

ENGYSYS – Ecole Doctorale des Sciences de l'Ingénierie et des Systèmes

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Van der Waals epitaxy of TaSe₂ and HfSe₂-based heterostructures on semiconducting substrates

Thesis supervised by Xavier WALLART

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Discipline **Micro et NanoTechnologies, Acoustique et Télécommunications**

Épitaxie de van der Waals d'hétérostructures à base de TaSe_2 et HfSe_2 sur substrats semiconducteurs

Thèse dirigée par Xavier WALLART

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Van der Waals epitaxy of TaSe₂ and HfSe₂-based heterostructures on semiconducting substrates

Abstract

Layered transition metal dichalcogenides (TMDCs) have attracted a significant attention in the last two decades owing to the large variety of properties they offer together with the unique ability of two-dimensional (2D) materials to be isolated in atomically thin layers or integrated in complex heterostructures regardless of the lattice mismatch. However, the lack of scalable fabrication techniques has hindered their use in practical applications. Especially, if molecular beam epitaxy (MBE) is a technique capable of growing high-quality semiconductors, the weak coupling between 2D layers represents a serious challenge for epitaxial growth because it favors rotational misalignment and twin formation. This makes the choice of an appropriate substrate an important and yet open question.

In this thesis, MBE is employed to grow TaSe₂ on GaP(1 1 1)B and GaAs(1 1 1)B substrates and HfSe₂ on GaP(1 1 1)B and Si(1 1 1). These semiconducting three-dimensional (3D) substrates are commercially available, but they require a passivation of their surface prior to 2D material growth. This has been achieved through an annealing under a Se flux for GaP and GaAs, whereas a self-limiting GaSe growth has allowed the deposition on a GaSe half-monolayer on Si. In each case, once the electronic properties and the morphology of the resulting surface has been fully characterized, the influence of the growth parameters during TMDC epitaxy is discussed. The focus on a metallic TMDC (TaSe₂) and a semiconducting one (HfSe₂) finally offers the opportunity to grow a 2D metal/semiconductor heterostructure.

In TaSe₂ monolayers, Mott insulating 1T or metallic 1H phase can be selectively grown at high or low substrate temperature, respectively. On the other hand, the stable H polytypes are favored in few-layers, for which the rotational alignment and crystallinity improve with increasing growth temperature. However, a rougher morphology is observed around 400–500 °C, whereas at higher temperature, a Se-deficiency is revealed in the TaSe₂ few-layers accompanied by an interdiffusion with the GaP substrate. Still, this substrate appears more suited than GaAs, which suffers from a large Se incorporation during TaSe₂ growth. The 1T-TaSe₂ monolayers reveal a moiré induced by the different GaP lattice parameter, in addition to the expected $\sqrt{13} \times \sqrt{13}$ charge density wave and Mott insulating phase stable at room temperature, contrasting with the metallic conductivity of H phases.

By contrast, HfSe₂ grown on GaP exhibits only the 1T phase, and its crystallinity is almost independent of the growth conditions, but rather depends on the annealing temperature. The thickness also plays an important role, the small lattice mismatch with GaP inducing a slight strain in thin layers which is relaxed with thickness. On Si substrates, however, HfSe₂ suffers from the instability of the GaSe half-monolayer and the formation of an intermediate SiSe_x phase. Electronic characterization suggests a n-type doping in thin HfSe₂ layers which is reduced in thicker films, leading to a high resistivity. This n-type character is largely preserved in the TaSe₂/HfSe₂ heterostructures although the latter suffer from a significant intermixing at the interface.

Keywords: transition metal dichalcogenides, two-dimensional materials, molecular beam epitaxy, heterostructures, photoemission spectroscopy, grazing incidence x-ray diffraction

Épitaxie de van der Waals d'hétérostructures à base de TaSe₂ et HfSe₂ sur substrats semi-conducteurs

Résumé

Les dichalcogénures de métaux de transition (TMDC) ont suscité un intérêt considérable au cours des deux dernières décennies en raison de la grande variété de propriétés qu'ils offrent, ainsi que de la capacité unique des matériaux bidimensionnels (2D) à pouvoir être isolés en couches atomiquement minces ou intégrés dans des hétérostructures complexes, quel que soit le désaccord de maille. Cependant, le manque de techniques de fabrication à grande échelle a freiné leur emploi pour des applications pratiques. Notamment, si l'épitaxie par jets moléculaires (MBE) est une technique permettant de produire des semi-conducteurs de haute qualité, le faible couplage entre les couches 2D représente un défi majeur pour la croissance épitaxiale, car il favorise le désalignement dans le plan et la formation de macles. Le choix d'un substrat approprié est donc une question importante, mais toujours ouverte.

Dans cette thèse, la MBE est utilisée pour faire croître du TaSe₂ sur des substrats de GaP(111)B et GaAs(111)B, et du HfSe₂ sur des substrats de GaP(111)B et Si(111). Ces substrats semi-conducteurs tridimensionnels (3D) sont disponibles commercialement, mais leur surface doit être passivée avant la croissance de matériaux 2D. Ceci a été réalisé par un recuit sous flux de Se pour GaP et GaAs, tandis qu'une croissance autolimitée de GaSe a permis le dépôt d'une demi-monocouche de GaSe sur Si. Dans chaque cas, une fois les propriétés électroniques et la morphologie de la surface obtenue entièrement caractérisées, l'influence des paramètres de croissance lors de l'épitaxie de TMDC est discutée. L'étude d'un TMDC métallique (TaSe₂) et d'un semi-conducteur (HfSe₂) offre enfin la possibilité de développer une hétérostructure métal/semi-conducteur 2D.

Dans les monocouches de TaSe₂, la phase isolante de Mott 1T ou la phase métallique 1H peuvent être sélectivement fabriquées à haute ou basse température du substrat, respectivement. En revanche, les polytypes H, plus stables, sont favorisés en multicouches, pour lesquelles l'alignement rotationnel et la cristallinité s'améliorent en augmentant la température de croissance. Cependant, une morphologie plus rugueuse est observée autour de 400–500 °C, tandis qu'à plus haute température, une déficience en Se est révélée dans les multicouches de TaSe₂ accompagnée d'une interdiffusion avec le substrat GaP. Cependant, ce substrat semble plus adapté que GaAs, qui souffre d'une importante incorporation de Se lors de la croissance de TaSe₂. Les monocouches 1T-TaSe₂ présentent un moiré induit par la différence de paramètre de maille par rapport à GaP, en plus de l'onde de densité de charge en $\sqrt{13} \times \sqrt{13}$ attendue pour ce matériau et de la phase isolante de Mott stable à température ambiante, contrastant avec la conductivité métallique des phases H.

En revanche, HfSe₂ préparé sur GaP ne forme que la phase 1T, et sa cristallinité est presque indépendante des conditions de croissance, mais dépend plutôt de la température de recuit. L'épaisseur joue également un rôle important, le faible désaccord de maille avec GaP induisant une légère contrainte dans les couches minces qui se relâche avec l'épaisseur. Sur substrats de silicium, cependant, HfSe₂ souffre de l'instabilité de la demi-monocouche de GaSe et de la formation d'une phase intermédiaire de SiSe_x. La caractérisation électronique suggère un dopage de type N dans les couches minces de HfSe₂, qui est réduit dans les couches plus épaisses, conduisant à une résistivité élevée. Ce dopage N est largement préservé dans les hétérostructures TaSe₂/HfSe₂, bien que ces dernières subissent une importante interdiffusion à l'interface.

Mots clés : dichalcogénures de métaux de transition, matériaux bidimensionnels, épitaxie par jets moléculaires, hétérostructures, spectroscopie de photoémission, diffraction des rayons x en incidence rasante

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Glossary

2D two-dimensionnal.

4PP four-point probe.

AFM atomic force microscopy.

ALD atomic layer deposition.

ARPES angle-resolved photoelectron spectroscopy.

CDW charge density wave.

CL core level.

CVD chemical vapor deposition.

CVT chemical vapor transport.

DOS density of states.

EDX energy-dispersive X-ray spectroscopy.

FCC face centered cubic.

FET field-effect transistor.

FFT fast-Fourier transform.

FIB focused ion beam.

FWHM full width at half maximum.

HAADF high-angle annular dark-field.

hBN hexagonal boron nitride.

HOPG highly-oriented pyrolytic graphene.

IEMN Institut d'Electronique, de Microélectronique et de Nanotechnologie.

IV current-voltage.

LEED low energy electron diffraction.

MBE molecular beam epitaxy.

ML monolayer.

MOCVD metal-organic chemical vapor deposition.

PH₃ phosphine.

PVD physical vapor deposition.

RHEED reflection high energy electron diffraction.

RMS root mean square.

SEM scanning electron microscopy.

STEM scanning transmission electron microscopy.

STM scanning tunneling microscopy.

STS scanning tunneling spectroscopy.

TMDC transition metal dichalcogenide.

UHV ultra-high vacuum.

UPS ultra-violet photoelectron spectroscopy.

UV ultraviolet.

vdW van der Waals.

XPD X-ray photoelectron diffraction.

XPS X-ray photoelectron spectroscopy.

XRD X-ray diffraction.

Introduction

The miniaturization of field-effect transistor (FET) devices has been so efficient to exponentially increase the device density for decades that, 60 years after the enunciation of Moore's law,¹ the latest technology nodes are still named after a length such as "3 nm" or "2 nm", even though these denominations no longer have a physical meaning since the shortest channel length should only reach ≈ 14 nm in 2025.² Indeed, as the device miniaturization is facing both technical challenges and physical limits, the current and future improvements rather consist in increasing the device density using different architectures (silicon-on-insulator, gate-all-around, ground plane), high- κ gate dielectrics, and vertical device stacking. To reduce further the channel length, a smaller semiconductor thickness would be highly desirable to overcome the short channel effect.³ However, the 3D semiconductors undergo a drastic decrease of their carrier mobility⁴ and thermal conductivity with thickness.⁵ A possible solution may lie in two-dimensional (2D) materials, which are crystals consisting of atomically thick layers containing covalent bonds over two different directions of space but that are held together by weak van der Waals (vdW) forces in the out-of-plane direction. The absence of dangling bonds on their surfaces explains they maintain good properties at very low thickness, and therefore makes them appealing for future electronics.⁶

Even though layered materials have been known for a long time, they only have attracted much attention since the successful exfoliation of single and few layers of graphene by Novoselov and Geim in 2004.⁷ This study not only proved the stability of individual 2D-layers, but also highlighted the gate control possibility it offers. However, since the metallic conductivity of graphene is not desirable for many applications, the need for semiconducting 2D materials has been recognized and transition metal dichalcogenides (TMDCs) have been rapidly identified as possible candidates.⁸ In particular, the discovery of a direct band gap in the monolayer MoS₂ in 2010⁹ has pioneered an intensive research on this material, but also more largely on TMDCs to explore the various properties they offer when they are thinned to the atomic scale.¹⁰ In this regard, metallic TMDCs are not only expected to be valuable as contact materials for 2D semiconductors,¹¹ but also exhibit exotic phenomena due to strong electron-electron interaction.¹²

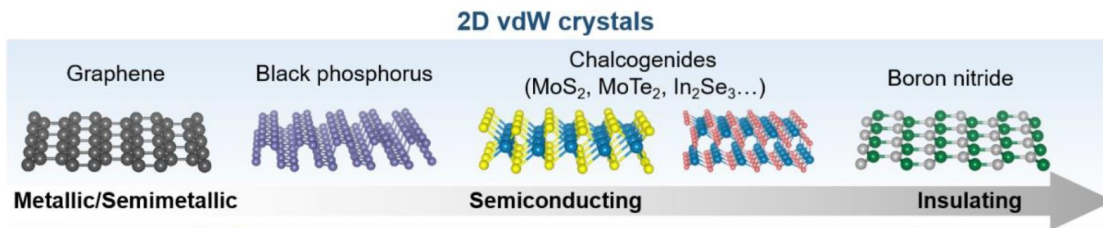


Figure 1: Some representatives of the main 2D-material families, reproduced from Yin *et al.*¹³.

The popularity of 2D materials mostly ought to the versatility of the top-down approach, consisting in the mechanical exfoliation of layers from a crystal followed by their transfer to the desired substrate or structure, and the good quality of the starting material which enabled the rapid demonstration of working devices.¹⁴ However, the method is not reliable and only small flakes are transferred, enabling few devices to be made. This leads us to consider a more

traditional approach, referred as bottom-up, in which the materials and heterostructures are formed on the targeted substrate using growth techniques such as molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD). They are scalable and mostly known for the 3D semiconductors, even though the growth of 2D materials using MBE was already pioneered by Koma *et al.*¹⁵ two decades before the exfoliation. At this time, the motivation was to benefit from the absence of interlayer covalent bonds in 2D materials to grow high quality heterostructures with sharp interfaces regardless of the lattice mismatch. In theory, this enables any combination of 2D materials to be made, in stark contrast with 3D materials for which the lattice mismatch inevitably induces strain or defects, as shown in Fig. 2. Given the limited choice of 2D substrates, the concept has been extended to grow 2D materials on 3D substrates when the surface of the latter is made free of dangling bonds through passivation strategies, or sufficiently inert, in the so-called "quasi vdW epitaxy".¹⁶ Nevertheless, the weakness of the vdW forces makes the growth of well-ordered 2D materials challenging since the interaction with the substrate is precisely what enables a coherent growth at the wafer scale in epitaxy. Different growth techniques and substrates have been considered to improve the crystallinity while achieving a wafer scale coverage with a controlled thickness, but no consensus has been reached yet. In this thesis, the MBE growth of HfSe_2 , a semiconducting TMDC with a high predicted mobility,¹⁷ and TaSe_2 , a metallic one with a suitable band alignment on the latter,¹⁸ is investigated on 3D semiconducting substrates, exploring the influence of the growth conditions and interaction with the substrates.

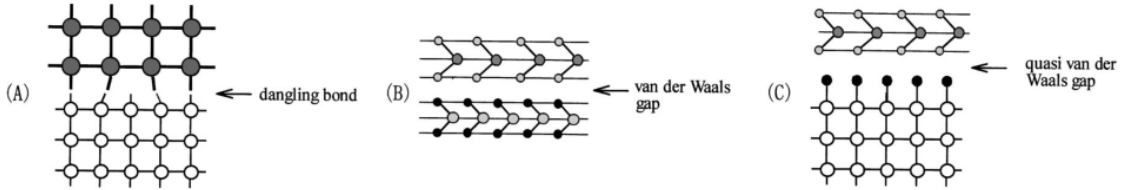


Figure 2: Schematic representation of (a) 3D epitaxy, (b) vdW epitaxy and (c) quasi vdW epitaxy, reproduced from Koma¹⁹.

In Chapter 1, the different families, properties and applications of TMDCs are introduced. The existing fabrication methods are briefly reviewed, and focusing on the bottom-up approaches, the main growth strategies as well as the available substrates are presented.

The experimental techniques that have been employed in this thesis are described in Chapter 2. First, the two MBE chambers, respectively dedicated to III-V and selenides compounds, are presented as well as the sample preparation procedures. Then, for each characterization technique, including photoemission spectroscopy, diffraction and scanning probe microscopy, the measurement principle is briefly introduced and the experimental details are provided, as well as the data analysis methods.

The growth of TaSe_2 , a metallic TMDC, on III-V substrates is examined in Chapter 3. The preparation of both GaP and GaAs surfaces is presented, including the growth of buffer layers and the passivation of the dangling bonds with Se atoms. The influence of the growth conditions on the phase formation, as well as on the morphology and crystallinity is investigated. Focusing mainly on GaP, the selective growth of 1T and 1H phases is demonstrated in monolayers. The rotational alignment of the monolayers is discussed, as well as the presence of a moiré. In addition, the investigation of the electronic properties reveals a charge density wave (CDW) and a band gap in the 1T monolayer. The influence of the thickness on the phase formation is then highlighted, as well as the role of the substrate in the degradation observed at higher temperature.

Chapter 4 is dedicated to semiconducting HfSe_2 and related heterostructures. The influence of the growth conditions and thickness are investigated on GaP substrates. The use of Si(111) substrate is also considered, as a self-limited GaSe growth is shown to efficiently passivate the

surface through the deposition of a half monolayer. The stability of this surface termination upon HfSe₂ growth is explored and HfSe₂ layers grown GaP and Si substrates are compared. Then, the metal-semiconductor HfSe₂/TaSe₂ heterostructures grown on GaP are studied, showing little charge transfer but significant interdiffusion. First attempts of electrical measurements of both lateral transport in HfSe₂ and in vertical heterostructures are finally presented.

Chapter 1

State of the art of transition metal dichalcogenide growth

In this chapter, the structure and electrical properties of the TMDCs are presented, as well as the potential applications for both the semiconducting and metallic ones. Then, the elaboration techniques are compared. In each case, a particular focus on HfSe_2 and TaSe_2 is made, but the lack of data specific to these two materials encourages us to look at the strategies employed for the growth of related compounds in order to identify the possible routes for improvement. In this regard, the influence of the growth conditions on the morphology, grain size and in-plane alignment are discussed. Finally, a survey of the available substrates highlights the surface passivation of III-V and Si as a promising approach for the development of 2D materials at larger scale.

1.1 Layered transition metal dichalcogenides

1.1.1 General properties of 2D-TMDCs

TMDCs are compounds made of one transition metal (d-block in the periodic table) for two chalcogen atoms (S, Se or Te). Not all chalcogenides are 2D-materials, but the elements that have been reported to form at least one layered structure are highlighted in the periodic table in Fig. 1.1. Note that other stoichiometries than 2 chalcogens for 1 metal exist, but this study will be restricted to dichalcogenides.

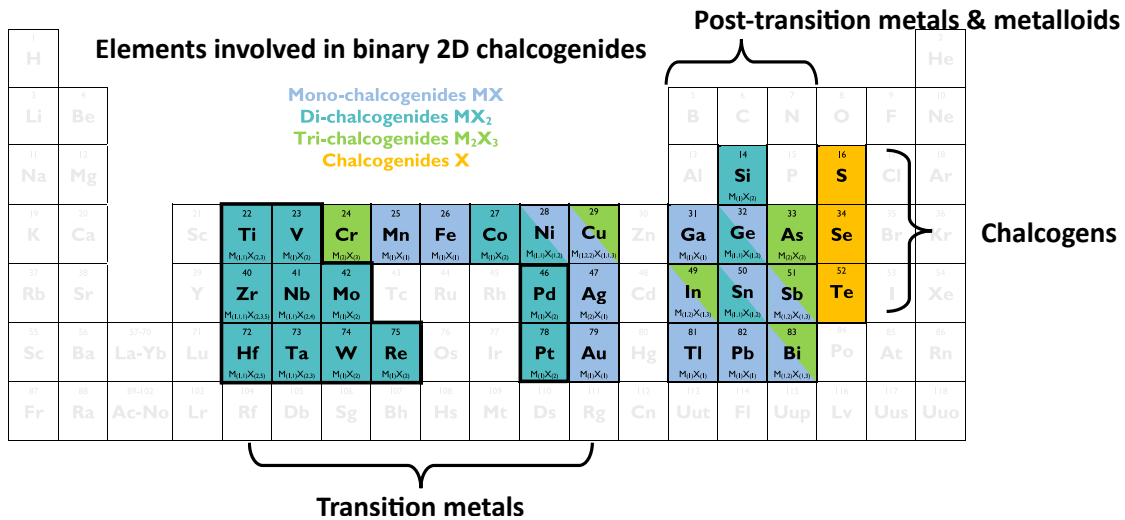


Figure 1.1: Periodic table of the elements involved in binary compounds for which at least one 2D structure has been reported, reproduced from Mortelmans *et al.*²⁰.

1.1.1.a Crystal structures of 2D-TMDCs

As any crystalline material, TMDCs exhibit periodic structures. However, in the layered ones, they are only covalently bounded along two directions, forming infinite thin sheets. Despite being 3 atoms-thick, they are called monolayers (MLs) because they are the thinnest structures that can be isolated. Several structures are found among the many combinations of atoms that form 2D-TMDCs. In the two most common, the metal atom is either in trigonal prismatic coordination in the 1H polymorph (Fig. 1.2 (a)), or in octahedral coordination in the 1T one (Fig. 1.2 (b)). Among the other structures, several variations of the 1T polymorph are referred as distorted phases since they are similar to the 1T one except that they are forming extra metal-to-metal bonds, the 1T' phase represented in Fig. 1.2 (c) being one example. Finally, a very distinctive orthorhombic structure is found in Pd dichalcogenides (Fig. 1.2 (d)).

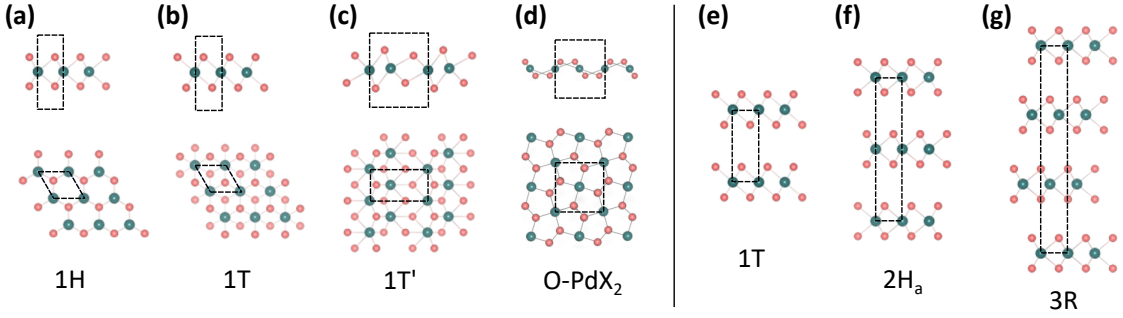


Figure 1.2: (a-d) Side and top views of different monolayer structures reported in TMDCs. (e-g) Most frequent polytypes in bulk TMDCs. Adapted from Kim *et al.*²¹.

A crystal is a regular arrangement of atoms in the three dimensions and, even if they can be thinned down to a ML, macroscopic TMDCs are composed of many of these MLs periodically stacked one over the other. Several 1T MLs are more likely to stack vertically at the same position (Fig. 1.2 (e)) while the 1H MLs are expected to be alternatively 180°-rotated in the 2H_a phase (Fig. 1.2 (f)), or to shift horizontally in the 3R phase (Fig. 1.2 (g)). Other stackings exist and they are usually denoted with an integer representing the number of MLs that are piled up until the sequence repeats, and a letter referring to the lattice type.²² The notation 1H does only refer to a monolayer since there is no report of a stacking of trigonal prismatic layers with a periodicity of 1.

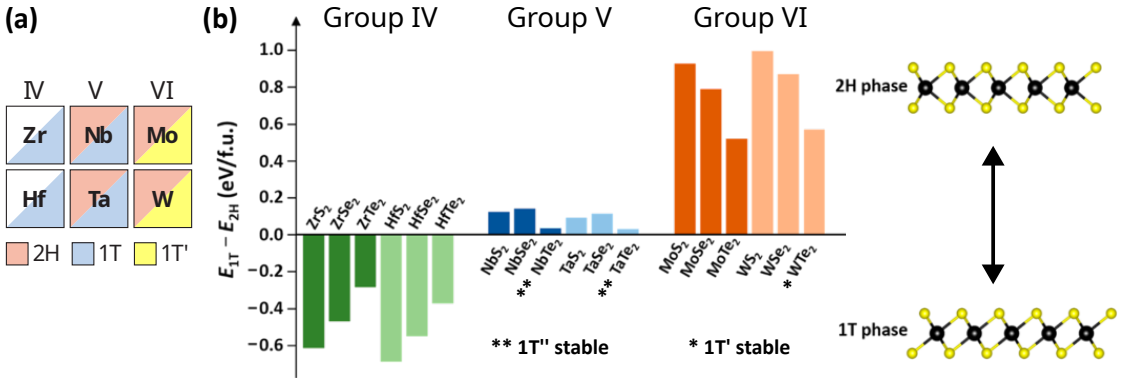


Figure 1.3: (a) Phases experimentally reported in TMDCs depending on the transition metal, adapted from Manzeli *et al.*²³. (b) Energy difference between 1T and 1H phase for different TMDCs estimated from density functional theory calculations, adapted from Wang *et al.*²⁴.

To predict which structure a given compound is expected to adopt, density functional theory calculations of the formation energy can be found in the literature. The energy difference between 1T and 1H phases is presented in Fig. 1.3. For Zr and Hf compounds, the energy difference is negative which means that the 1T phase is more stable. In Nb and Ta ones, the energy difference is very small, so even if the 1H phase is the stable one, the 1T structure may be also be encountered as a metastable phase. Finally, in Mo and W compounds the 1H is largely more favored compared to the 1T phase. However, this calculation does not investigate the distorted 1T' and 1T'' phases. Other studies have shown that the 1T' is comparatively more stable than the 1T phase,^{25,26} which is confirmed experimentally by the observation of 1T' as a metastable phase. The 1H remains however the stable phase for Mo and W compounds, except for WTe₂ in which the 1T' is slightly lower in energy.²⁵ Similarly, TaTe₂ and NbTe₂ crystallize in the less common 1T'' structure.^{27,28} As evidenced by the periodic table, it is clear that TMDCs with metal atoms from the same column usually share the same structure. The TMDCs are therefore classified into groups corresponding to the column from which the metal atom originates. The groups as well as the structures have a critical influence on the properties discussed in the next paragraph.

1.1.1.b Electronic properties of 2D-TMDCs

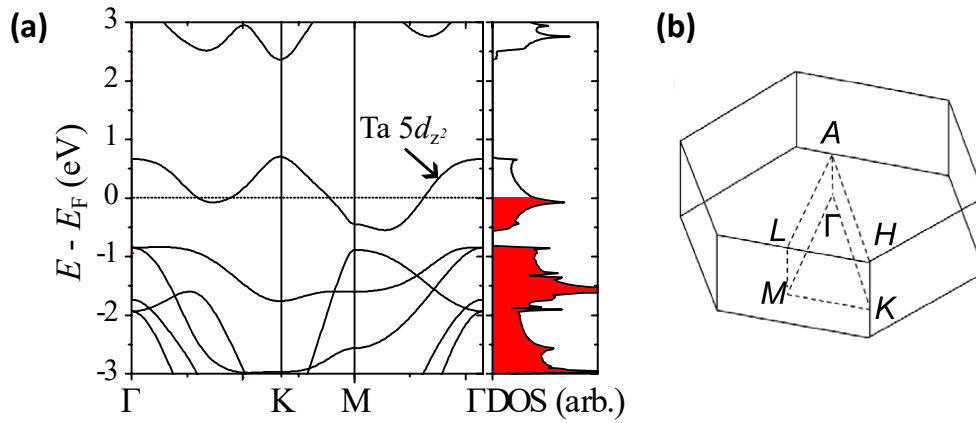


Figure 1.4: (a) Calculated band structure and density of states (DOS) in a 1H-TaSe₂ monolayer.²⁹ (b) Geometry of the first Brillouin zone of a hexagonal crystal.³⁰

As any crystalline material, the electronic properties of the TMDCs are determined by their band structure (Fig. 1.4 (a)). It establishes the allowed energies of an electron in the material as a function of its momentum. The integration of the band structure over the Brillouin zone (Fig. 1.4 (b)) gives the density of available states as a function of energy. It features both regions with non-zero available states, corresponding to the bands, and energy ranges where no states are allowed. As known from Fermi exclusion principle, two electrons cannot share the same state, so the bands are filled with electrons from the lowest energy to the highest until the charge neutrality is reached. The energy of the highest occupied state is called the Fermi energy, denoted E_F .

Because electrons need available states to move, the bands that only contain filled states do not contribute to the electrical conductivity.³¹ As a consequence, materials in which the Fermi level is between two bands corresponds to insulators. When the energy gap between the last filled band and the nearest empty band, also called the band gap, is only a few eV, electrons can be thermally excited from the valence band to the conduction band, and the material is semiconducting. Extra charge carriers, electrons in the conduction band, or empty states (holes) in the valence band, can also be injected in the material to increase the conductivity through chemical or electrostatic doping.

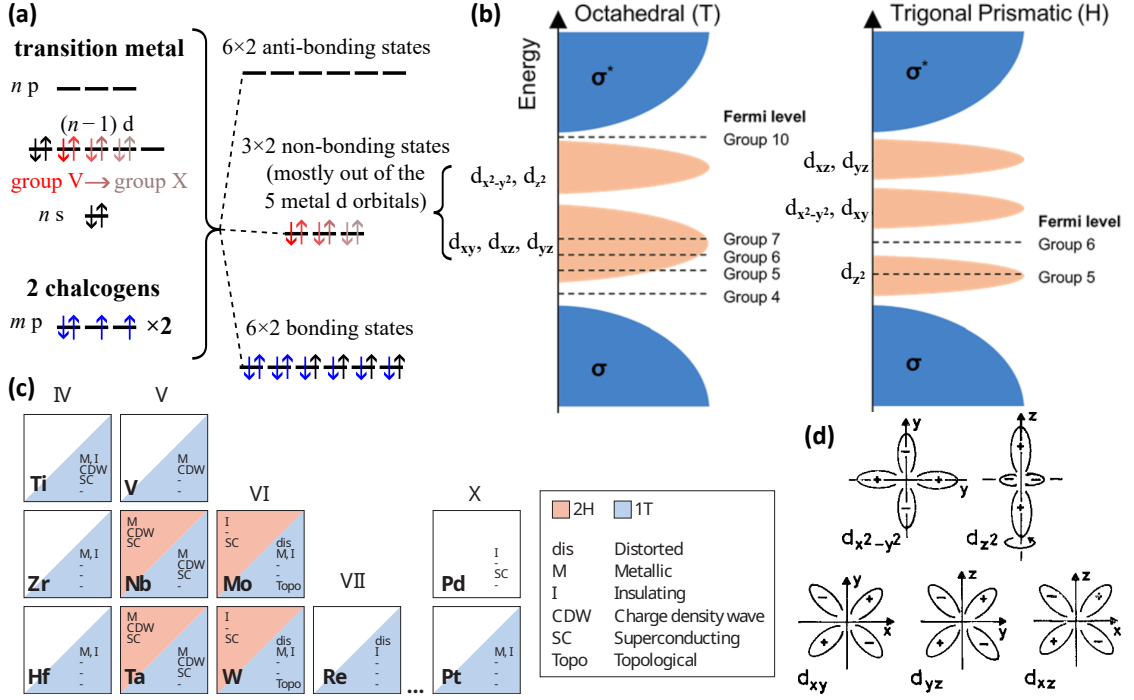


Figure 1.5: (a) Orbitals in TMDCs before and after covalent bonding. The electrons are represented as arrows pointing either upwards or downwards as function of their spin. (b) Qualitative representation of the energy bands in TMDC depending on the structure and position of the Fermi energy, reproduced from Kim *et al.*²¹. (c) Summary of the structures and properties found in TMDCs depending on the transition metal, reproduced from Manzeli *et al.*²³. (d) Schematics of the five d orbitals, reproduced from Wilson *et al.*³².

The electronic structure of TMDC compounds is represented in Fig. 1.5 (a). Since each chalcogen lacks 2 electrons to complete its electronic configuration, 4 electrons are required to form the 6 covalent bonds, leading to an oxidation state of +4 for the transition metal. Any additional d electrons occupy 3 non-bonding bands that have been mostly ascribed to the remaining d orbitals. They are represented in orange in the energy diagram in Fig. 1.5 (b) for the two most frequent transition metal atom coordinations. In the 1T monolayer, the inversion symmetry of the octahedral coordination causes the degeneracy of the non-hybridized d_{xy} , d_{xz} and d_{yz} orbitals. They are empty in group IV, and completely filled with 6 electrons in group X. These compounds are thus semiconducting whereas for the transition metals in between, the 1T phase is expected to be metallic. Hence, despite the octahedral configuration is more stable from the steric repulsion point of view,³³ it leads to a non-optimal electronic configuration for group V to VII which favors other structures as reported in Fig. 1.5 (c). Among them, the trigonal prismatic coordination breaks the inversion symmetry, and the d_{z^2} orbital becomes the lowest energy state.³² It is completely filled with 2 electrons in group VI TMDCs, making the 2H phase stable and semiconducting, while it remains metallic in group V with a single electron. Distorted 1T-phases also splits the energy levels and provides extra metal-metal bonds for electron pairing. If 1T'-TaTe₂ and 1T'-WTe₂ stay metallic or semimetallic,^{34,35} a particular atomic arrangement makes Re compounds semiconducting.^{36,37}

Note that this description is only valid at a certain extent since a band cannot be uniquely attributed as calculations show a significant mixing of the orbitals.³⁸ Moreover, the bands may overlap because of the dispersion relation, causing some discrepancies with respect to the above discussion. For instance, Ti compounds are either metallic or semimetallic despite being in group IV. Similarly, tellurides tend to be semimetallic, as in Zr and Hf compounds^{39,40} following the gen-

eral trend of a decrease of the band gap descending in the chalcogen column. Finally, some group X compounds undergo a semiconductor-to-semimetal transition with increasing thickness^{41–43} which can be ascribed to a reduction of the electron confinement.⁴⁴

1.1.1.c Collective electronic states in metallic TMDCs

In the previous paragraph, some TMDCs with partially filled bands have been noticed to exhibit lattice distortions and insulating states, showing the instability of the metallic state. Although various concepts have been proposed to describe the underlying phenomena,^{12,45} the collective electronic states such as the CDWs and Mott insulating phase can be understood in this framework. Here, their origin is discussed through a very simplified picture, stating in one-dimension.

One-dimensional model

In the 1930s, Peierls demonstrated that a 1D-chain of atoms with one free electron per atom can minimize its energy by a small displacement of the atoms, so that the periodicity of the system becomes twice the initial atom spacing. Such a periodic distortion of the lattice, which is accompanied with a modulation of the electronic density, is what is called a CDW.⁴⁶ This results in the opening of a small gap at the Fermi energy level. As shown in Fig. 1.6, the filled states, below E_F , are moved downwards. As a consequence, the system effectively reduces its energy for small atomic displacements, for which the elastic energy cost is comparatively smaller.⁴⁶ The decrease of the total energy is maximum at 0 K, but as the thermal energy $k_B T$ becomes comparable to the formed gap, some states below E_F become empty while some others above E_F are filled and consequently, the energy gain is reduced and the CDW becomes unstable. It is worth noting that in Fig. 1.6, the metallic band was considered half-filled, so that the wave vector at the Fermi level k_F is exactly half of the reciprocal space vector, leading to a doubling of the real space lattice. In practical, a band gap could open for any value of k_F and the resulting CDW periodicity can be either commensurate or incommensurate with the material lattice.⁴⁷

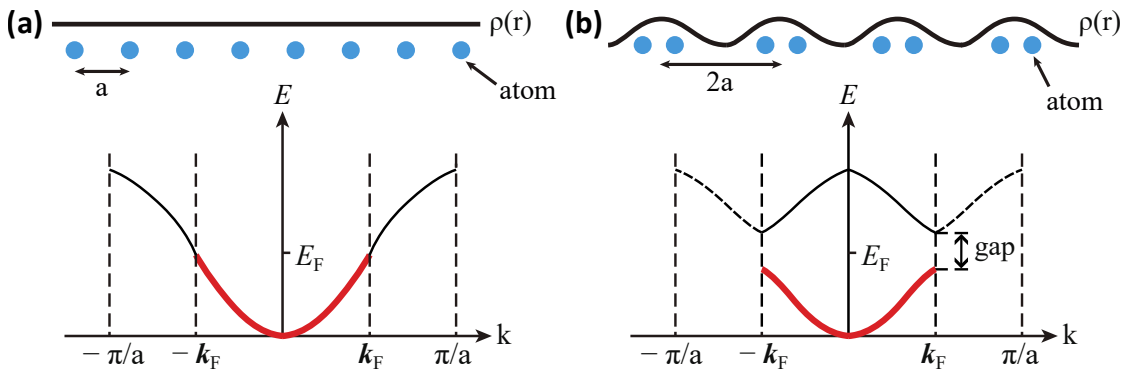


Figure 1.6: Illustration of the Peierls instability, adapted from Wen *et al.*⁴⁸. The metallic 1D-chain of atoms (a) rearrange to form an insulator with a double period (b).

2D and 3D-materials case

Few systems can be considered as purely 1D, so more realistic materials are now considered, for which the reciprocal space extends over 2 or 3 dimensions. In Fig. 1.7 (a) the Brillouin zone is considered two dimensional, which is valid for a monolayer TMDC, and the vertical scale depicts the energy. In this case, the Fermi level becomes a surface and its intersection with the energy bands are lines. They can be experimentally revealed using angle-resolved photoelectron spectroscopy (ARPES) and an example for TaSe₂ is shown in Fig. 1.7 (c). Upon the presence of a CDW, the bands are folded in a reduced Brillouin zone and a band gap opens at its boundary

(Fig. 1.7 (b)). However, contrary to the one-dimensional case, it cannot perfectly coincide with the intersection of the bands with the Fermi surface. Hence, the bands are moved away from the Fermi surface in specific regions of the reciprocal space,⁴⁹ while they still cross it in some others as seen in Fig. 1.7 (d). This results in a reduction of the local density of states, sometimes referred as a pseudogap, as observed in NbSe₂⁵⁰ (Fig. 1.7 (e)), but the material remains metallic.

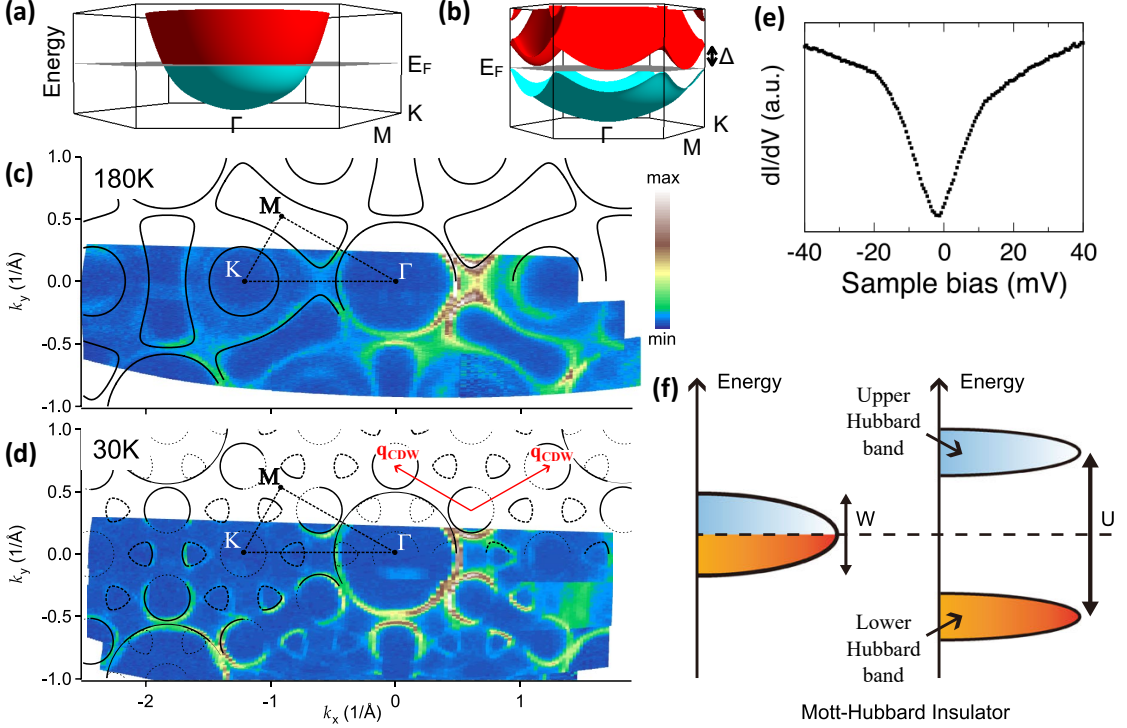


Figure 1.7: (a-b) Schematic of a metallic band in a hypothetical 2D crystal (a) without and (b) with Peierls distortion.⁵⁰ (c-d) Fermi surface of 2H-TaSe₂⁵¹ (c) in the absence and (d) presence of a 3×3 CDW. (e) Pseudogap revealed by scanning tunneling spectroscopy (STS) in a 2H-NbSe₂ crystal in the presence of a 3×3 CDW.⁵⁰ The dI/dV signal is considered proportional to the density of states. (f) Schematic of the Mott-Hubbard transition.⁵²

Since the Peierls instability is insufficient to describe the insulating states observed in many TMDCs with partially filled bands, other models have been proposed. One of them was developed by Mott and Hubbard to explain the insulating states in transition metal oxides based on the electron localization caused by electron-electron interactions. For this, they consider an array of identical sites having a half-filled degenerated state. The repulsive Coulomb interaction U will make the energy of an already occupied site differ from a non-occupied one, so that the system minimizes its energy if the electrons are evenly distributed.⁵³ However, as the interatomic distances decrease, the electron hopping makes the energy levels become bands that may overlap and enable the electron transport. Nevertheless, if U is greater than the bandwidth W , a half-filled energy band is still expected to split into two separate bands, as depicted in Fig. 1.7 (f), one being entirely filled and the other one empty, hence the system is expected to be insulating.⁵⁴ Because of the lower dimensionality, the interaction U between two electrons is stronger in a 2D material due to a reduced screening by other electrons, whereas the hopping, responsible for electron delocalization, is decreased.⁵⁵ This makes the electron localization more likely in 2D materials although the interplay with (i) spin interactions, leading to magnetic ordering, (ii) lattice distortions, as discussed above, and (iii) with the chalcogen p-band must also be considered.⁵³

1.1.2 Semiconducting TMDCs

1.1.2.a Overview

In this paragraph, the properties of the semiconducting TMDCs and their applications are reviewed. As the most determinant features, their band gap energies are presented in Fig. 1.8.

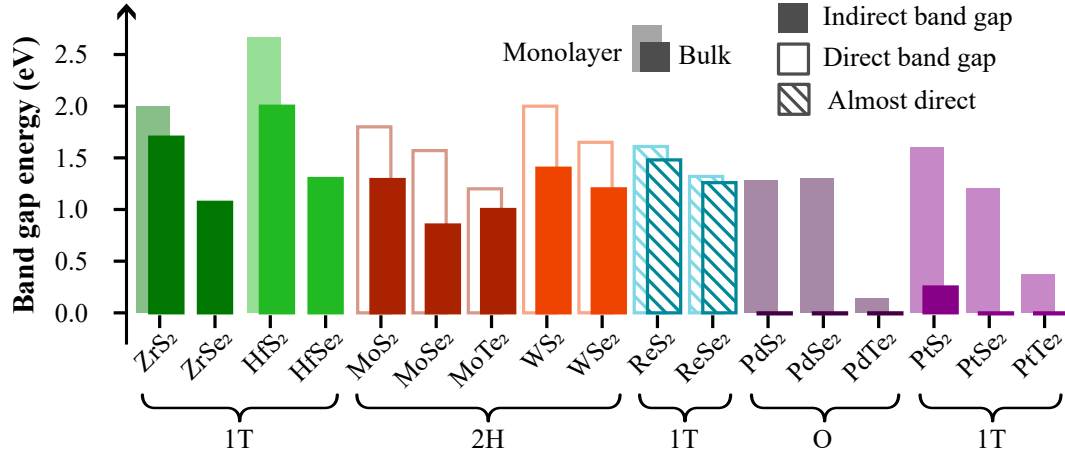


Figure 1.8: Experimental band gaps in semi-conducting TMDCs, based on values reported in the literature.^{21,30} The direct and indirect band gaps are close in Re compounds regardless of the thickness.⁵⁶ For ZrSe₂ and HfSe₂, only values for few layers have been reported, but the thickness does not seem to have a large influence.³⁰

Among them, the group VI dichalcogenides have attracted most of the attention because of their direct-to-indirect band gap transition with thickness. They appear particularly suited for opto-electronic applications since the light-matter interaction is strongly favored in direct band gap materials, as illustrated by the enhancement of the photo-luminescence in monolayer samples.⁵⁷ In addition, this emission can be spectrally very narrow thanks to the large binding energy of excitons.⁵⁸

The 5 direct band gap TMDC monolayers provide a bunch of wavelengths between 627 nm (WS₂) and 1127 nm (MoTe₂), with an entire tunability within this range using alloys.^{59,60} The band gap can be further reduced in heterostructures,⁶¹ or by increasing the number of layers, however at the cost of a rapid decrease of the photoluminescence intensity in the latter case.⁵⁷

Almost all dichalcogenides exhibit this band gap dependence to thickness, but this is particularly pronounced in group X dichalcogenides,⁶² with a 1.6 to 0.25 eV shift in PtS₂⁶³ and complete semiconductor to semimetal transition in PtSe₂ and PtTe₂,^{41,43} opening applications in mid-infrared and broadband photodetectors.⁶⁴ As regards photovoltaic applications, group VI TMDCs have also been considered first since one monolayer of MoS₂ or MoSe₂ can absorb as much of the solar spectrum as 50 nm of Si or 15 nm of GaAs, despite having wider band gap.⁶⁵ Still, the absorbance of a single monolayer remains very low so the recent studies have focused on 50-300 nm-thick TMDC absorbers^{66,67} and few of them reached an efficiency of 5 %.^{68,69} Alternatively, the TMDCs have been used in 2D-3D heterostructures with Si⁷⁰ and GaAs,⁷¹ and their integration was also proposed for semi-transparent solar windows,⁷² lightweight and flexible solar panels⁷³ or tandem solar cells.⁷⁴

A different approach to harvest the solar energy is the photocatalytic production of H₂ through water splitting. In this case, 2D materials are promising thanks to their large specific surface area and good stability in water.⁷⁵ Still, they must have their valence band below -5.67 eV and their conduction band above -4.44 eV with respect to the vacuum to be suitable,⁷⁶ a condition fulfilled by MoS₂, WS₂, PtS₂, and PtSe₂.⁷⁵

Besides, the monolayer 1H structure has broken inversion symmetry which makes the K and K' valleys inequivalent in the Brillouin zone. This induces a coupling between the direction of the electron momentum and polarized light.⁷⁷ Interestingly, in the centrosymmetric bilayer 2H structure, an applied electric field can also break the symmetry to enable the valley Hall effect.⁷⁸ This experiment opens the path toward the so-called valleytronics since the transported information lies in the valley rather than in the charge. Nevertheless, the observation of these effects at room temperature remains currently challenging since valley depolarization time is very short compared to the exciton lifetime.⁷⁹

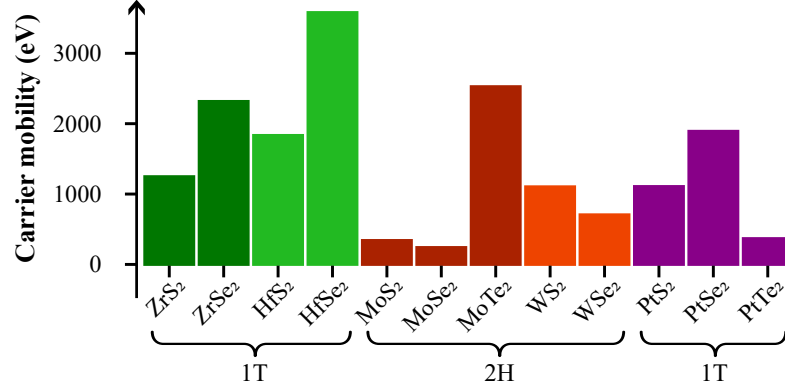


Figure 1.9: Phonon-limited electron mobility calculated using local density approximation by Zhang *et al.*¹⁷.

Regarding applications in electronics, semiconducting 2D-materials are of significant interest for FETs with very high on/off ratios because they can be atomically thin, which enables a good control of their carrier density through electrostatic gating.¹⁰ With many compounds having moderate band gaps, TMDCs appear as good candidates. A high carrier mobility would also be desirable for this application, but the achieved mobilities have remained modest in these compounds compared to other bulk semiconductors. Still, considering the decrease of the carrier mobility with thickness in 3D-materials,⁴ TMDCs could surpass the performance of Si in the future transistor architectures.² Since the experimental values strongly depends on the quality of the material, contacts and interfaces, Fig. 1.9 presents the expected electron mobilities if the acoustic photons were the only source of scattering. Based on this calculation, HfSe₂ appears as the most promising material, with an upper limit of carrier mobility 10 times higher than in MoS₂ despite the latter is far more studied. For this reason, it deserves a closer look.

1.1.2.b Hafnium diselenide

As many of the group IV TMDCs, HfSe₂ has been scarcely studied. Apart from few mentions of the 2H phase,⁸⁰ it is almost always found in the 1T phase. Its band gap, approximately 1.1 eV, is indirect and does not significantly vary with the thickness,³⁰ indicating a weak interlayer coupling.⁶² Thus, if this material does not seem particularly interesting from a physicist point of view, it offers an advantage for practical applications since its properties are relatively invariant to thickness inhomogeneity. With a bandgap similar to silicon, and a possibly higher mobility, it could be reasonably considered for future applications in electronics. However, the results of the few experimental studies available in the literature, reproduced in Table 1.1, are currently far from the $3600 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ calculated by Zhang *et al.*¹⁷. Different hypotheses could explain this discrepancy.

First, HfSe₂ is a polar material, and it has been suggested that the large in plane static dielectric constant in 1T polytypes would lead to polar-optical phonon scattering that significantly decreases the mobility.⁸¹ Effectively, Keshri *et al.* calculated a much lower mobility using a method that includes the scattering by optical phonons.⁸²

Resistivity ($\Omega\cdot\text{cm}$)	Mobility ($\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)	Extraction method	Contact material	Reference
0.02	1.59	vdP/Hall		Radhakrishnan <i>et al.</i> ⁸³
	0.22	FET	Cr/Au	Kang <i>et al.</i> ⁸⁴
	2.16–3.04	FET	Cr/Au	Kang <i>et al.</i> ⁸⁵
	2.6–6.5	FET	Au	Yin <i>et al.</i> ⁸⁶
	1–4	FET	Al ₂ O ₃ /Cr/Au	Mleczko <i>et al.</i> ³⁰
800		4PP		Liu <i>et al.</i> ⁸⁷

Table 1.1: Experimentally determined electrical transport properties of HfSe₂ layers. 4PP: Four-point probe. vdP: van der Pauw.

Extrinsic reasons have also been raised because a high density of defects has been observed using scanning tunneling microscopy (STM) on a cleaved HfSe₂ surface,⁸⁸ and such defect densities are known to affect the carrier mobility in other TMDCs.⁸⁹ Liu *et al.* reported that samples stored 3 months under vacuum exhibited a Se deficiency and a strong electron doping,⁸⁷ which may explain the much lower resistivity found by Radhakrishnan *et al.*⁸³. Moreover, HfSe₂ oxidizes very easily in air,^{88,90} which raises an additional challenge for device processing. Nevertheless, this could also offer several advantages since HfO₂ is a high- κ dielectric with a large band gap.⁹¹ The oxidation of the top layers by an O₂ plasma treatment has been used to reduce the HfSe₂ channel thickness without degrading the mobility, which improved the FET performance.⁸⁵ A superior interface quality was also noticed when replacing Al₂O₃ with HfO₂ in a metal-insulator-semiconductor structure.³⁰ This suggests a particular compatibility between HfSe₂ and its native oxide, similarly to the Si/SiO₂ couple.

Finally, it should be mentioned that the performance of 2D material-based devices is usually hindered by high contact resistances. Because very few studies have been performed on HfSe₂, it is still possible that improvements could be made with new contact strategies, in which metallic dichalcogenides could play a role.

1.1.3 Metallic TMDCs

1.1.3.a Overview

Metallic TMDCs have been mostly studied from a pure research perspective. However, in this paragraph, a focus will be given on the current and future applications of these materials.

First, they are interesting as electrical contacts, especially for 2D-materials. The different compounds and polytypes cover a wide range of work functions, some of which are particularly large especially in sulfides. It makes them suitable for contacting p-type semiconductors, for which high work function materials are sometimes lacking. However, it should be noted that some semiconducting TMDCs also have large electron affinity, making the contact with n-type TMDCs such as HfSe₂ also feasible.¹⁸ One advantage of such 2D-dimensional contacts is their ability to combine electrical conductivity with a good transparency since they can be thinned down to few monolayers,⁹² which could be useful for top contacts in optoelectronic devices.

Also taking advantage of both the layered structure and good electrical conductivity, metallic TMDCs are promising for the fabrication of batteries. The layered structure not only enables large contact surface, but can also store small ions such as Li⁺ or Na⁺. Several metallic TMDCs have been considered for this application, including the metastable 1T-MoS₂ and 1T-WSe₂.⁹³ However, in these cases, the performances were strongly degraded if the semiconducting phase was used instead. Larger specific capacities have been achieved later with TaSe₂, for which both phases have presented promising results.^{94,95}

Several metallic TMDCs have been reported to have a relatively high temperature superconductivity, among which the highest T_c have been found in Nb compounds, up to 7.4 K for

NbSe₂.⁹⁶ This property has been exploited in Josephson junctions, a superconductor-insulator-superconductor heterostructure, with potential applications in quantum electronics.^{97,98} Regarding CDW and Mott insulators, a possibility to make a multi-step non-volatile resistive switching was recently demonstrated in 1T-TaS₂.⁹⁹ However, the device required to be cooled down to 165 K to exhibit the high resistivity state, strongly limiting the potential applications. By contrast, the monolayer 1T-TaSe₂ is a Mott insulator at room temperature,⁵⁵ which gives an interesting perspective for the fabrication of memristive devices.

Finally, with both superconductivity, reported up to 3.8 K,¹⁰⁰ and a Mott insulating phase, up to 530 K, in addition to the standard metallic behavior, TaSe₂ appears as a very versatile material.

1.1.3.b Tantalum diselenide

As most of the group V TMDCs, the energy difference between the 1T and 1H monolayers is small which means that both are easily produced. In addition, the different stacking possibilities for the H-monolayer, combined with the existence of mixed 1T and 1H compounds make TaSe₂ one of the dichalcogenide with the largest number of reported polytypes.²²

The phase stability of the bulk compounds has already been established in the 1960s and the resulting phase diagram is reproduced Fig. 1.10. From this, it is clearly seen that the 1T phase is stable only at high temperature while two different H-phases are stable at room temperature, namely the 2H_a and 4H_c. In addition, 4H_b and 6R polytypes, which are composed of alternating 1T and 1H layers, are stable at intermediate temperatures. Finally, the 3R phase is metastable at every temperature but can result from the conversion of 1T into 1H layers at low temperature,¹⁰¹ or is usually produced in the presence of a small excess of Ta atoms,¹⁰² as for the 2H_b¹⁰³ and 4H_a phases¹⁰⁴ which are other stacking sequences of H-layers.

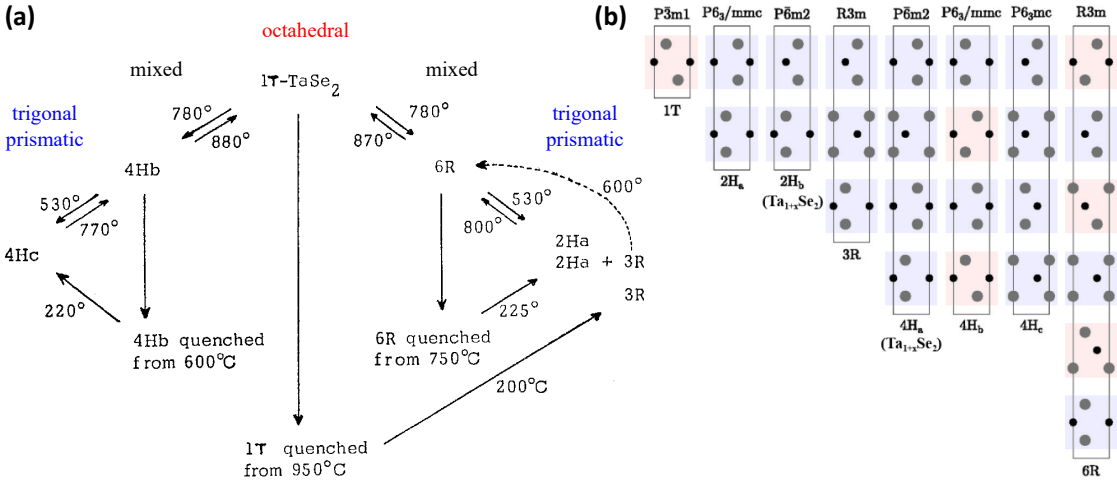


Figure 1.10: (a) Phase transitions in bulk TaSe₂, reproduced from Wilson *et al.*³². (b) TaSe₂ polytypes, adapted from Katzke *et al.*²².

The electronic properties and CDW of the different polytypes have been summarized in Table 1.2. Despite being metastable at room temperature, the 1T phase has been the most studied because it exhibits a $\sqrt{13} \times \sqrt{13}$ CDW which is commensurate up to 473 K.¹⁰⁵ 1T-TaSe₂ is metallic at every temperature, but its surface is a Mott insulator below 250 K.¹⁰⁶ In monolayer, though, it has been shown to be insulating well above room temperature.⁵⁵ It should be noted that the true origin of the gap in 1T-TaSe₂ is still under debate,¹⁰⁷ but this question is beyond the scope of this work so it will be referred as a Mott gap for convenience.

By contrast, the H-phases only undergo CDW transitions below 122 K, but they also exhibit superconductivity. Interestingly, the critical temperature for superconductivity is lower in the

Phase	Electrical properties	Charge density waves
1T	Mott insulator < 530 K ⁵⁵ (ML only)	$\sqrt{13} \times \sqrt{13}$ (CCDW < 473 K, ICCDW < 600 K ¹⁰⁵)
2H _a	SC < 0.14 K ¹⁰⁸	$\sqrt{3} \times \sqrt{3}$ (CCDW < 90 K, ICCDW < 122 K ¹⁰⁵)
3R	SC < 0.6-1.6 K ^{109,110}	$\sqrt{3} \times \sqrt{3}$ ¹⁰⁹ (ICCDW < 90 K, weak ¹¹⁰)
4H _a	SC < 2.9 K ¹¹¹	$\sqrt{3} \times \sqrt{3}$ (< 106-115 K ^{104,111})
4H _b		$\sqrt{13} \times \sqrt{13}$ (CCDW < 410 K ¹⁰⁵) plus $\sqrt{3} \times \sqrt{3}$ (ICCDW < 75 K ¹⁰⁵)
6R		Similar to 4H _b ¹¹²

Table 1.2: Electrical properties and CDW in TaSe₂ phases. If not specified, the compounds are metallic. SC: superconducting CCDW: commensurate CDW. ICCDW: incommensurate CDW.

2H¹⁰⁸ phase compared to the 3R^{109,110} and 4H_c¹¹¹ ones. Many studies have improved the critical temperature in different TaSe₂ polytypes, including 1T, through doping,^{113,114} alloying¹¹⁵ and self-intercalation.^{100,104} From this, it appears that any source of disorder may in fact be beneficial to the superconductivity because it tends to suppress the competing CDW,¹¹⁶ or more exactly its commensurability.¹¹⁷

Finally, the 4H_b and 6R polytypes combine properties of both 1T and 1H layers, with the coexistence of two CDWs.

1.1.4 Electrical contacts on 2D-materials

The importance of good contacts has been highlighted for the use of semiconducting dichalcogenides in electronic applications. In theory, the quality of a semiconductor contact depends on the height of the Schottky barriers, which are determined through the Shottky-Mott rule,¹¹⁵

$$\delta_n = \Phi_M - X_{sc} \quad (1.1)$$

$$\delta_p = X_{sc} + E_g - \Phi_M \quad (1.2)$$

where δ_n and δ_p are the energy barriers for electrons and holes respectively, Φ_M is the metal work function, X_{sc} is the semiconductor electron affinity and E_g the semiconductor band gap. However, this is rarely valid because of metal induced gap states that are unavoidable at metal-semiconductor junction. In addition, the direct evaporation of 3D metals on 2D materials usually causes damages as shown in Fig. 1.11 (a). As a result, the Fermi level is almost pinned at the semiconductor-metal interface and the barrier height is nearly independent on the metal work function.¹¹⁵ To overcome this issue, many strategies have been employed, which can be divided into two categories as summarized in Table 1.3.

Strategies	Reducing Fermi-level pinning	Opting for in-plane Shottky barriers
3D metals	Flat metal contacts Passivating buffer layer	Edge contacts Hybridization of the underlying 2D
2D metals	2D buffer under a 3D metal Vertical 2D-heterostructures	Seamless metal-semiconductor junction

Table 1.3: Summary of the strategies used to decrease the contact resistance with semiconducting TMDCs.

The first one consists in reducing the Fermi-level pinning by preventing the formation of surface states. As an illustration, the intercalation of a thin insulating layer, made of oxide^{118,119} or LiF,¹²⁰ has been shown to lower the contact resistance. It has also been observed that conventional metals damage less 2D layers when they are deposited by mechanical exfoliation¹¹⁵ or onto a removable polymer buffer layer,¹²¹ resulting in an atomically flat 2D/metal interface with a preserved vdW gap on top of the 2D material (Fig. 1.11 (b)). In this regard, the use of 2D materials appears as a straightforward way to achieve smooth interface, either through the introduction of a thin 2D buffer layer under the 3D metal, as demonstrated with Co/hBN¹²² and Ag/graphene¹²³ contacts, or using the 2D material as a whole contact,^{92,124,125} the TMDC family providing a large choice of metals and semi-metals. If this approach largely prevents the Fermi-level pinning, the vdW gap and, at a larger extent, the insulating buffer layers, add a tunneling barrier as a downside.

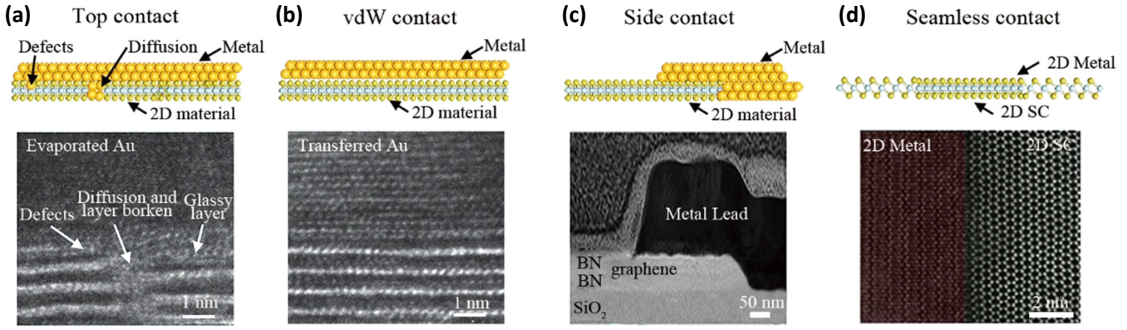


Figure 1.11: Various contact strategies, reproduced from Chen *et al.*¹²⁶.

The second approach consists in transferring the Schottky-barrier from a vertical vdW interface to an in-plane covalent one. Using 3D contacts, it is genuinely achieved by edge contacts, as illustrated in Fig. 1.11 (c), taking advantage of the dangling bonds at the termination of the foil to covalently connect the 2D-layer.¹²⁷ However, a similar outcome can also be obtained in top contacts when a strong hybridization of the TMDC with the metal occurs, resulting in the metallization of the underlying layers.^{128,129} The Schottky-barrier is no longer between the metal and the metallized TMDC, but between the latter and the pristine TMDC instead. Finally, both the hybridized and edge contacts result in a lateral junction and benefit from the suppression of the vdW barrier as well as the superior in-plane conductivity of the TMDCs.

It is also possible to combine this strategy with the use of a 2D metallic material by making a lateral metal-semiconductor junction as depicted in Fig. 1.11 (d). This contact is called seamless because it enables to minimize the creation of defects using two materials that have a similar structure.¹²⁶ Practically, it has been fabricated using a two-step growth,¹³⁰ or by locally converting the semiconducting material into a metallic one through a phase transformation from 1H into 1T in group VI TMDCs,¹³¹ a chemical reaction from MoS₂ into Mo₂C,¹³² or a thickness variation in PtSe₂.¹³³

Finally, a low contact resistance is obtained by associating a low(high) work function metal to n(p)-type material, provided that one of the above strategies is employed to overcome the Fermi-level pinning.

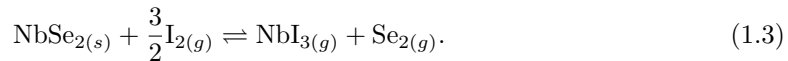
1.2 Elaboration of transition metal dichalcogenides

For many of the aforementioned properties and their use in applications, the material quality is crucial. The latter strongly depends on the elaboration method. In this section, the growth of millimeter scale crystals is presented first because it has enabled most of the advances with TMDCs thanks to a small quantity of defects. Then, the methods to obtain thin layers, either

by exfoliation of the bulk crystals (top-down approach), or by growth methods (bottom-up) are presented in the perspective of large scale applications, also calling for a control of the thickness and a uniform coverage over large areas.

1.2.1 Synthesis of bulk TMDC crystals

The growth of pure dichalcogenide single crystals has been made possible in the early 1960s with the development of the chemical vapor transport (CVT) method for the growth of material with high melting point.¹³⁴ The process is illustrated in Fig. 1.12 (a) and can be described as follows. First, the precursors are introduced in a sealed chamber, usually a quartz ampule with typically few grams per litre of the transport agent.¹³⁵ The precursors may be the pure elemental constituents, introduced in the desired stoichiometry,¹³⁶ or a powder of the compound, which is synthesized first to ensure a perfect homogeneity.^{137–139} Then, the ampule is placed in a two-zone furnace so that the precursor evaporates in the high temperature zone and is transported by a transport agent to the low temperature zone where it crystallizes. The transport agent is not supposed to be incorporated in the crystal hence a small amount of it can transport a large quantity of material through many cycles. The most common transport agents are halogens since volatile metal halide compounds can be formed based on the following reaction¹⁴⁰



I_2 has been the most common choice, essentially for practical reasons since it is less toxic and solid at room temperature.¹³⁵ However Br_2 and, in rare occasions, Cl_2 ¹⁴¹ have also been used, especially with Mo and W compounds for which I_2 has been less successful.^{142,143} Alternative halogen sources such as ammonium halides (NH_4Cl , NH_4Br , NH_4I) have been proposed but seemed less effective, probably because they release undesired gaseous species.¹⁴³ Transition metal halides MCl_5 ¹⁴⁴ and chalcogen halides SeCl_4 and TeCl_4 ¹³⁵ genuinely overcome this issue since they contain only the elements involved in the reaction. Finally, excess S¹³⁶ and Se^{135,139} have also been shown to promote transport alone, avoiding halogen contamination. Depending on the growth conditions and transport agent, different doping types have been obtained^{139,145} but this can also be achieved by introducing dopants in the initial charge.¹⁴¹

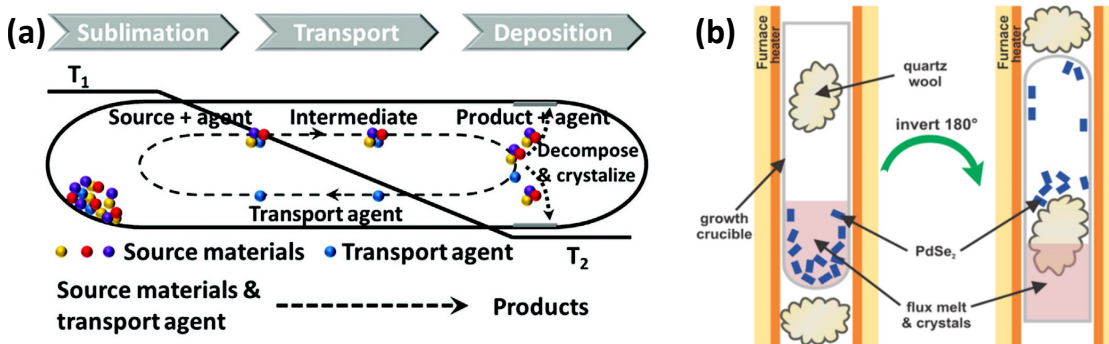


Figure 1.12: (a) Principle of the CVT, (b) flux method.

The CVT appears thus as a versatile tool for growing millimeter-large TMDC crystals, however the interest has slightly declined in the last decades in favor of the flux method. The latter can be described as an equivalent of CVT that involves liquid instead of vapor. The elemental precursors are dissolved in a solvent, called flux, which is slowly cooled to induce the crystallization. The flux should have a low melting point and a high boiling point, and must not form stable compounds with the reactants.¹⁴⁶ For TMDC synthesis, Sn,¹⁴⁷ CuSe¹⁴⁸ or $\text{Na}_x\text{K}_{1-x}\text{Cl}$ ^{149,150} fluxes have been used. As an alternative, the chalcogen is introduced in large excess and used as

a solvent in the self-flux variant of this technique.^{42,151,152} A single temperature is necessary in this case, typically between 850 °C⁴² and 1100 °C.¹⁵³ After a homogenization time, the melt is cooled at very slow rate, only few degrees per hour,¹⁴⁷ making the whole process duration comparable to CVT. Finally, the crystals are filtered from the flux, for instance using centrifugation, as represented in Fig. 1.12 (b), or dissolution of the melt.^{147,149,150}

The crystals grown by the flux method have shown a superior quality, with a density of defects of 10^{11} cm^{-2} based on STM images,¹⁵³ which is one order of magnitude below those grown by CVT.¹⁵⁴ This resulted in extraordinary properties, such as a huge low-temperature carrier mobility of $167\,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and a magnetoresistance of 1 750 000 % reported in WTe_2 ,¹⁵¹ which would not be achievable without this extremely low defect density. However, as downsides, both methods require long growth at high temperature and mostly produce thick crystals of large but uncontrolled dimensions, requiring further processing for integration as discussed next.

1.2.2 Transfer techniques

A control over the thickness is effectively mandatory for many applications. This is especially true for some TMDCs that reveal their properties when the number of layers is decreased. For instance, 1T-TaSe₂ becomes a Mott insulator in monolayer, whereas in group VI TMDCs, the bandgap becomes direct. In addition, the layers usually have to be deposited on a given substrate or structure to be integrated into a device. Hence, exfoliation and transfer techniques have played a significant role in the development of 2D materials physics.

1.2.2.a Liquid-phase exfoliation

It has long been known that 2D-materials could be dispersed in liquids.^{155,156} In the case of TMDCs, the exfoliation is facilitated with the choice an appropriate solvent, along with the use of ultrasonication to dissociate the layers and centrifugation to eliminate the unexfoliated material.¹⁵⁷ This process, however, produces nanosheets of small lateral size¹⁵⁸ because of the fragmentation of the layers during the sonication and centrifugation steps.¹⁵⁹

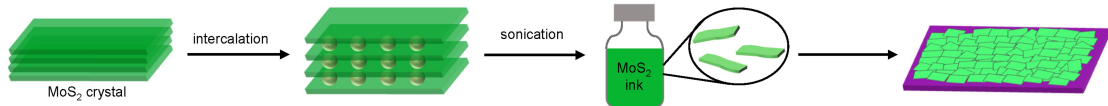


Figure 1.13: Schematics of the liquid exfoliation process using ion intercalation, adapted from Lin *et al.*¹⁶⁰.

An efficient way to force the layer exfoliation consists in the intercalation of ions as depicted in Fig. 1.13. The use of Li ions seems particularly convenient, due to its inclination to intercalate TMDC crystals¹⁶¹ which are easily dispersed in water afterwards.¹⁶² This method produces much larger flakes¹⁵⁸ and favors the exfoliation of monolayers. However, it also induces a phase change from 2H to 1T in MoS_2 .¹⁶³ This phenomenon has been explained by the modification in the phase stability upon electrostatic doping because of their different ionization energies.¹⁶⁴ To prevent this effect, it has been proposed to replace Li by large ammonium molecules which induce less undesired doping.¹⁶⁰ In this case, however, the intercalation must be electrolytically triggered as it was in the first studies.¹⁶⁵

Finally, in spite of some advances, the size of flakes produced by liquid exfoliation remains small, which inevitably degrades the properties. Thanks to its high scalability and a low cost, this technique can still find some applications for which a uniform surface coverage is more important than a good crystalline quality. However, concerning electronics, the rapid progress in the integration of 2D-materials has essentially been unlocked by the mechanical exfoliation instead.

1.2.2.b Mechanical exfoliation

The possibility of isolating a single monolayer of graphene was demonstrated by Novoselov *et al.* using mechanical exfoliation.⁷ At that time they did not discuss reproducibility of their transfer technique, hence following studies were dedicated to the improvement of the exfoliation yield especially toward larger flakes.¹⁶⁶ The exfoliation techniques can be applied to other 2D materials for which the adhesive strength of the vdW interaction is lower compared to their in-plane tensile strength.¹⁶⁷ A typical exfoliation procedure is represented in Fig. 1.14 (a). First the material is attached to an adhesive carrier surface, usually a polymer, to be pulled off from the bulk. Then, the layers are released on the target surface through the debond, usually thermally activated,¹⁶⁸ or dissolution of the carrier. During both stages, a particular care should be given to remove slowly the carrier with a small angle to prevent the formation of cracks. Still, the number of transferred layers is generally uncontrolled and the size of the flakes very small. In addition, the polymers leave residues that require additional cleaning steps to be removed.¹⁶⁹

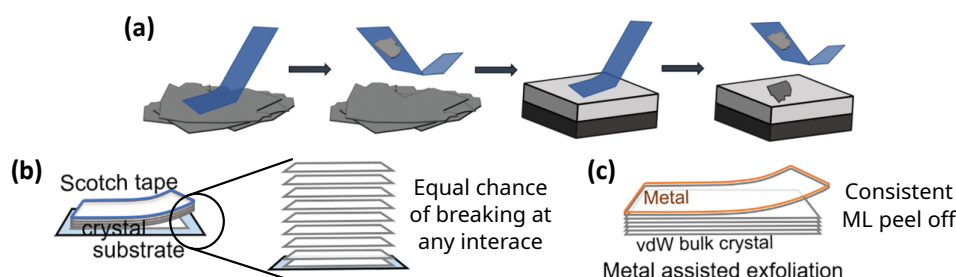


Figure 1.14: (a) Basic adhesive tape exfoliation procedure, reproduced from Yang *et al.*¹⁷⁰, (b-c) Comparison between polymer and metal exfoliation, adapted from Liu *et al.*¹⁷¹.

To circumvent these issues, it has been proposed to use metals instead of polymers.¹⁷² This method was first introduced by Magda *et al.* who exploited the strong adhesion of MoS₂ on gold to isolate a large monolayer flake.¹⁷³ The latter was then transferred on the desired substrate using tape while the metal was chemically etched. In this first report, the extra MoS₂ layers were lost, whereas Shim *et al.* developed a process to consistently cleave each individual layer of a thick 2D-material by controlling the crack propagation thanks to the strong interaction of graphene with Ni.¹⁷⁴ In the case of TMDCs, gold has been the prevailing choice since it provides a sufficient adhesive energy to exfoliate most 2D-materials,¹⁷⁵ and it is less affected by the oxidation which significantly lowers the yield for other metals.¹⁷⁶ To avoid the damage caused by a direct evaporation of gold on a TMDC, it has been proposed to transfer the Au film from a flexible substrate.¹⁷⁷ This approach also enables the metal to be patterned and used as electrical contacts in the transfer via contact method.¹⁷⁸

Finally, in few years the many limitations of the mechanical exfoliation have been overcome, and large monolayers have been transferred with minimal damage and residues. Still, progress remains to be made toward automation, but more importantly, the flake size is also limited by the availability of large crystals. For this reason, the mechanical exfoliation is nowadays commonly used to transfer layers grown using chemical vapor deposition (CVD).

1.2.3 Chemical vapor deposition

The CVD regroups the thin films synthesis methods that involve chemical reactions in vapour phase. Unlike the CVT method, presented in Section 1.2.1, which occurred in a sealed environment, CVD reactors enable the introduction and exhaust of gaseous species and a control over the pressure. Another difference is the presence of a substrate as thin layers are usually targeted in this case. Depending on the precursor choice, the solid-source and gas-source CVD are distinguished, but many variations of these techniques were reported, among which atomic layer deposition (ALD) is worth mentioning.

1.2.3.a Solid-source CVD

In the case of solid sources, metal oxide powders are generally used as precursors^{179,180} since the pure transition metals have very high sublimation temperatures. Similarly to the CVT case, the addition of alkali metal halides (e. g. NaCl, KI) also promotes their evaporation.^{181,182} More occasionally, transition metal halides (e. g. NbCl₅, WCl₆) were directly used.^{183,184} The metal and chalcogen precursors are disposed in a different position of a tube furnace so that their temperature can be separately controlled.¹⁸⁵ Then, an inert carrier gas, usually Ar^{179,186} or N₂,¹⁸⁰ sometimes mixed with H₂,¹⁸² flows from the chalcogen precursor to the metal precursor and the substrate nearby in order to transport the species. It maintains a control over the pressure and provides another tuning knob.

Typical CVD-grown TMDCs form micrometer-large triangular flakes, that eventually merge to form a polycrystalline film. However, the full coverage of the substrate with uniform thickness has appeared challenging. By tuning the Mo partial pressure, Yu *et al.* have shown a sufficient control of the layers thickness up to 4 ML thanks to the influence of the substrate.¹⁸³ However the grain size was only few tens or hundreds of nanometers in this case. The deposition of reduced graphene oxides and other aromatic molecules have been used to promote the lateral growth on amorphous SiO₂ substrate.^{187,188} Alternatively, the addition of Cu, first introduced by Liu *et al.*,¹⁸⁹ hampers the growth of a second layer, resulting in 30 μm -large monolayer flakes.¹⁹⁰ Other strategies to increase the grain size included, for instance, the introduction of a NiO barrier to reduce the Mo flux,¹⁹¹ or the etching of the unstable nucleus using a O₂ flux.¹⁹² In the last case, grain size up to 350 μm have been demonstrated, but the full coverage was not possible since the growth rate decreased with time. Another common issue is the spatial non-uniformity resulting from the precursor concentration gradient.¹⁷⁹ Where the flux is too large, the grain size is reduced because of the high nucleation density, whereas it is limited by the insufficient coverage when it is too low.¹⁸⁶

Finally, despite promising results concerning the grain size, this technique lacks of scalability due to the difficulty to obtain a large-scale coverage, as well as the high growth temperatures, typically between 650 and 850 °C,¹⁸² which limits the choice of substrates and therefore may require the use of transfer techniques for the integration of the layers into devices.

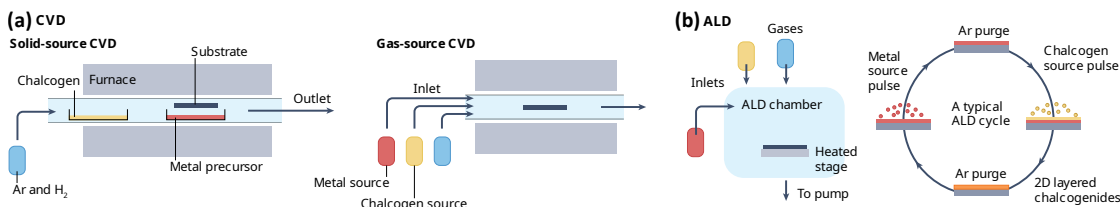


Figure 1.15: (a) Solid-source CVD, (b) gas-source CVD, (c) ALD, reproduced from Zhang *et al.*¹⁸⁵.

1.2.3.b Gas-source CVD

The gas-source variant of the CVD is intended to overcome the difficulty to maintain a stable and uniform precursor flux from a solid source using gaseous reactants instead, whose individual partial pressures can be finely adjusted using a mass flow controller.¹⁸⁵ Because metal-organic precursors are the most common, this technique is indistinctively referred as MOCVD. As the precursors can be evaporated or bubbled outside the chamber, a lower growth temperature can be used, but it should remain sufficient to allow the precursor decomposition.¹⁹³ For this reason, hot wall reactors, in which a gas phase reactions can occur upstream, are distinguished from the cold wall systems, in which an induction heater confines the reactions close to the substrate.¹⁹⁴ Two-temperature-zone tubes were also used to form large grains at low temperature, but this configuration resembles the solid source case and suffered from the same spatial inhomogeneity.¹⁹³ Instead, most MOCVD studies have highlighted the ability to grow films of controlled thickness

and uniform coverage at wafer scale, making this technique suitable for batch fabrication.¹⁹⁵ Apart from smaller grain size, the main downside is the carbon contamination, that has been mostly reported when organic chalcogen precursors were used to replace the toxic H_2S and H_2Se gases^{194,196,197} but could also arise from the metal precursor.¹⁹⁸

Various alternative CVD methods have been proposed to increase the grain size, including the addition of H_2O vapor¹⁹⁸ or the use of liquid precursors dip- or spin-coated prior to the growth^{199,200} or supplied by the capillary action.²⁰¹ Others have focused on the improvement of the thickness uniformity and increased of the growth rate.²⁰² In the next section the ALD is presented as a rare method capable of a conformal coverage.^{203,204}

1.2.3.c Atomic layer deposition

ALD differs from other CVD methods by the sequential supply of the precursors.²⁰³ Each of them is introduced separately, so that it adsorbs and reacts on the surface until all reaction sites are consumed or protected by the steric repulsion of the other adsorbed molecules. Then the excess precursor and by-products are purged so that the next precursor only reacts with the surface groups deposited at the previous stage. This cycle enables the growth of a maximum of one monolayer of the desired material, and may be repeated as many times as required. This self-limiting process is expected to provide a very precise control of the thickness with large-area uniformity²⁰⁴ and the possibility of covering non-flat surfaces.²⁰⁴ Nevertheless, in practice, much less than a monolayer may be grown because of the steric hindrance of the molecules,²⁰⁵ substantially lowering the growth rate and the control over the thickness. The second particularity of the ALD process is the ability to deposit at very low temperature, which makes it compatible with back-end of line processing and temperature sensitive substrates such as polymers for flexible electronics. To reach very low growth temperatures, the assistance of a plasma has been commonly used, enabling the growth of crystalline TMDCs down to 100 °C, however at the cost of a very small grain size.²⁰⁶

Finally, in the review of the CVD methods, a general trend of a high crystallinity at high growth temperature versus a large-scale uniformity at low temperature has been outlined. The physical vapor deposition (PVD) presented next mostly follows the same scheme.

1.2.4 Physical vapor deposition

PVD designates thin film elaboration methods that involve phase changes through an intermediate vapor phase, without chemical reactions with other species.

In the most straightforward strategies, the bulk form of the material is used as a single precursor, which is sublimated and deposited on the desired substrate.¹⁸⁵ As a simple option, MoS_2 and WS_2 have been thermally evaporated in a tube furnace under Ar flux in a configuration similar to the solid-source CVD.^{207,208} However this method requires high growth temperature and is not applicable to every material. For instance, in the growth of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloys, elemental Se have been added to compensate for the MoSe_2 decomposition into Mo_3Se_4 .²⁰⁹ To circumvent the high sublimation temperatures of these materials, alternative methods have been employed.

Among them, the pulsed laser deposition method uses high-power laser pulses to ablate the material from a target. The growth can occur in vacuum, however a background Ar pressure has been shown to be beneficial for MoS_2 and WS_2 growth.^{210,211} For this technique, optimized growth temperatures were reported from 450 °C²¹² to 800 °C.²¹⁰ Despite the deposited material is expected to have the same composition than the target, a target with excess S content has been required to obtain a perfectly stoichiometric MoS_2 film at 700 °C.²¹³

In the radio frequency magnetron sputtering method, the vaporization of the TMDC target is caused by the impacts of an ionized inert gas, usually Ar. Crystalline WS_2 have been successfully grown at 300 °C,²¹⁴ and MoS_2 at 400 °C while it was amorphous at room temperature.²¹⁵ In addition, the MoS_2 layers were not stoichiometric, possibly because the light S atoms are

preferably sputtered by Ar. Due to the poor quality of the as-grown samples, a post growth annealing has been used after sputtering in most of the studies. It is usually performed under Ar with a chalcogen supply^{216,217} although it has also been shown to be beneficial without.²¹⁸ Since the relevance of a growth at low growth temperature is hindered by the need of this annealing step, an option to recrystallize the film using electron beam irradiation has been proposed.²¹⁹ Moreover, these techniques require the availability of the bulk form of the desired material in sufficient quality.

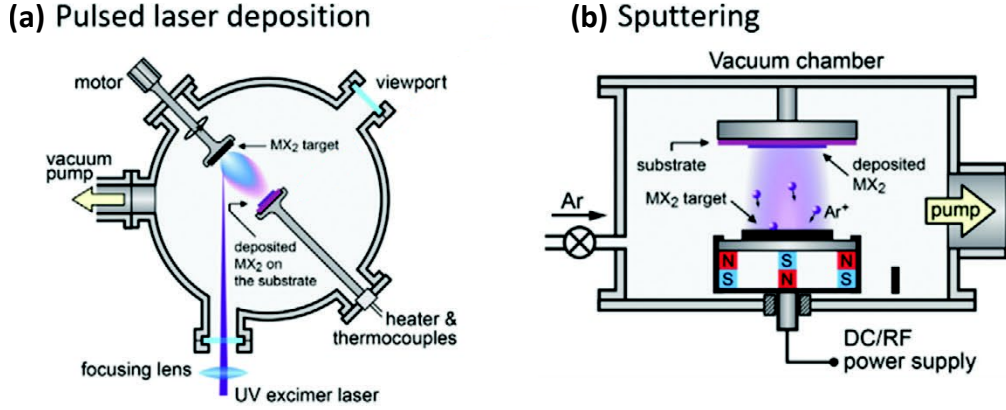


Figure 1.16: (a) Schematics of the PVD and (b) magnetron sputtering techniques, reproduced from Mattinen *et al.*²⁰³.

Alternatively, the elemental constituents may be supplied from different sources, either simultaneously or during two distinct steps. A single step growth has been achieved with the magnetron sputtering of a Mo target in a S atmosphere.²²⁰ Besides that, this is mostly the strategy used in MBE, a versatile tool that allows several elements to be co-deposited in ultra-high vacuum. In this case, the sublimation of refractory metals is generally achieved using an e-beam evaporator, while effusions cells are commonly used for Se and Te. The high vapor pressure of sulfur makes it less suitable for MBE although a solution consists in using dissociated H₂S in a plasma cell in the so-called gas source MBE.^{221,222} The use of high purity elements and vacuum conditions makes this technique expensive, but it allows the growth of high purity layers and enables a high controllability. In addition, it achieves an excellent stoichiometry and a good control of the thickness thanks to the three-temperature method. For this, the substrate temperature is comprised between the sublimation temperature of the two constituents, so that the growth is limited by the less volatile.²²³ In the case of TMDCs, the high melting point of transition metals and the high vapor pressure of chalcogens make this range particularly large, as demonstrated by successful growths reported from 170 °C²²⁴ to 900 °C.²²⁵ The low growth rate explains that a coherent epitaxial growth is more easily maintained compared to other PVD methods, but the absence of covalent bonds makes a high crystallinity still difficult to achieve for 2D materials as will be discussed throughout this manuscript.

As for two step growths, the chalcogenization of a predeposited metal coating has been proposed as a simple way to achieve wafer scale coverage. Transition metals are first deposited at low temperature by sputtering²²⁶ or e-beam evaporation,²²⁷ and then annealed at high temperature under a Ar/H₂S gas mixture or chalcogen vapor.^{228,229} Alternatively, a low temperature sulfuration has been demonstrated using plasma enhanced CVD for temperature sensitive substrates.^{230,231} It has been noted that the deposition order has an influence, since the deposition of Se first resulted in less-oriented TaSe₂ grains on Au(111) substrate possibly due to interfacial Se.²³² If the method enables the horizontal growth of thin layers, thick layers tend to be vertically oriented instead.²²⁸ In addition, surface roughening caused by metal agglomeration is an issue that has been solved by a chalcogen deposition at very low temperature prior to an annealing under thermally cracked S and Se.²³³ Recently, a new method called hypotaxy used a

reported graphene template on the metal film to achieve single crystal TMDCs growth during the chalcogenization step.²³⁴ The graphene monolayer being evaporated at the end of the process, this opens the path of growing high quality TMDC on any substrate.

1.2.5 Comparison of the growth techniques

Finally, a large panel of elaboration techniques has been reviewed and a summary of their typical characteristics is presented in Table 1.4. The transfer methods are not included since they require one of these techniques to produce the material first.

	CVT/ Flux	Solid-source CVD	MOCVD	MBE	PLD/ sputtering
Temperature range (°C)	900-1200	600-850 ¹⁸²	300-750 ²³⁵	200-900 ^{224,236}	300-800 ^{210,214}
Grain size	1-10 mm	0.1-300 μm	0.04-100 μm ^{193,221}	20-500 nm ²³⁶	5-20 nm ^{213,214}
Typical defect	chalcogen vacancies	chalcogen vacancies	carbon contamination ¹⁹⁷	grain boundaries	low crystallinity
Coverage	poor	challenging	variable	uniform ²³⁷	uniform ²¹¹

Table 1.4: Summary of the characteristics of the different elaboration methods.

As previously discussed for CVD and PVD methods, it appears clearly that the techniques operating at high temperature achieve good crystallinity but at the cost of a non-uniform coverage. Note that the variability in the results obtained in MOCVD is typically related to the different system configurations, either similar to solid-source CVD or MBE.

If the good device performances demonstrated from TMDC flakes produced by CVT, flux or CVD confirm the superior quality of the materials grown with these methods, a transfer technique was generally employed to extract the desired number of MLs from a bulk crystal, or the devices were directly fabricated on a single flake. These methods are obviously not scalable. On the other hand, few reports have demonstrated operating devices from a wafer-scale continuous layer.

Among the methods able to control the thickness over a large area, MBE offers several advantages. First, it covers a wide temperature range compared to other techniques, which is made possible because the substrate temperature is decoupled from the precursor evaporation. In addition, the use of a high vacuum environment and high purity elemental sources avoids the contamination arising from the halogen transport agent or metal-organic molecules. Up to now, the results have been modest in term of grain size, however the high controllability opens rooms for improvements.

Therefore, MBE is now considered to grow HfSe₂ and TaSe₂, and a detailed review of the existing results concerning the growth of these two materials is presented next.

1.2.6 State of the art of TaSe₂ and HfSe₂ growth by MBE

1.2.6.a Growth of TaSe₂

The experiments that have reported TaSe₂ growth by MBE are listed in Table 1.5. The monolayers have always been grown on graphitized SiC substrates, and highlight a clear trend with respect to the temperature. The 1H phase is always formed at low temperature while the 1T one appears at high temperature. However, the transition temperature of 490 °C found by Nakata *et al.*²³⁸ is significantly lower than the one reported by the group of Crommie.²³⁹ Although it seems unusual that a metastable phase, the 1T one, is favored at high growth temperature, this is inconsistent with the results obtained using CVD.²⁴⁰ With this technique, the transition temperature is around 750 °C, closer to the phase stability in bulk (800 °C).¹⁰¹ It is thus possible that the energy difference between the 1T and 1H phases is reduced with increasing

temperature. Then, the growth of the 1T phase may be kinetically favored in MBE owing to a greater inclination for growing metastable phases, leading to a lower transition temperature.

Substrate	Temperature (°C)	Thickness (ML)	Phase	Author (Year) Reference
graphene/SiC	450	1	1H	Nakata (2018) ²³⁸
	490		1H+1T	
	560		1T	
graphene/SiC	550	1	1H	Ryu/Crommie (2018) ²⁴¹
graphene/SiC	660	1	1T+1H	Chen/Crommie (2020) ²⁴²
graphene/SiC	660	1	1T	Ruan/Crommie (2020) ²⁴³
graphene/SiC	450	1	1H	Lee/Crommie (2024) ²³⁹
	600		1H+1T	
	750		1T	
graphene/SiC	650	1	1T	Lin (2020) ¹⁰⁷
MoS ₂ , MoTe ₂ , ...	300-340	3-10	1T-like	Shimada (1991) ²⁴⁴
... SnSe ₂	420-650		1H-like	
	410		4H _b +6R	
GaAs-Se	495	16	2H _a +2H _b	Shimada (1996) ²⁴⁵
	590	15	2H _a +2H _b	
AlN/Si	450+ ann.650	4	2H+1T-like	Tsoutsou (2016) ¹⁸
HfSe ₂ /AlN/Si			2H+1T-like	
MoSe ₂ /AlN/Si			2H	
Al ₂ O ₃	500+	6, 10, 18, 52	3R Ta _{1+x} Se ₂	Tanaka (2020) ¹⁰⁰
SiC	ann.700	6, 10, 50		

Table 1.5: Summary of the MBE-grown TaSe₂ layers reported in the literature.

Looking at the multilayers, various substrates and thicknesses have been explored. However, the trends are less evident because many different stackings have been reported, and sometimes the polytypes could not be precisely identified. Obviously, the 1T phase does no longer dominate at high growth temperature. Looking at the experiments of Shimada *et al.*^{244,245}, it seems to be rather the opposite. In these cases, 1T clusters are believed to be quenched in the layers at low temperature while they are converted into the H phases at higher temperature. This indicates a strong influence of the thickness that will have to be clarified in the following experiments. It can also be noted that a post-growth annealing was used in the experiments of Tsoutsou *et al.* and Tanaka *et al.*, which could help toward the formation of purer materials. Especially, the 3R phase is supposed to be obtained by annealing the 1T phase in bulk¹⁰¹ but it has also been mentioned that excess Ta atoms can favor its formation.¹⁰⁰

1.2.6.b Growth of HfSe₂

By contrast to TaSe₂, very few MBE growths have been reported for HfSe₂ as shown in Table 1.6. The influence of the thickness, growth temperature or substrate were only scarcely discussed. Yue *et al.* noticed that the film is smooth and well-aligned with respect to the substrate in monolayer whereas it becomes rough and polycrystalline as the thickness increases.²⁴⁶ They also showed that layers grown at higher temperature are more resistant to oxidation, suggesting a better crystalline quality. Then, Aretouli *et al.* reported a disordered surface as-grown whose crystallinity was improved after annealing.²⁴⁷ Finally, Li *et al.* have chosen an amorphous surface on purpose to get a polycrystalline material.²⁴⁸ When it was possible to determine the polytype, only the 1T phase has been found, as expected for this material.

Substrate	Temperature (°C)	Thickness (ML)	Phase	Author (Year) Reference
MoS ₂ , HOPG	450-550	≈24	1T	Yue/Barton (2015) ²⁴⁶
MoS ₂ , HOPG	-	1-few	1T	Yue/Barton (2015) ²⁴⁹
AlN/Si	570+ann.810	6	1T	Aretouli (2015) ²⁴⁷
SiO ₂ /Si	750	5-15 nm	-	Li (2022) ²⁴⁸

Table 1.6: Summary of the MBE-grown HfSe₂ layers reported in the literature. HOPG stands for highly-oriented pyrolytic graphene

Still, the authors have not studied the crystallinity of these layers. Regarding the electronic properties, a resistive switching has been reported by Li *et al.*, but neither the resistivity nor the carrier mobility have been measured.²⁴⁸

1.3 Main guidelines for van der Waals epitaxy

In this section, the possible strategies to improve the growth of TaSe₂ and HfSe₂ by MBE will be reviewed based on the progress that have been made with other TMDCs. Even if the focus is made on MBE, some useful insights may also be taken from CVD and MOCVD experiments.

1.3.1 Influence of the growth parameters

Since one advantage of the MBE is the tunability provided by parameters such as the substrate temperature, flux ratios and the growth rate that can be controlled independently, it is of significant interest to know their respective influence on the crystal quality and film morphology. For this, a more fundamental understanding of the growth thermodynamics and kinetics is required.

1.3.1.a Morphology

In the general theory of epitaxy, three possible growth modes are identified depending on the surface and interface energy.²⁵⁰ In the Frank-van der Merwe growth mode, the epitaxial film grows layer-by-layer, resulting in a homogeneous thickness (Fig. 1.17 (a)). It corresponds to a complete wettability of the substrate by the film, which requires a lower surface energy for the film and the film-substrate interface than for the substrate alone. Conversely, if these conditions are not fulfilled, the Volmer-Weber growth mode takes place and results in the formation of isolated islands that do not cover the surface (Fig. 1.17 (b)). An intermediate growth mode, named Stranski-Krastanov, occurs when the film wets the substrate but is constrained by the lattice mismatch. In this case, a 3D growth appears after the deposition of a certain thickness (Fig. 1.17 (c)) because the elastic energy cost increases the interfacial energy. This effect is normally not expected in vdW epitaxy for which immediate lattice relaxation occurs.²⁵¹ Still, Zhang *et al.*⁴³ have calculated a slight increase of the PtSe₂ interlayer binding energy with thickness, consistent with the particularly large interlayer coupling in this TMDC,⁶² while a much smaller graphene-PtSe₂ interaction was predicted. In such case, a deposition of PtSe₂ layer on highly-oriented pyrolytic graphene (HOPG) is expected to form thick PtSe₂ clusters rather than an uniform layer, as confirmed by the observation of a 3D growth mode at high temperature.⁴³ It is worth noting that compared to the [0001] planes, which are free of dangling bonds in 2D materials, the surface energy of the lateral planes is much larger. This competing effect favors a 2D growth at low temperature, when the surface of the grains is sufficiently small compared to their borders.⁴³

In addition to this thermodynamic point of view, kinetic effects should not be overlooked. Compared to 3D materials, the absence of dangling bonds on a perfect 2D surface hinders the nucleation and promotes the diffusion of adatoms in vdW epitaxy. As a result, a significant

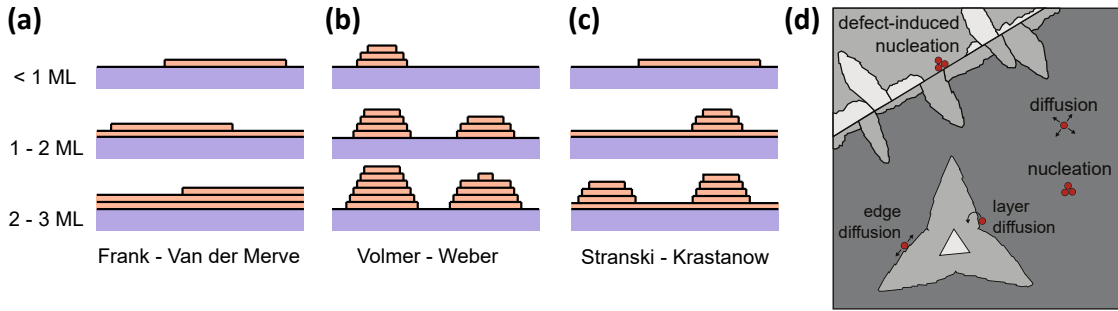


Figure 1.17: (a-c) Schematics growth modes, reproduced from Pohl *et al.*²⁵². (b) Illustration of the processes involved during vdW epitaxy, reproduced from Rajan *et al.*²⁵³.

number of grains may nucleate from the step edges, leading to more defects and a non-uniform coverage as illustrated in Fig. 1.17 (d).²⁵³ Also, if the layer is more defective than the substrate, the nucleation will be favored on the existing TMDC layers, resulting in multi-layer islands. In this regard, a sufficient chalcogen supply is required to avoid metal agglomeration, which inevitably induces 3D growth.²⁵⁴ To obtain a complete MoS₂ monolayer, a two-step MBE growth has been reported, consisting of a relatively short initial stage, not less than 3 hours though, at relatively low temperature, 750 °C still, to promote the nucleation, and followed by a slower coalescence stage in which the temperature was increased and the growth rate reduced to switch to a more thermodynamically controlled growth.²²⁵ This strategy is not dissimilar to the more widespread usage of a post growth annealing which is known to improve the morphology. For instance, Pacuski *et al.* have obtained an almost complete MoSe₂ monolayer coverage using a low growth temperature (300 °C) followed by a high temperature annealing (700-750 °C) to flatten the surface, and repeated the process several times.²⁵⁵ In both studies, the total growth duration was more than 10 h, so a new approach referred as nucleation-assisted growth was proposed.²⁵³ It consists in creating defects on the substrate before the growth, for instance using Ge evaporation on HOPG, so that it can serve as nucleation sites for the TMDC layer.

Although these methods were effective for monolayer growth, it should be noted that the case of few-layers, which is not well documented, seems not less tricky. In two different studies, a 3D growth has been reported to take place after few monolayers were deposited.^{224,256} For VSe₂ growth, the reduction of the substrate temperature down to 170 °C was successful to recover a 2D growth²²⁴ whereas for NbSe₂, it has been achieved through the interruption of the metal supply and the use of a cracking Se cell.²⁵⁶ The reasons behind these effects are not clear yet and will require further investigation.

1.3.1.b Grain size

Besides the coverage, the second bottleneck for TMDC growth is the poor crystallinity resulting from the high density of small nuclei that produces as many grain boundaries upon coalescence.

To address this, the most straightforward and explored strategy lies in the reduction of the nucleation density through an improved lateral diffusion of the adatoms. The chalcogen being usually provided in large excess, it concerns mostly the transition metal atom which remains much longer adsorbed on the surface.²⁵⁷ During this time, the adsorbed atoms diffuse until they reach either another adatom to form a nucleus, or a preexisting nucleus. The distance they can travel corresponds roughly to the average distance between two adatoms, and also to the distance between nuclei after enough of them have been formed. Therefore, the diffusion length is strongly dependent of the adatom density, which is an equilibrium between the number of impinging atoms, related to the growth rate, and the incorporated atoms, related to how fast they can move over this distance. The energy barrier for the atom diffusion, which depends on

many parameters including the surface and the atom itself,²⁵⁷ can be overcome by increasing the substrate temperature.

Thus, it is no surprise that multiple studies reported a decrease of the nucleation density with increasing growth temperature, and decreasing the growth rate.^{236,254,258} By contrast, the influence of the chalcogen on the metal diffusion is not evident. Rajan *et al.* found that a high Se/metal ratio increases the TiSe_2 and NbSe_2 grain size at 500 °C, when the Se desorption rate is important, while it has little influence at 300 °C.²³⁶ Besides, Yue *et al.* not only reported a decrease of the nucleation density at 500 °C under high Se flux, but also observed a reduction of the growth rate which was explained by the drop of the W sticking coefficient on HOPG.²⁵⁴ They calculated that a pure WSe_2 nucleus must contain at least 15 W atoms to be stable whereas a 3-atom metallic W nucleus is already stable at a similar temperature. Thus, they suggested that Se atoms prevents the formation of metal clusters that would act as nucleation sites.

Finally, these two studies have respectively demonstrated a monolayer flake as large as 600 nm for TiSe_2 growth at 600 °C,²³⁶ and a 8 ML-thick island of 1.2 μm ,²⁵⁴ confirming that a low nucleation density is favorable for the crystallinity. However, no continuous films were reported as it could be predicted from the previous section. This trade-off situation was perfectly illustrated by the comparison of CVD and MBE techniques, the former leading to in-homogeneous coverage and the latter suffering from low grain size. In the next section, however, a possible solution is proposed based on the ability of MBE to grow layers with relatively good in-plane alignment with the substrate lattice.

1.3.1.c In-plane alignment

TMDCs have a 3-fold symmetry, which means they are invariant by a rotation of 120°. Two grains with the same orientation can be expected to coalesce whereas a grain boundary will be inevitably formed otherwise. The most frequent situation is the specific case of two grains rotated by 60° as depicted in Fig. 1.18 (a), also called mirrors twins, since both are randomly formed on a hexagonal lattice. This issue is of significant importance since mirror twin boundaries induce mid-gap states²⁵⁹ and metallic conductivity²⁶⁰ in semiconducting TMDCs. In addition, the properties that emerge from the lack of inversion symmetry in 1H monolayers or 3R polytypes, such as the spin and valley polarization, can only be revealed in crystals having a single orientation.²⁶¹

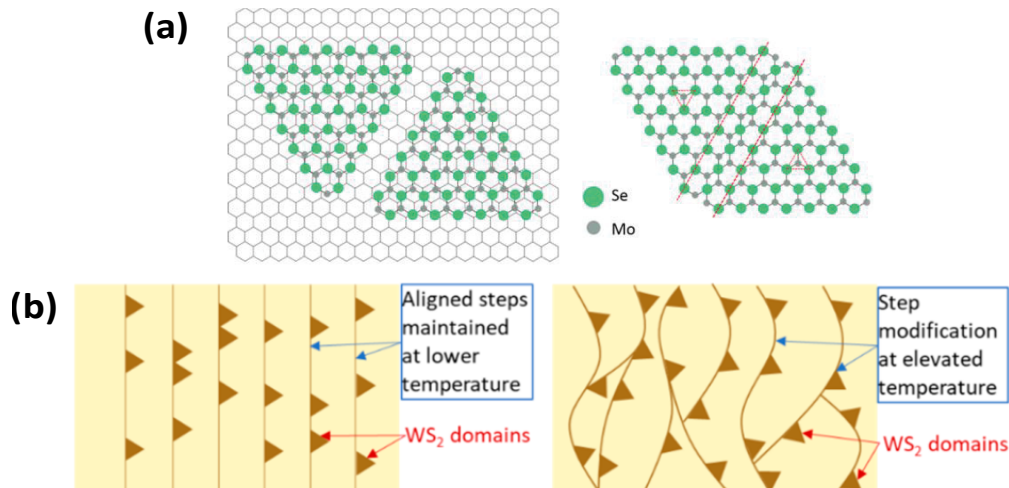


Figure 1.18: (a) Schematic of mirrors twins and the formation of a grain boundary after stitching, reproduced from Ma *et al.*²⁶², (b) Principle of the step-edge guided epitaxy, reproduced from Chubarov *et al.*²⁶³.

To avoid the grain boundaries, the choice of a substrate having the same symmetry as the layer is a determining factor. Still, because of the weak vdW interaction, grown 2D layers usually exhibit a large in-plane angular dispersion. A significant reduction of this residual misorientation has been shown by an increase of the growth temperature and reduction of the growth rate.²⁶⁴ Similarly, a huge improvement toward the suppression of mirror twins has been reported by increasing the temperature²⁶⁵ and chalcogen over metal flux ratio in CVD,²⁶⁶ and decreasing the metal flux in MBE.²²⁵ Such conditions are expected to favor the thermodynamics over the kinetics so that the most energetically stable configuration is predominantly formed. Apart from the substrate symmetry, the presence of atomic steps also has a strong influence on the grain alignment.²⁶⁶ To avoid a random nucleation, a control of the step orientation and density may be a necessity, as depicted in Fig. 1.18 (b).²⁶³ This can be achieved using substrates with a specific miscut angle along a desired direction.²⁶⁷ Note that the miscut breaks the rotational symmetry of the substrate, which explains that single oriented WSe₂ have been achieved indifferently on (100), (110) and (111) Au terraces from a highly misoriented foil.²⁶⁵

Besides, it has been shown that for Mo-dichalcogenides, the most stable form of mirror twin boundaries is Mo-rich.²⁶⁸ As a consequence, they are more likely to be formed in metal-rich conditions. For instance, they have been shown to emerge from the migration of S vacancies after an annealing at 700 °C²⁶⁹ or from the absorption of excess Mo at 350 °C.²⁷⁰ Conversely, thanks to the ability of the grain boundaries to migrate,²⁷¹ it could be possible to cure the inversion domain boundaries during a post-growth annealing in a chalcogen-rich atmosphere.^{272,273}

1.3.1.d Summary

In conclusion, the influence of the growth parameters in the aspects discussed above have been compiled in Table 1.7.

	Temperature	Growth rate	Chalcogen/metal ratio	Post-growth annealing
Morphology	Degrades	-	Improves	Improves
Grain size	Improves	Degrades	Improves	Improves
In-plane orientation	Improves	Degrades	Improves	Improves
Stoichiometry/Faultlessness	Degrades	Degrades	Improves	(Depends)

Table 1.7: Influence of the growth parameters on different figures of merit of the vdW epitaxy.

As already evidenced earlier, the temperature usually leads to a trade-off situation between an enhanced crystallinity and a degraded morphology because of the increase adatom mobility. In addition to the grain boundaries resulting from an uncontrolled in-plane alignment and small grain size, point defects may also be a concern. In MoS₂, it has been determined that they were mostly metal anti-sites (Mo replacing S) and S vacancies,²⁷⁴ implying a correlation with poor stoichiometry. Therefore, an insufficient chalcogen supply and a too high temperature are expected to be detrimental, although the influence of the growth rate has also been highlighted.²⁵⁷ Finally, it seems that a high chalcogen pressure, a low growth rate and the use of a post growth annealing are always beneficial, provided that the selenium supply is sufficient during the annealing step. However, the substrate also plays an important role in all the processes that have been discussed, and will be the subject of the next section.

1.3.2 Substrates for van der Waals epitaxy

Despite the van der Waals epitaxy is supposed to be independent of the lattice mismatch, the different surface energies of 2D-substrates still influence the growth thermodynamics and kinetics.²⁷⁵ In addition, the vdW interaction is sufficient to align the layer with respect to the substrate lattice.²⁷⁶ A single crystalline substrate having the same symmetry as the layer is therefore desired.

1.3.2.a 2D-substrates

As theorized by Koma *et al.* in the 1980s, the vdW epitaxy requires a 2D substrate. However, bulk 2D materials are rare, and apart from those synthesized by the CVT and flux methods, the naturally occurring ones are graphite, MoS_2 ²⁷⁷ and micas. After the initial work of Koma *et al.*²⁷⁸, very few authors reported growths on TMDCs.^{244,249,279} Even if the good alignment of the two TMDCs layers has been remarked,²⁸⁰ their use is hindered by the large defect density they contain,²⁴⁹ their relatively low thermal stability, and the small size of the available crystals.

Micas are comparatively more easily purchased as substrates. They form a family of layered minerals having similar structures but different compositions. For instance, both muscovite mica ($\text{KAl}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$)^{264,281,282} and fluorophlogopite mica ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$)^{283,284} have been used. Their structure is actually monoclinic²⁸⁵ but the cleavage planes are relatively close to a hexagonal symmetry, as seen in Fig. 1.19 (a). Therefore, it has been possible to align a majority of WSe_2 domains below 1.25° of residual misorientation although few other orientations have been identified at specific angles.²⁶⁴

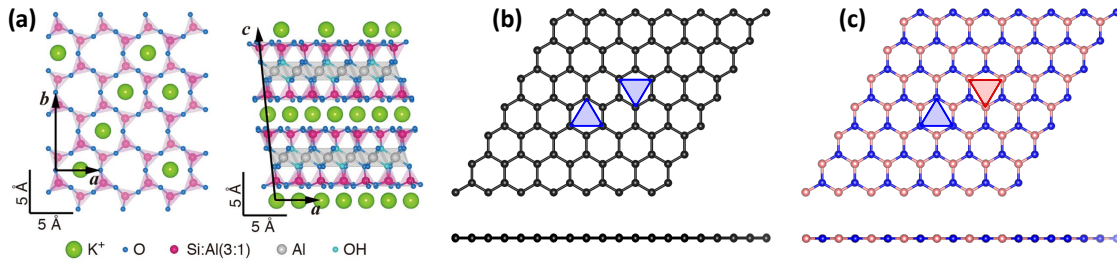


Figure 1.19: (a) Crystal structure of muscovite mica with partial coverage of K^+ ions after cleavage, reproduced from Arai *et al.*²⁸⁶. (b) Crystal structure of graphene. The blue triangles illustrate the two equivalent orientations of a triangular lattice on it. (c) Crystal structure of a hexagonal boron nitride (hBN) monolayer. In this case, the two triangles are inequivalent.

Still, the most natural choice when looking for a good quality 2D material with high chemical and thermal stability is graphene, whose structure is represented in Fig. 1.19 (b). The corresponding bulk material is graphite, which can be produced in a more ordered form, although not monocrystalline, denoted HOPG. It has been used by many groups, and monolayer flakes up to 600 nm have been grown by MBE on this substrate,²³⁶ suggesting a very high adatom mobility and low nucleation density. However, as a downside, the grains form predominantly along the step edges making the uniform coverage difficult to achieve.²⁷⁹ Finally, the metallic character is an issue for the fabrication of most electronic devices, for which the layers have to be transferred on an insulating substrate.

By contrast, hBN which has a similar layered hexagonal structure, is a large band gap insulator²⁸⁷ highly desirable for the encapsulation of electrical devices since it provides a charge impurity-free environment.²⁸⁸ It has also a very high chemical and thermal stability, and unlike graphene, the presence of two different atoms in the hBN single layer reduce its symmetry to 3-fold, making it a perfect choice for TMDC growth. Poh *et al.* and Pacuski *et al.* have demonstrated 60° aligned MoSe_2 grains,^{255,289} while Fu *et al.* and Zhang *et al.* have successfully eliminated mirror twins at higher growth temperatures.^{225,290} In these studies, exfoliated flakes were used as a substrate, even if the growth of TMDCs on hBN prepared by CVD on SiC,²⁹¹ Ir(111)²⁹² and Ru(0001)²⁹³ has also been reported. This raises the question of the availability of large-scale and high-quality hBN. This is why other substrates are still worth considering.

1.3.2.b 3D-substrates

Since the early age of the vdW epitaxy, Koma *et al.* recognized that 3D materials could also be suitable substrates, provided that they are sufficiently inert.¹⁵ The example that was given at this time is $\text{CaF}_2(111)$ for which few TMDC growths have now been reported.^{16,294,295} The F-terminated (111) faces not only have a lower surface energy,^{296,297} but it also benefits from a 3-fold symmetry inherited from the face centered cubic (FCC) structure. As shown in Fig. 1.20, even if the top layer of a (111) surface is a hexagonal arrangement of atoms, the atoms underneath effectively break the mirror symmetry. The combined influence of the different layers is much more likely to favor a unique grain alignment in the case a 3D substrate than it is in graphite, the interlayer distance being much larger in the latter.

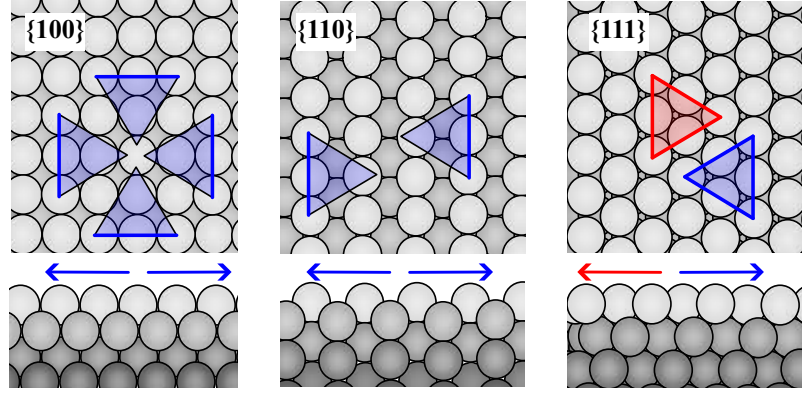


Figure 1.20: (a) Comparison of three surface orientations of a mono-atomic FCC structure, adapted from Ibach *et al.*²⁹⁸. The blue triangles indicate different orientations of a TMDC lattice that would have an equivalent interaction energy with the FCC surface. The thick borders highlight the directions exhibiting high number of coincidences between the two lattices. The red triangle on the $\{111\}$ surface represents a mirror twin whose energy should differ from that of the blue one since this surface lacks a mirror symmetry as shown by the side view below.

Also stable and more widespread materials, oxides have attracted a much larger interest, especially for CVD and MOCVD because of their high temperature stability. The growth on amorphous oxides seemed appealing for mass production, enabling for instance device staking,¹⁹⁵ and easier exfoliation thanks to lower binding energies.²⁹⁹ Particularly SiO_2 has been considered because of its compatibility with standard Si substrates. However, El Kazzi *et al.* reported a significant Mo and S diffusion through a native SiO_2 oxide while this effect could be avoided using ALD-deposited Al_2O_3 instead. In addition, the layers grown on amorphous substrates are randomly oriented, whereas comparing crystalline SiO_2 and $\alpha\text{-Al}_2\text{O}_3$ substrates Paul *et al.* confirmed that MoS_2 grains with preferential orientation could only be grown on sapphire.²⁹⁹ Some authors reported both 0 and 30 ° orientations on the $\text{Al}_2\text{O}_3(0001)$ surface^{191,300} while other reports predominant 0° and 60° corresponding to mirror twins.³⁰¹ This discrepancy may be explained by different surface preparations since a 30° azimuthal rotation of the WSe_2 lattice has been obtained by changing the initial surface reconstruction.³⁰² In theory, the (1000) plane has only a 3-fold symmetry which should favor the growth of oriented grains without mirror twins, but the large unit-cell of sapphire contains two mirrored layers having the same termination in opposite directions. Therefore, a careful preparation has been required to achieve step bunching and expose only the lowest energy planes, and finally suppress the mirror twins.³⁰³

Owing to exceptional dielectric properties, including a high relative permittivity,³⁰⁴ SrTiO_3 is another commercially available oxide substrate that has been considered for TMDC growth. It has a perovskite cubic structure, making the (111) surface favorable to single oriented domains, as confirmed by the reduced number of misoriented grains compared to (100) and (110)

surfaces.^{305–307} Nevertheless, the (100) orientation has been used to induce strain in PtTe_2 ³⁰⁸ and promote the metastable phase of WSe_2 ,³⁰⁹ which suggests a large interaction with this substrate.

Apart from oxides, III-nitrides exhibit also a high temperature stability. They are not available as bulk substrates but the recent advances in the growth of AlN and GaN on Si ,³¹⁰ Al_2O_3 ³¹¹ and SiC ³¹² make them potential candidates. The group of Dimoulas studied selenides grown on AlN on $\text{Si}(111)$.^{18,247,313} Although the absence of rotational domains was claimed,³¹³ the wurtzite structure presents alternated layers in which the direction of the Al-N bond is rotated by 180° , making it prone to mirror twin formation. In the case of MoS_2 grown on GaN , the layer appeared strongly bonded to the substrate but the epitaxy is still possible thanks to the small lattice mismatch between these materials.²²² However, the interaction with the substrate has been suspected to favor the metastable 1T phase, which may not be desired.

At this stage, it is worth mentioning that silicon, despite a good thermal stability, is not suitable since it is expected to react with both chalcogens and transition metals.^{314,315} Recently, direct synthesis on $\text{Si}(111)$ has been investigated by the group of Singh *et al.*^{316,317} using a chalcogen pre-growth wetting to prevent the formation of metal-Si bonds. However, the growth and annealing temperature were limited to 550°C . The same group compared different substrates in CVD and showed that the Si surface exhibited the worst morphology, with few-layer islands and an incomplete coverage.²⁸²

Metallic substrates have been strongly considered following the good results obtained for hBN and graphene synthesis. Copper, for instance, is very soft at high temperature which helps the grain stitching for perfect coalescence.³¹⁸ However, the graphene synthesis is in this case highly simplified by a catalytic effect which enables the growth of exactly one ML.³¹⁹ By contrast, a lower temperature must be used for TMDC synthesis and the reactivity of most metals with chalcogens limits essentially the choice of substrate to Au.³²⁰ Although more recent studies have focused on the step-edge guided epitaxy to suppress the mirror twins,²⁶⁶ Bana *et al.* successfully grew a single oriented MoS_2 on $\text{Au}(111)$ regardless of the substrate atomic steps,²⁶¹ demonstrating the potential of this substrate for growing high quality TMDCs. Still, this technique is difficult to scale since it requires both the preparation of a large-area single-crystalline gold surface, and the possibility to transfer the layer since a metallic substrate is usually not desired.²⁶⁶

Finally, despite of the large diversity of 3D crystals, no ideal candidate has been identified for large scale TMDC growth.

1.3.2.c Surface passivation of 3D substrates

One possibility to extend the list of suitable substrates is to address the issues of the dangling bonds through surface passivation techniques. A typical example is the well-known preparation of bilayer graphene on SiC ,³²¹ providing a single crystalline 2D surface at wafer scale. Despite the popularity of this method, this case will not be discussed as it is not different from HOPG and because graphene is metallic.

Instead, it would be more appealing to search for semiconducting substrates, for which the possibility of doping provides an extra versatility. Interestingly, the chalcogen atoms are known to reduce the density of deep surface traps on III-V semiconductors,³²² suggesting an efficient suppression of dangling bonds and a preservation of their semiconducting character. These materials appear thus highly compatible with the growth of TMDCs. Hence, it is not surprising that GaAs, as the most widespread of them, has been already used for vdW epitaxy since 1990.²⁸¹ Note that in this early study, the sulfur-termination of the surface was obtained through a chemical treatment with $(\text{HN}_4)_2\text{S}_2$ before the NbSe_2 and MoSe_2 growth, whereas the more recent studies shows that it could be prepared in the MBE chamber through an annealing under a low pressure of the desired chalcogen.³²³ Still, the substrate needs to be deoxidized and the growth of a GaAs buffer layer may be useful to obtain a smooth surface.²³⁷

The structure of GaAs is presented in Fig. 1.21 (a). It is worth noting that the $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ directions are not equivalent in a zinc-blende structure composed of two different atoms. The Ga-terminated surface is denoted GaAs(111)A while GaAs(111)B designates the As-terminated surface. In their pioneering work, Ueno *et al.* did not notice any difference between (111)A and (111)B orientations, and the following studies have been mainly restricted to the (111)B.^{224,237,256} Nevertheless, Ohtake *et al.* studied the influence of the GaAs substrate orientation on the growth of MoS₂.³²⁴ Surprisingly, the layer had a preferential orientation on (100), (110) and (111)B surfaces despite the different symmetries. This was explained by the presence of a 2×1 reconstruction on the (100) surface and the fact that the layer always aligned along the direction with the highest atomic density, regardless of the lattice mismatch. Still, the film grown on the (111)B surface exhibited the smoothest morphology. Comparing the (111)A and (111)B substrate orientations, larger MoS₂ grains have been observed on the latter, suggesting an enhanced surface diffusion on GaAs(111)B.³²⁵ Finally, Ohtake *et al.* established that the electronic passivation of this surface could be achieved if 3/4 of the top As atoms are replaced with Se atoms, as represented in Fig. 1.21 (b),³²⁶ contrasting with a previous work which determined a full substitution of the top As atoms by Se, and the presence of extra Se atoms in the deeper As layers.³²⁷

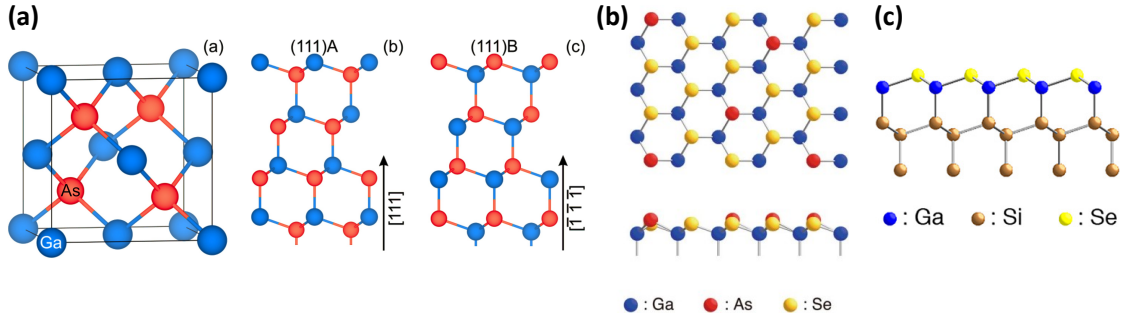


Figure 1.21: (a) GaAs structure and side view of the (111)A and (111)B surfaces, adapted from Bakulin *et al.*³²⁸. (b) Model for the Se-terminated GaAs(111)B surface proposed by Ohtake *et al.*, reproduced from Ohtake *et al.*³²⁶. (c) Model for the GaSe-terminated Si, reproduced from Ohtake *et al.*³²⁹.

Concerning other III-V compounds, the literature on the chalcogen passivation of (111)B surfaces is scarce. The sulfur passivation of InAs³³⁰ and GaP³³¹ were reported, whereas for InP, it has been shown to convert rapidly into few layer In₂Se₃ under selenium pressure at 500 °C.³³² By contrast, Se-terminated GaP is expected to have a better thermal stability, owing to a sublimation temperature 50 °C higher than GaAs,^{333,334} and has recently shown encouraging results for WSe₂ growth.³³⁵ In addition, GaP has a small lattice mismatch with Si which opens a possibility for TMDCs integration on Si. However, the few attempts of GaP heteroepitaxy on Si(111) have so far been unpromising^{336,337} as the difference of polarity induces anti-phase domains.³³⁸

A more straightforward approach has been explored toward the integration of TMDC on Si. It is well known that gallium selenide, another 2D-material, can be grown directly on Si.²⁵¹ Interestingly, thanks to very close lattice parameters, half a monolayer of GaSe forms at the surface of the bulk Si substrate.³³⁹ This substrate termination, represented in Fig. 1.21 (c), provides a large surface band gap³⁴⁰ and an efficient chemical passivation.³⁴¹ In addition, the absence of rotational domains for GaSe half layer prepared at sufficiently high temperature^{342,343} makes it promising for the growth of single oriented TMDCs. Ohtake *et al.* compared bare Si(111), As-terminated Si(111) and GaSe-terminated Si(111) for the growth of MoSe₂, and confirmed that Mo reacts with Si in the first two cases, demonstrating that As does not provide a sufficient barrier to prevent MoSi₂ formation, whereas the GaSe passivation was effective since only Mo-Se bonds were detected.³²⁹ Nevertheless, the use of a too high Se pressure during the growth results in a surface roughening attributed to the formation of Ga₂Se₃, and the apparition of Mo-Si bonds, consistent with the degradation of the GaSe-surface termination.

Conclusion

In the first section, a survey of the properties and applications of TMDCs has pinpointed HfSe_2 as a promising semiconducting material for electronic applications. Among metallic compounds, TaSe_2 not only appeared interesting as a potential contact, in the H-polytypes, but also as a room temperature Mott insulator, in the 1T phase.

However, the practical applications for these materials are currently hindered by the lack of scalable elaboration technique. MBE is suggested as a possible candidate, but a good crystallinity is difficult to achieve along with a uniform thickness coverage in vdW epitaxy.

Nevertheless, the recent studies highlight that more importantly than an enhanced surface diffusion, the key to improve the crystallinity could be a good alignment of the layer with respect to the substrate. A high growth temperature, low growth rate and sufficient Se supply seem to be the suitable conditions to achieve this. The substrate is also believed to play a major role and, in this perspective, the $\text{GaP}(1\ 1\ 1)\text{B}$ surface seems promising, owing to its 3-fold symmetry, possible passivation by Se atoms and relatively high thermal stability. Still, because the use of a cheap and widespread substrate is always a key for the adoption of any technology at larger scale, the $\text{Si}(1\ 1\ 1)$ is also worth considering, but requires a passivation layer.

Experimental techniques

2.1 Molecular Beam epitaxy

2.1.1 System overview

The MBE cluster at IEMN is composed of two growth chambers, dedicated to III-V and selenides compounds, respectively, and an analysis chamber equipped with low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS) and ultra-violet photoelectron spectroscopy (UPS). They are connected by a tube divided in different sections maintained under ultra-high vacuum (UHV). At both ends, introduction chambers are used to load and unload samples on a carrier.

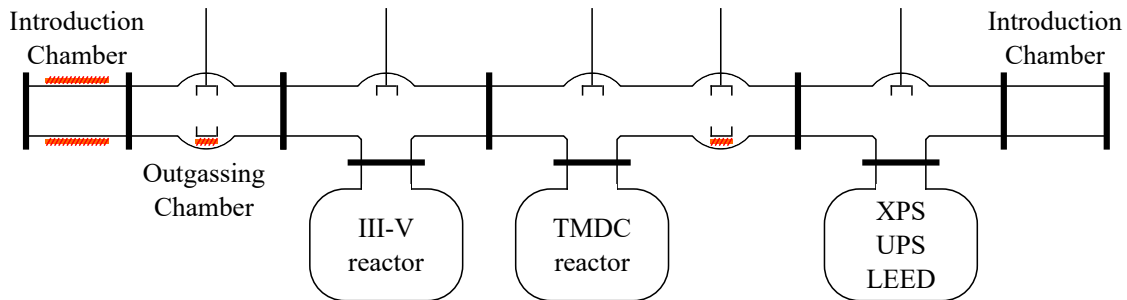


Figure 2.1: Overview of the MBE cluster at IEMN.

2.1.2 Sample introduction

GaP and GaAs substrates

GaP(111)B and GaAs(111)B substrates were purchased from *Ensemble3 sp. z o.o.* and *AXT Inc.* respectively. They are cleaved into small pieces and glued with indium on 3" Si wafers. In some cases, two pieces of substrates with different doping are glued on the same Si wafer. After introduction in the system, they are first outgassed 12 h at 100 °C under secondary vacuum and then 1-2 h at 200 °C under UHV.

Si substrates

One-side polished 3" Si(111) wafers are first cleaned under a O₂ plasma of 100 W for 2 min, deoxidized for 2 min in a 1 % HF solution, rinsed in deionized water, dried under N₂ and finally introduced under vacuum less than 10 min after deoxidation. In this case, the wafers are

directly transferred under UHV when the pressure reaches the 10^{-8} Torr range in the introduction chamber and then outgassed 1-2 h at 200 °C.

2.1.3 III-V deoxidation and homoepitaxy

The III-V substrates are first deoxidized in a *Riber C21* reactor. It contains cells for various elements, including an effusion cell for Ga and a valve cracker cell for As, a high temperature gas injector for phosphine (PH_3) and a radio-frequency hydrogen plasma cell. The PH_3 flux is controlled by a mass-flowmeter up to 10 sccm. The molecules are then cracked at 850 °C in the high temperature gas injector to produce mostly highly reactive P_2 . The plasma cell enables the production of reactive H radicals from a 3 sccm H_2 flux containing 2 % of Ar at 600 W. For GaP and GaAs regrowth, the Ga flux is calibrated from the period of the reflection high energy electron diffraction (RHEED) oscillations³⁴⁴ in a layer-by-layer growth mode during GaAs(001) homoepitaxy. The equivalent As flux is determined by slowly decreasing the valve aperture until the 2×4 GaAs(001) surface reconstruction turns to a 4×2 one, indicating a change from As-rich to Ga-rich conditions. The deoxidation and growth procedures are detailed in Section 3.1.

2.1.4 Surface passivation and TMDC growth

The surface termination of III-V and Si substrates as well as the growth of TMDC are performed in a reactor from *Vinci Technologies* represented in Fig. 2.2. It is equipped with an electron-beam evaporator for transition metals, In, Ga and Se effusion cells, a Se valve cracker cell and a H-plasma cell. A cryopanel filled with liquid nitrogen, an ionic pump and cryogenic pump enable to achieve a base pressure below 5×10^{-10} Torr.

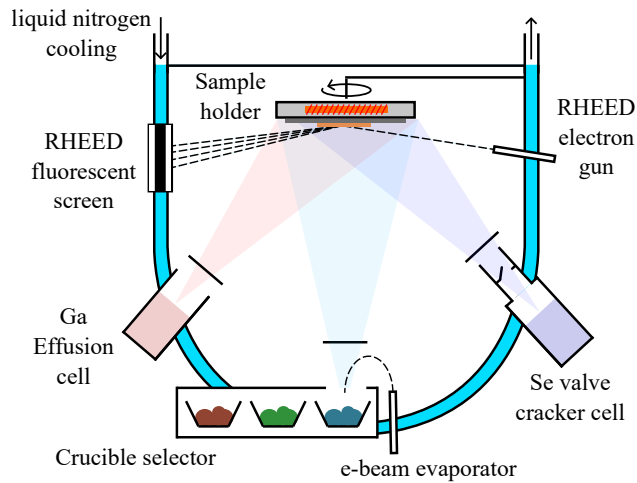


Figure 2.2: Growth chamber dedicated to TMDCs.

Transition metals are evaporated from elemental sources using a *Telemark 575* electron gun operating a 10 kV. The Hf and Ta flux are measured using quartz microbalances. One is positioned below the sample holder to adjust the flux before the growth. The second is closer to the crucible and is used during the growth to monitor a possible drift of the evaporation rate. A metal deposition rate of 0.001–0.002 Å/s is targeted, leading to TMDC growth rates of 0.004–0.007 Å/s (i. e. 2–4 ML/h), except for thick and high growth rate HfSe₂ samples for which TMDC growth rates in the 0.040–0.050 Å/s range are employed.

Regarding selenium, only the *Riber VCOR 110* valve cracker cell was used throughout this work with an evaporator temperature regulated at 190 °C and a cracking zone set at 425 °C to avoid Se deposition on the valve. These temperatures are lowered down to 136 and 325 °C respectively for experiments at low Se flux. The selenium to metal atomic ratios are deduced

from the growth rates measured using the quartz microbalance below the sample holder. In addition, a beam equivalent pressure, reported as "Se flux", is measured using a Bayart-Alpert ion gauge. For GaSe-terminated Si surface preparation, Ga is evaporated from a standard effusion cell operating typically at 880 °C to get a flux of circa 0.15 Å/s.

The substrate temperature is measured using a thermocouple placed behind the sample, and for temperatures greater than 350 °C, using a pyrometer working at a wavelength of 2.2 μm and calibrated against the InSb melting point at 525 °C. The difference between both methods is typically 25 °C or less, but the reported values are systematically those from the pyrometer when it can be measured. Note that for Si substrate, only the thermocouple values are considered because of the transparency of the substrate at the pyrometer wavelength. For GaP substrates, the In at the backside enables the measurement.

If not specified, the standard annealing duration, either for Se-passivation or post-growth annealing of the layers, is 3 min. During the experiments, heating and cooling rates are 25 °C/min for Si substrates and 20 °C/min for GaP and GaAs to avoid temperature overshoot. For the final cooling, the heating is turned off and the temperature decreases quicker than 100 °C/min. The layers are always exposed to Se during annealing. The Se flux is turned on when the sample reaches 250 °C when heated and turned off at 450 °C when cooled to avoid Se deposition.

2.1.5 Mask for in-situ patterning

For the growth of patterned layers and localized metallic contacts in the MBE chamber, a physical mask was designed and is presented in Fig. 2.3 (a). The motifs were laser-cut by Flavie Braud in a Ta shutter to ensure a sufficient mechanical resistance at high temperature. Then it was attached to a translator arm in the chamber so that it can be placed at a desired position under the sample, as in Fig. 2.3 (b), or completely retracted. The distance between the mask and the sample is about 3 cm to let the Se beam reach the sample from the left side, which was also cut for this purpose. This however causes a small broadening of the patterns, first because of the enlargement of the projected shadow with distance, and second because of the non-negligible spatial extent of the metal source. The crucibles being 45 cm below the sample, these would result in a broadening of circa 7 % of the motif plus 7 % of the few millimeters electron gun sweeping span over the source. For this reason, only millimeter scale motifs have been considered. The mask design with the expected dimensions is provided in Appendix A.

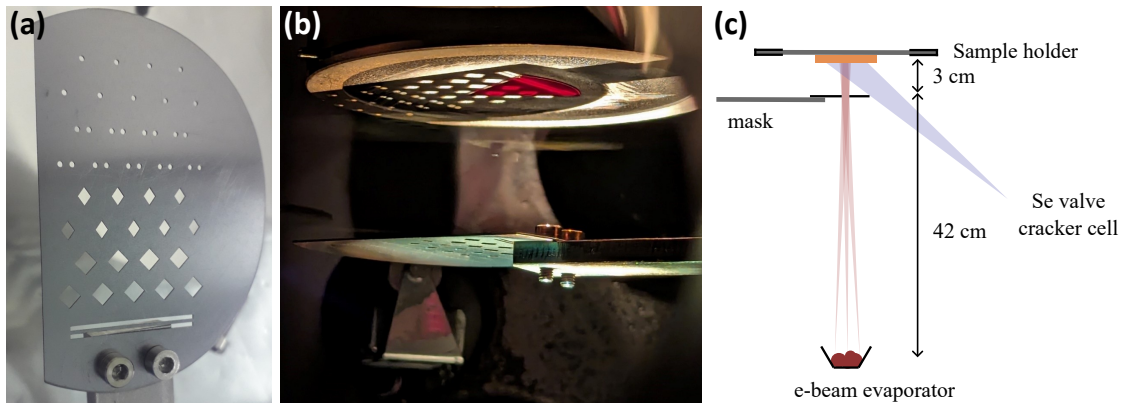


Figure 2.3: (a) Picture of the mask. (b) Usage of the mask in the MBE chamber. The light coming from the electron beam evaporator reveals the shadow of the mask on the sample during the growth. (c) Schematic of the mask and source disposition in the chamber.

This mask is also intended to be multipurpose. Hence, it contains squares, diamonds, circles, and lines so that various structures can be formed by only uniaxial translations of the mask, including Hall squares and staggered vertical heterostructures.

2.1.6 Selenium capping

For ex-situ measurements, including STM, X-ray diffraction (XRD) and Raman spectroscopy, the samples are capped with a 20 to 50 nm-thick amorphous selenium layer to protect them from oxidation. For this, the substrate temperature is maintained below 20 °C while selenium is deposited at a rate of 0.5 to 2 Å/s. The effective deposition of Se is confirmed by the disappearance of the RHEED pattern in a few seconds, after which the latter is turned off to avoid adventitious heating.

For the debonding of the GaP substrate from the Si wafer, a hot plate is first stabilized at 170 °C. The sample is placed on it and the GaP substrate is lifted using a scalpel in less than 30 s to avoid Se evaporation. A color change usually occurs in few seconds and is attributed to the crystallization of the Se capping, which does not necessarily make it less protective.³⁴⁵

2.2 Photoelectron spectroscopy techniques

2.2.1 Electron photoemission

Photoemission spectroscopy consists in the measurement of the kinetic energy E_{kinetic} of photoemitted electrons upon excitation by photons of energy $h\nu$ in order to deduce their binding energy E_{binding} in the material. Based on the schematic in Fig. 2.4, the relation between these two energies is³⁴⁶

$$E_{\text{binding}} = h\nu - E_{\text{kinetic}} - \Phi_{\text{spec}} \quad (2.1)$$

where h is the Plank constant, ν is the photon frequency and Φ_{spec} is the spectrometer work function. The photon energy required for the measurement of core levels (CLs) corresponds to X-rays (XPS) while ultraviolet (UV) radiation is preferred for valence levels (UPS).

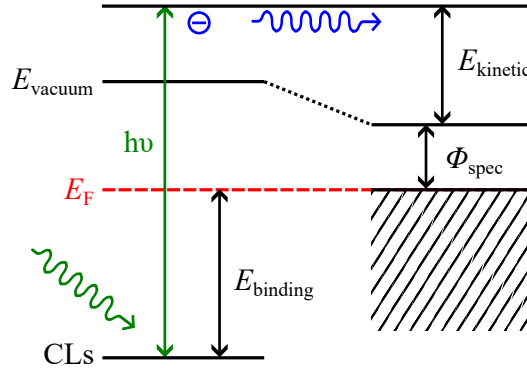


Figure 2.4: Energy diagram of a photoemitted electron collected by the analyzer.

2.2.2 Instrument

XPS and UPS experiments are performed in a chamber with a base pressure of 2×10^{-10} Torr equipped with a *Physical Electronics PHI 5600* instrument represented in Fig. 2.5. For XPS experiments, an Al anode emits $K\alpha$ X-rays having an energy of 1487.6 eV. The monochromator filters the other wavelengths and reduce the linewidth so that a full width at half maximum (FWHM) of 0.5 eV is achieved on the Ag 3d core level. The angle between the Al X-ray source and the analyzer is 90°. Electrons are collected within a 14° acceptance angle.

The measurement of the electron kinetic energy is achieved by a hemispherical analyzer. Electrons are deflected by the electric field between the inner and outer sphere, and the detector collects only electrons having a kinetic energy between $E_{\text{pass}} - \Delta E/2$ and $E_{\text{pass}} + \Delta E/2$, where

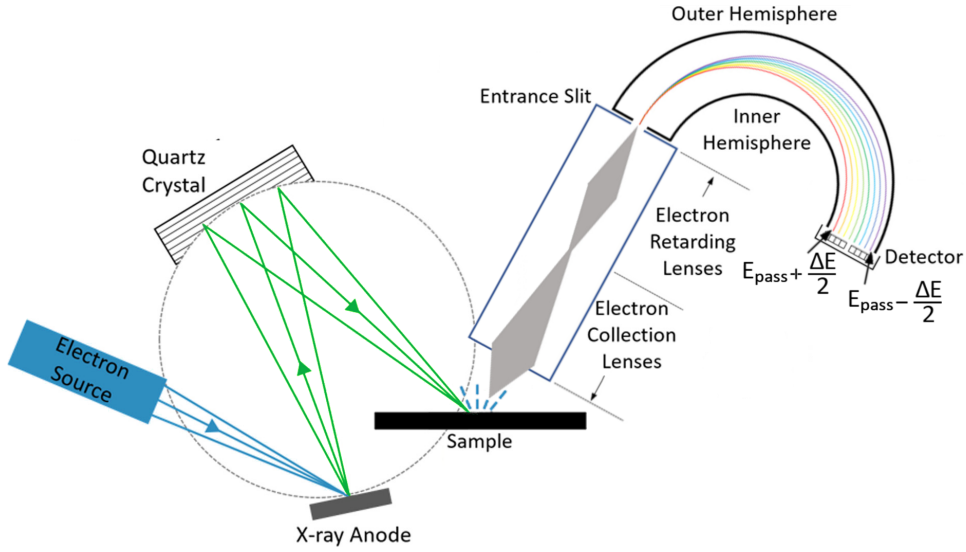


Figure 2.5: Schematic of the XPS instrument, adapted from Stevie *et al.*³⁴⁶.

ΔE is the resolution and E_{pass} is the pass energy. To ensure a constant energy resolution over the spectrum, all electrons are measured using the same pass energy E_{pass} . For this, the kinetic energy of the photoemitted electrons is adjusted using retarding electronic lenses, so that a scan over the different retard energies enables the reconstruction of the energy spectrum.

For the acquisition of the whole spectrum, the pass energy and energy step are 58.7 eV and 0.5 eV. To improve the resolution in small scans, they are reduced to 11.8 eV and 0.05 eV, respectively.

2.2.3 Core level spectra analysis

The binding energy of the core electrons is not only a characteristic of the emitting element, but is also slightly modified by the chemical environment of the atom. Hence it provides valuable information on the covalent bonds present in a compound through the general rule that the more an atom is bonded to electronegative atoms, the larger the binding energy.

Because a given atom can be found in several nonequivalent chemical environments, the core level spectra have been decomposed using the *PHI MultiPak 9.9.3* software. For this, a Shirley background³⁴⁷ is first subtracted. Except for *s* CLs, each chemical environment is expected to produce a doublet because of the spin orbit coupling. For this reason, they are fitted using two peaks of equal width for which the branching ratio and the energy separation are fixed to the values in Table 2.1. Each peak is a pseudo-Voigt function made of a sum of a Lorentzian and a Gaussian, for which the Gaussian proportion is at least 80 %.

Core level	Area ratio	Spin orbit coupling (eV)
Si 2 <i>p</i>	1:0.5	0.61
P 2 <i>p</i>	1:0.5	0.86
Ga 3 <i>d</i>	1:0.67	0.44
As 3 <i>d</i>	1:0.67	0.69
Se 3 <i>d</i>	1:0.67	0.86
Hf 4 <i>f</i>	1:0.75	1.67
Ta 4 <i>f</i>	1:0.75	1.92

Table 2.1: Doublet branching ratio and energy separation for core level decomposition in XPS.^{348,349}

In TaSe₂, the metallicity of the compound causes an asymmetry of the core levels which is better described by Doniach-Sunjc functions.³⁵⁰ Even though it has a theoretical basis, it corresponds to a deformation of a Lorentzian line shape so it should be convoluted to a Gaussian peak to take into account the experimental broadening of the system. In addition, the Doniach-Sunjc function has an infinite area due to the tail. Doniach-Sunjc-Shirley (DSS) line shapes,³⁵¹ implemented in the *Casa XPS* software,³⁵² solution this issue by introducing an energy cut-off.

Doped substrates are used to avoid surface charging effects upon photoelectron emission. Still, in the presence of a band bending at the surface of a semiconductor, surface photovoltage is expected to occur because the photogenerated carriers are separated by the electric field. In this case, the surface typically charges negatively on p-doped substrates, and positively on n-doped substrates, reducing the effective band bending and shifting the whole energy spectra, as represented in Fig. 2.6.³⁵³ In the case of TaSe₂, which is expected to be metallic, or semiconducting with a band gap inferior to the instrument resolution,²⁴² a photovoltage ranging between +0.2 and -0.2 eV is measured through the position of the Fermi level cut-off and is compensated in the presented spectra. This effect cannot be corrected in semiconducting samples but it is shown to reach a similar magnitude through the comparison of HfSe₂ layers grown on GaP substrates of different doping types.

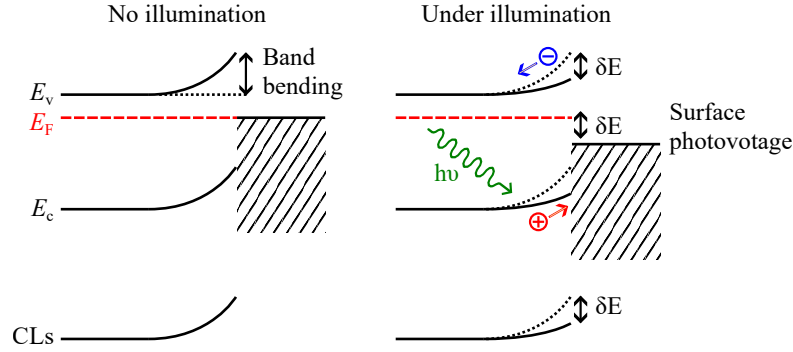


Figure 2.6: Illustration of surface photovoltage in a metal deposited on an n-type semiconductor.

2.2.4 Quantitative analysis

To compare the intensities originating from different atoms or electronic shells in XPS, an appropriate normalization by sensitivity factors is required. For this, the configuration represented in Fig. 2.7 (a) is considered, where γ is the angle between the source and the analyzer and θ is the take-off angle with respect to the surface plane. Then, the contribution of a layer of thickness dz at depth z to the XPS intensity dI_X of a core level from a chemical element X is

$$dI_X(z) = N_X(z) \cdot T(E_X) \cdot A(\theta) \cdot \Delta\Omega \cdot \Phi(\theta) \cdot \sigma_X(\gamma) \cdot \exp\left(\frac{-z}{\lambda(E_X) \sin \theta}\right) dz \quad (2.2)$$

where N_X is the concentration of the atom X , T is the analyzer transmission and detection efficiency for electrons of energy E_X , A is the probed area, $\Delta\Omega$ is the solid angle acceptance of the analyzer, Φ is the photon flux, λ is the inelastic mean free path, and

$$\sigma_X(\gamma) = \sigma_X \left(1 - \frac{\beta_X}{4} (3(\cos \gamma)^2 - 1)\right) = \sigma_X \left(1 + \frac{\beta_X}{4}\right) \quad (2.3)$$

where σ_X is the subshell photoionization cross-section and β_X is the asymmetry parameter, respectively, for a given subshell of atom X . The simplification of the expression of σ_X comes from $\gamma = 90^\circ$ in the setup. The inelastic mean free path λ is the average distance an electron travels in material before experiencing an inelastic collision.³⁵⁴ As illustrated in Fig. 2.7 (b), it

is a reasonable approximation of the characteristic length of the exponential decay of the XPS signal with depth. In theory, elastic collisions should also be taken into account, leading to the effective attenuation length,³⁵⁵ but its calculation is more complex since elastically scattered electrons can still contribute the CL intensity whereas the inelastically scattered ones would irremediably be lost in the background if collected.

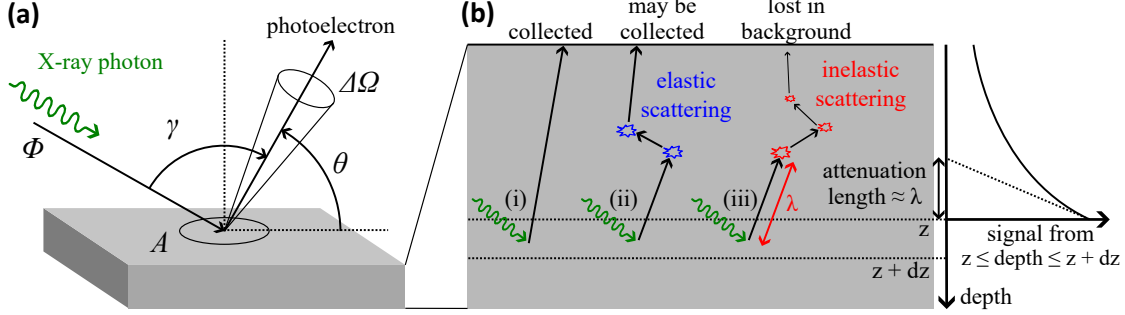


Figure 2.7: (a) Geometry of the photoemission experiments. (b) Interpretation of the electron inelastic mean free path and attenuation length, through three examples of scattering paths for photoelectrons emitted at a depth z .

Considering a bulk material for which N_X is constant in space, the integration of equation 2.2 gives the reference intensity for element X in a bulk material

$$I_X^\infty = \int_0^\infty dI_X(z) = N_X \cdot T(E_X) \cdot A(\theta) \cdot \Delta\Omega \cdot \Phi(\theta) \cdot \sigma_X \left(1 + \frac{\beta_X}{4}\right) \cdot \lambda(E_X) \sin \theta. \quad (2.4)$$

Now, considering two different chemical elements X and Y in a bulk compound, the ratio of their core level intensity measured at the same take off angle becomes

$$\frac{I_X^\infty}{I_Y^\infty} = \frac{N_X \cdot \sigma_X \left(1 + \frac{\beta_X}{4}\right) \lambda(E_X)}{N_Y \cdot \sigma_Y \left(1 + \frac{\beta_Y}{4}\right) \lambda(E_Y)}. \quad (2.5)$$

Among the remaining factors, σ_X and β_X have been calculated in the literature and are reproduced in Table 2.2 for the core levels of interest. The inelastic mean free path has been calculated thanks to the *NIST database*.³⁵⁶ For Si, the data from Tanuma *et al.* have been used,³⁵⁷ while for other compounds it is derived from the TPP-2M equation³⁵⁸ and the input parameters in Table 2.3. The results are presented in Table 2.4. It can be observed that electrons with smaller kinetic energy escape less easily from a given material. Similarly, dense materials with smaller band gap seems to attenuate more the signal.

Core level	Photoionization cross-section	Asymmetry parameter	Kinetic energy (eV)
Si 2p	0.817	1.01	1386.9
P 2p	1.192	1.09	1357
Ga 3d	1.085	1.004	1467
As 3d	1.821	1.052	1445
Se 3d	2.294	1.076	1433
Hf 4f	7.52	1.046	1468.2
Ta 4f	8.62	1.044	1463

Table 2.2: Photoionization cross sections are from Scofield *et al.*³⁵⁹, Asymmetry parameter are from linearly interpolated from Reilman *et al.*³⁶⁰.

Material	Band gap (eV)	Density (kg.dm ⁻³)	Number of valence electrons
GaSe	2.0 ³⁶¹	5.07	9
GaP	2.24	4.138	8
GaAs	1.424	5.318	8
HfSe ₂	1.1	7.467	16
TaSe ₂	0	8.647	17

Table 2.3: Material properties for inelastic mean free path calculation.

Core levels	Si 2p	P 2p	Ga 3d	As 3d	Se 3d	Hf 4f	Ta 4f
$\lambda_{\text{Si}}(E_X)$ (Å)	31.66	-	-	-	-	-	-
$\lambda_{\text{GaSe}}(E_X)$ (Å)	29.82	-	31.16	-	30.21	-	-
$\lambda_{\text{GaP}}(E_X)$ (Å)	-	28.57	30.38	-	-	-	-
$\lambda_{\text{GaAs}}(E_X)$ (Å)	-	-	30.19	29.83	-	-	-
$\lambda_{\text{HfSe}_2}(E_X)$ (Å)	26.39	25.95	27.57	27.25	27.07	27.59	27.5
$\lambda_{\text{TaSe}_2}(E_X)$ (Å)	-	23.97	25.46	25.16	25	25.47	25.40

Table 2.4: Inelastic mean free paths calculated using the *NIST database*.³⁵⁶

Finally, the composition of a compound can be experimentally determined from the experimental intensities I_X and I_Y through the reverse equation

$$\frac{N_X}{N_Y} = \frac{I_X \cdot \sigma_Y \left(1 + \frac{\beta_Y}{4}\right) \lambda(E_Y)}{I_Y \cdot \sigma_X \left(1 + \frac{\beta_X}{4}\right) \lambda(E_X)} \quad (2.6)$$

provided that the thickness t of the compound is large compared to the inelastic mean free path $\lambda(E_X)$ and $\lambda(E_Y)$. For this reason, the compositions will be calculated from measurements at an emission angle $\theta = 25^\circ$ so that the probed depth is reduced as a consequence of the $\sin \theta$ factor in Equation 2.2.

2.2.5 Thickness determination

2.2.5.a Equivalent homogeneous thickness model

In case of a film whose thickness is not large compared to the inelastic mean free path, the quantitative analysis enables the thickness to be determined by comparing the XPS signal from an atom in the film and another in the substrate. For this, the general Equation 2.2 is now integrated over the ranges $[0, t]$ and $[t, +\infty[$ respectively, where t is the thickness to be estimated, which gives³⁶²

$$\begin{aligned} I_X^{\text{film}}(t) &= \int_0^t dI_X(z) \\ &= N_X \cdot T \cdot A \cdot \Delta\Omega \cdot \Phi \cdot \sigma_X \left(1 + \frac{\beta_X}{4}\right) \cdot \lambda_{\text{film}}(E_X) \sin \theta \left[1 - \exp\left(\frac{-t}{\lambda_{\text{film}}(E_X) \sin \theta}\right)\right] \end{aligned} \quad (2.7)$$

and

$$\begin{aligned} I_Y^{\text{subs}}(t) &= \int_t^\infty dI_Y(z) \\ &= N_Y \cdot T \cdot A \cdot \Delta\Omega \cdot \Phi \cdot \sigma_Y \left(1 + \frac{\beta_Y}{4}\right) \cdot \lambda_{\text{subs}}(E_Y) \sin \theta \exp\left(\frac{-t}{\lambda_{\text{film}}(E_Y) \sin \theta}\right). \end{aligned} \quad (2.8)$$

Finally, the ratio of the two signals becomes

$$\frac{I_X^{\text{film}}}{I_Y^{\text{subs}}} = \frac{N_X \sigma_X \left(1 + \frac{\beta_X}{4}\right) \lambda_{\text{film}}(E_X)}{N_Y \sigma_Y \left(1 + \frac{\beta_Y}{4}\right) \lambda_{\text{subs}}(E_Y)} \cdot \frac{1 - \exp\left(\frac{-t}{\lambda_{\text{film}}(E_X) \sin \theta}\right)}{\exp\left(\frac{-t}{\lambda_{\text{film}}(E_Y) \sin \theta}\right)}. \quad (2.9)$$

If the composition of the two materials is known, t remains as the single unknown and the latter equation can be numerically solved to estimate the thickness. This could be done for any couple of an atom from the substrate and another from the layer, but because the metal atoms are expected to diffuse less, only Ta, Hf, Ga and Si have been considered for thickness determination. Similarly, this can be done at various emission angles θ and the thickness presented in this manuscript are usually a mean of the estimations made at 25, 45 and 75° to average possible photodiffraction effects.

Finally, a relatively good accordance observed between the thickness estimated through this method and the number of MLs revealed on scanning transmission electron microscopy (STEM) images, when available, confirms that the thickness uncertainty is below 1 ML for samples up to 5 ML-thick. Above this thickness, the signal from the substrate is too low for precise determination. For samples less than 1 ML-thick, the thickness estimation is usually lower than the surface coverage observed on atomic force microscopy (AFM) images, requiring a slight modification of the model as discussed next. Still, the method correctly reveals the thickness variations between samples, and thus can be used to compare different ones and gauge the real thickness by analogy to reference samples for which the thickness is known from other methods.

2.2.5.b Incomplete monolayer model

In the model presented above, the calculated thickness corresponds to the thickness of an hypothetical homogeneous film that would lead to the same atomic X/Y ratio. This calculated thickness can take any positive value, whereas in reality, the number of monolayers at a given position must be an integer, and for this reason the thickness is unlikely to be homogeneous over the sample. In general, the calculated thickness will be interpreted as the average thickness of film, but this is only an approximation since the XPS intensity attenuation is not linear with overlayer thickness. This becomes non negligible when the film contains large thickness variations, or when the number of layers is very small.

In the case of a film containing only 1 or 0 ML areas, the model is adapted to calculate the coverage α (which rigorously corresponds to the average thickness in ML), by solving the equation

$$\frac{I_X^{\text{film}}}{I_Y^{\text{subs}}} = \frac{I_X^\infty}{I_Y^\infty} \cdot \frac{\alpha \left[1 - \exp\left(\frac{-t_{\text{ML}}}{\lambda_{\text{film}}(E_X) \sin \theta}\right)\right]}{(1 - \alpha) + \alpha \exp\left(\frac{-t_{\text{ML}}}{\lambda_{\text{film}}(E_Y) \sin \theta}\right)} \quad (2.10)$$

instead where t_{ML} is the thickness of one monolayer of the considered material, and

$$I_X^\infty = N_X \sigma_X \left(1 + \frac{\beta_X}{4}\right) \lambda_{\text{film}}(E_X), \quad I_Y^\infty = N_Y \sigma_Y \left(1 + \frac{\beta_Y}{4}\right) \lambda_{\text{film}}(E_Y). \quad (2.11)$$

The difference between the coverage (Eq. 2.10) and the equivalent homogeneous thickness (Eq. 2.9) is shown in Fig. 2.8 (b) by plotting one as function of the other and considering the average of the 3 angles used in this manuscript. It is clear that the equivalent thickness underestimates the coverage. For instance, the difference represents 6 % of absolute coverage at 50 % of TaSe₂ monolayer coverage on GaP, meaning that without this correction, the thickness would be estimated at 0.44 ML instead of 0.50 ML. This model will be used for every sample having a thickness below 1 ML, whereas no correction is considered for thicker films since this effect will become negligible as long as the morphology is not too degraded.

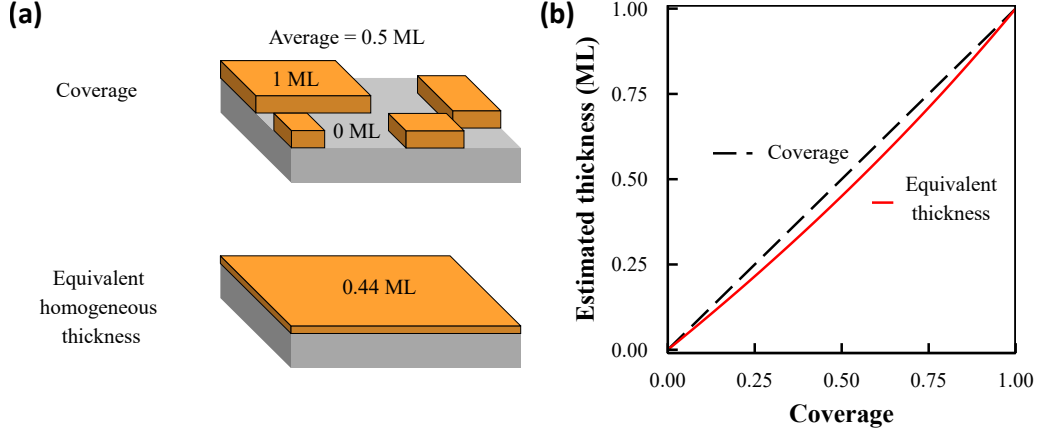


Figure 2.8: (a) Schematic representation of the coverage and the equivalent homogeneous thickness. (b) Estimation of the correction achieved using the incomplete monolayer model (dashed line) instead of the equivalent homogeneous thickness (red line) for a TaSe₂ monolayer on GaP.

2.2.5.c Three-layer model

In case of an heterostructure consisting of two thin films on a substrate, the thickness of both can be deduced from two coupled equations using the same method as for the equivalent homogeneous thickness model.

The intensity ratio between atoms X and Y respectively from the top and bottom layers is

$$\frac{I_X^{\text{top}}}{I_Y^{\text{bottom}}} = \frac{I_X^\infty}{I_Y^\infty} \cdot \frac{1 - \exp\left(\frac{-t_{\text{top}}}{\lambda_{\text{top}}(E_X) \sin \theta}\right)}{\exp\left(\frac{-t_{\text{top}}}{\lambda_{\text{top}}(E_Y) \sin \theta}\right) \left[1 - \exp\left(\frac{-t_{\text{bottom}}}{\lambda_{\text{bottom}}(E_Y) \sin \theta}\right)\right]} \quad (2.12)$$

while the intensity ratio between the atoms Y in the bottom layer and Z in the substrate gives

$$\frac{I_Y^{\text{bottom}}}{I_Z^{\text{subs}}} = \frac{I_Y^\infty}{I_Z^\infty} \cdot \frac{\exp\left(\frac{-t_{\text{top}}}{\lambda_{\text{top}}(E_Y) \sin \theta}\right) \left[1 - \exp\left(\frac{-t_{\text{bottom}}}{\lambda_{\text{bottom}}(E_Y) \sin \theta}\right)\right]}{\exp\left(\frac{-t_{\text{top}}}{\lambda_{\text{top}}(E_Z) \sin \theta}\right) \exp\left(\frac{-t_{\text{bottom}}}{\lambda_{\text{bottom}}(E_Z) \sin \theta}\right) \left[1 - \exp\left(\frac{-t_{\text{subs}}}{\lambda_{\text{subs}}(E_Z) \sin \theta}\right)\right]} \quad (2.13)$$

This set of equations rapidly converge toward a unique solution for t_{top} and t_{bottom} , meaning that it is possible to measure the thickness of an heterostructure without intermediate measurement of the first deposited layer.

Nevertheless, since the signal from the substrate may become very weak after the growth of the top layer, the measurement of the bottom layer thickness t_{bottom} in HfSe₂/TaSe₂/GaP and TaSe₂/HfSe₂/GaP heterostructures in Chapter 4 have been performed before growth of the top layer. Then, the thickness of the top layer t_{top} has been determined through Equation 2.12 only and assuming that the bottom layer thickness does not vary afterward.

Inversely, in the case of HfSe₂/GaSe/Si heterostructures, the signal from the half-monolayer GaSe is not reliable after HfSe₂ growth and the ratio between the atom X from the top layer (i.e. Hf) is compared to the atoms Z from the substrate instead (i.e. Si) using

$$\frac{I_X^{\text{bottom}}}{I_Z^{\text{subs}}} = \frac{I_X^\infty}{I_Z^\infty} \cdot \frac{1 - \exp\left(\frac{-t_{\text{top}}}{\lambda_{\text{top}}(E_X) \sin \theta}\right)}{\exp\left(\frac{-t_{\text{top}}}{\lambda_{\text{top}}(E_Z) \sin \theta}\right) \exp\left(\frac{-t_{\text{bottom}}}{\lambda_{\text{bottom}}(E_Z) \sin \theta}\right) \left[1 - \exp\left(\frac{-t_{\text{subs}}}{\lambda_{\text{subs}}(E_Z) \sin \theta}\right)\right]} \quad (2.14)$$

In this particular case, the thickness t_{bottom} is assumed to be 0.5 ML GaSe.

2.2.6 X-ray photoelectron diffraction

Photoemitted electrons are easily scattered by neighboring atoms and according to the calculation reproduced in Fig. 2.9, this scattering is not isotropic. For this reason, the samples are normally aligned parallel to one of the cleavage planes and the acceptance angle of the analyzer is fixed at its higher value (14°) to improve the reproducibility of the quantitative analysis.

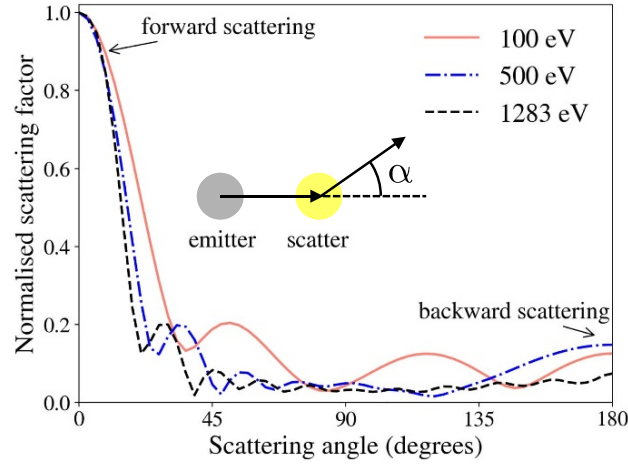


Figure 2.9: Calculated scattering by a Se atom.³⁶³

However, it is also possible to study the evolution of a core level signal as function of the emission angle to determine the position of neighboring atoms relatively to the emitting ones. This usually requires simulations to interpret the X-ray photoelectron diffraction (XPD) pattern when multiple scattering occurs, but for atomically thin layers and electrons having a sufficiently high kinetic energy, for which the forward scattering dominates, it is possible to consider a single scattering event.

For this, the setup was slightly modified to favor the angular resolution over the spatial resolution, and the signal intensity over the energy resolution. First, a Mg anode for which the overall transmission is less sensitive to the emission angle was used. It produces non-monochromatic X-rays with a main emission line $K\alpha$ at 1253.6 eV. The pass energy and energy step were increased to 46.95 eV and 0.4 eV respectively, while the analyzer acceptance angle was reduced to 4° . The signal intensity was measured as the area of the peaks above a Shirley background.

2.2.7 Ultraviolet photoelectron spectroscopy

For valence band measurement, UV photons are produced from a He plasma with main emission lines at $h\nu = 21.2$ eV for HeI and $h\nu = 40.8$ eV for HeII, whose ratio can be tuned by adjusting the pressure and power of the plasma. They are particularly narrow, and also intense concerning HeI, which allows a low pass energy for the analyzer ($E_{\text{pass}} = 2.95$ eV) to be used, leading to an improved energy resolution with respect to the X-ray sources. Another characteristic of UPS is the extreme surface sensitivity, because the very low kinetic energy of the photoemitted electrons results in a short attenuation length. This low kinetic energy of the photoemitted electrons also implies a limitation in the wave number k of the electrons that can be measured, as the energy of the free electron is expressed as

$$E_{\text{kinetic}} = \frac{\hbar^2 k^2}{2m} \quad (2.15)$$

where $\hbar$ is the reduced Planck constant and m its mass. Deducing the kinetic energy from the photoemission Equation 2.1, this gives the following expression for the wave number

$$k = \frac{\sqrt{2m(\hbar\nu - E_{\text{binding}} - \Phi_{\text{spec}})}}{\hbar}. \quad (2.16)$$

Then, the electron wave vector is decomposed as $\vec{k} = \vec{k}_{\perp} + \vec{k}_{\parallel}$ where $\vec{k}_{\parallel}$ denotes the component parallel to the sample surface. The maximum $k_{\parallel}$ that can be analyzed is limited by the half acceptance angle α

$$k_{\parallel} = k \sin \alpha. \quad (2.17)$$

Finally, TMDCs typically have an in-plane lattice parameter around $3.5 \text{ \AA}$, which corresponds to a periodicity of reciprocal space of $2.1 \text{ \AA}^{-1}$. Hence, for $\alpha = 7^\circ$, it appears that only a small proportion of the Brillouin zone is probed in UPS since $k_{\parallel\text{max}} = 0.26 \text{ \AA}^{-1}$ using HeI whereas in XPS $k_{\parallel\text{max}} = 2.40 \text{ \AA}^{-1}$ is sufficient to cover an entire period of the reciprocal space as illustrated in Fig. 2.10. In this work, the valence band is measured in UPS normal to the surface ($\theta = 0^\circ$), i.e. around Γ .

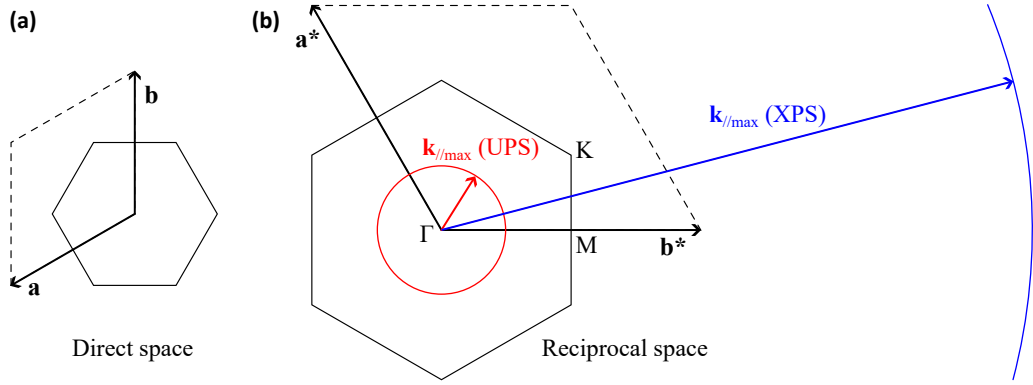


Figure 2.10: (a) Schematic a TMDC lattice in the direct space. (b) Corresponding reciprocal space lattice and Brillouin zone. The circles illustrate the regions probed using UPS ($\hbar\nu = 21.2 \text{ eV}$) and XPS ($\hbar\nu = 1487.6 \text{ eV}$) at scale for TaSe_2 ($a = 3.44 \text{ \AA}$).

Besides that, UPS is used for work function determination. In this case, a bias $V = -3 \text{ V}$ is applied to the sample so that the photomitted electrons are guaranteed to reach the detector regardless of the work function difference. The maximum binding energy of the photoelectrons is therefore limited at the emission by the sample work function hence

$$E_{\text{binding}}^{\text{max}} = \hbar\nu - \Phi_{\text{sample}}. \quad (2.18)$$

However, because of the polarization V , it will reach the detector with the energy

$$E_{\text{kinetic}} = \hbar\nu - E_{\text{binding}}^{\text{max}} - \Phi_{\text{spec}} - eV = \hbar\nu - E_{\text{binding}}^{\text{apparent}} - \Phi_{\text{spec}}. \quad (2.19)$$

where $E_{\text{binding}}^{\text{apparent}}$ is the apparent binding energy, deduced from Equation 2.1, for the low energy electron cutoff. By combining Equations 2.18 and 2.19, the sample work function can be deduced from

$$\Phi_{\text{sample}} = \hbar\nu - E_{\text{binding}}^{\text{apparent}} + eV. \quad (2.20)$$

2.3 Raman spectroscopy

Raman spectroscopy is a convenient characterization technique for 2D materials. It consists in the measurement of wavelength shifts caused by the inelastic scattering of light by phonons, the vibrations of the atomic lattice. It notably enables the phases to be identified, the presence or absence of certain modes being related to the material symmetries.³⁶⁴ The main active Raman modes for 1T and 2H phases are schematized in Fig. 2.11 (a) and the experimental shifts observed in the literature for TaSe₂ and HfSe₂ are reported in Table 2.5. This technique also provides an indication of the crystalline quality through the width of the Raman peaks, and can be used for thickness determination based on peak intensity ratios³⁶⁵ or previously reported frequency shifts.³⁶⁶

Material	Mode	Raman shift (cm ⁻¹)
1T-HfSe ₂	E _g	146 ³⁶⁷
	A _{1g}	199 ³⁶⁷
2H-TaSe ₂	E _{2g} ¹	208-210 ^{368,369}
	A _{1g}	231-236 ^{368,369}
1T-TaSe ₂	E _g	177 ³⁶⁹
	A _{1g}	185-187 ^{369,370}
	CDW-related	60-100 ^{240,370} 154 ³⁶⁹

Table 2.5: Main active Raman modes observed in HfSe₂ and TaSe₂. Note that peak positions for 1T-TaSe₂ are still debated.³⁷¹

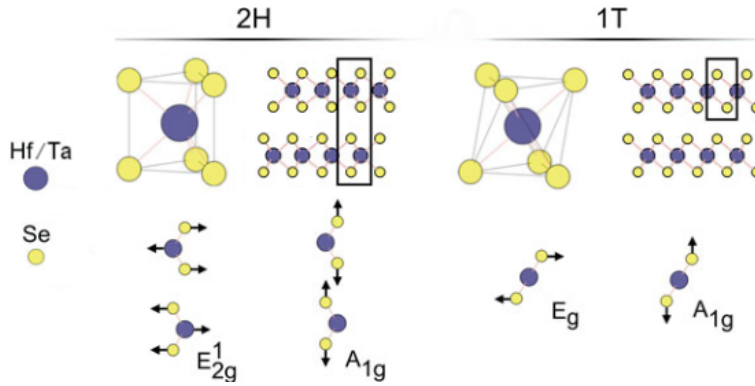


Figure 2.11: (a) Schematic of the main Raman modes in TMDCs, adapted from Cruz *et al.*³⁷².

The experiments were done at IEMN by Dominique Vignaud, Flavie Braud and Chiara Crivello using a *Horiba Scientific LabRAM HR* instrument with a laser wavelength of 473.1 nm, a power of 10 mW and a beam size of about 1 μm^2 using a $\times 100$ objective. A diffraction grating of 1800 gr/mm was used to achieve an energy resolution of 0.5 cm^{-1} . Because the laser rapidly degrades the layers, attenuation filters are added to reduce the power to 1 mW. In this case, an acquisition of 4 s is preferentially chosen to avoid saturation of the substrate peak on the detector, and then are repeated between 2 and 50 times to average the spectra. The spectra are always compared with the one measured on the bare substrate in similar conditions, the later presenting minor peaks in the region of interest.

2.4 Diffraction techniques

Diffraction techniques enable the structure of the materials to be probed thanks to the reflection of a wave on the atomic planes. The condition for constructive interference in Fig. 2.12 (a) is expressed as the Bragg's law³⁷³

$$n\lambda = 2d_{hkl} \sin \theta \quad (2.21)$$

where λ is the wavelength, d_{hkl} is the distance between (hkl) planes, θ is the incidence angle and n is an integer. In this case, $n = 1$ since we will only consider first order diffraction. An equivalent formulation is the Laue condition

$$\mathbf{k}_d - \mathbf{k}_i = \mathbf{G} \quad (2.22)$$

where $\mathbf{k}_i$ and $\mathbf{k}_d$ are the incident and diffracted wave vectors respectively, for which the energy conservation imposes $|\mathbf{k}_i| = |\mathbf{k}_d|$, and $\mathbf{G}$ is a vector of the reciprocal lattice. The vectors that satisfy this criterion can be geometrically determined in the reciprocal space by the Ewald construction represented in Fig. 2.12 (b).

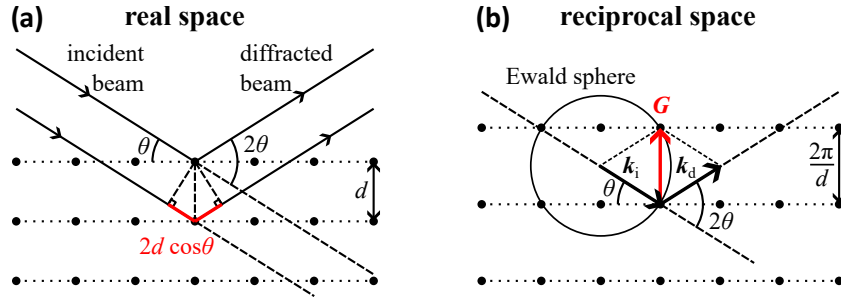


Figure 2.12: (a) Schematic of the diffraction condition by a periodic arrangement of atoms³⁷⁴ (b) Illustration of the Laue diffraction condition verified by the intersection of the Ewald sphere, of radius k_i , with a point of the reciprocal lattice.

2.4.1 X-ray diffraction

The interference requires a certain number of planes to produce a sharp peak. In thin films, the width is related to the thickness.³⁷⁵ In this work, the layers are typically below 10 nm which implies a large broadening in addition to a very weak intensity in the out-of-plane configuration where the reflection occurs on the atomic planes parallel to the surface. For this reason, the measurements are performed at a grazing incidence in the in-plane configuration. In this case, the incidence angle is close to the critical angle for total external reflection and the beam is diffracted by atomic planes perpendicular to the surface. The experiments were done at *Institut Chevreul* using a *Rigaku Smartlab* diffractometer under the support of Lydia Karamazin and Pascal Roussel. As represented in Fig. 2.13 (a), the out-of-plane angles θ and ω are set to 0.5° to ensure a sufficient reflection. Non-monochromatic X-rays are produced by a Cu rotating anode, with main emission lines $K\alpha_1$ at $1.5406 \text{ \AA}$, $K\alpha_2$ at $1.5444 \text{ \AA}$, and $K\beta$ at $1.3922 \text{ \AA}$. For the presented calculations, the mean value for $K\alpha$ $\lambda=1.5418 \text{ \AA}$ is considered. The beam divergence is reduced using 0.114° Soller slits unless otherwise specified.

The sample is first aligned along a crystalline direction of the substrate using the procedure schematized in Fig. 2.13 (b). The source to detector angle, denoted $2\theta_\chi$, is set to the substrate $\{2\bar{2}0\}$ diffraction angle, and then the sample is rotated along its azimuth, denoted φ . As illustrated by the example in Fig. 2.13 (d), it typically reveals 6 peaks whose height may vary because of the shape of the sample and non-ideal alignment. It is worth mentioning that XRD diffractograms are always symmetric, explaining why the same peaks are found along

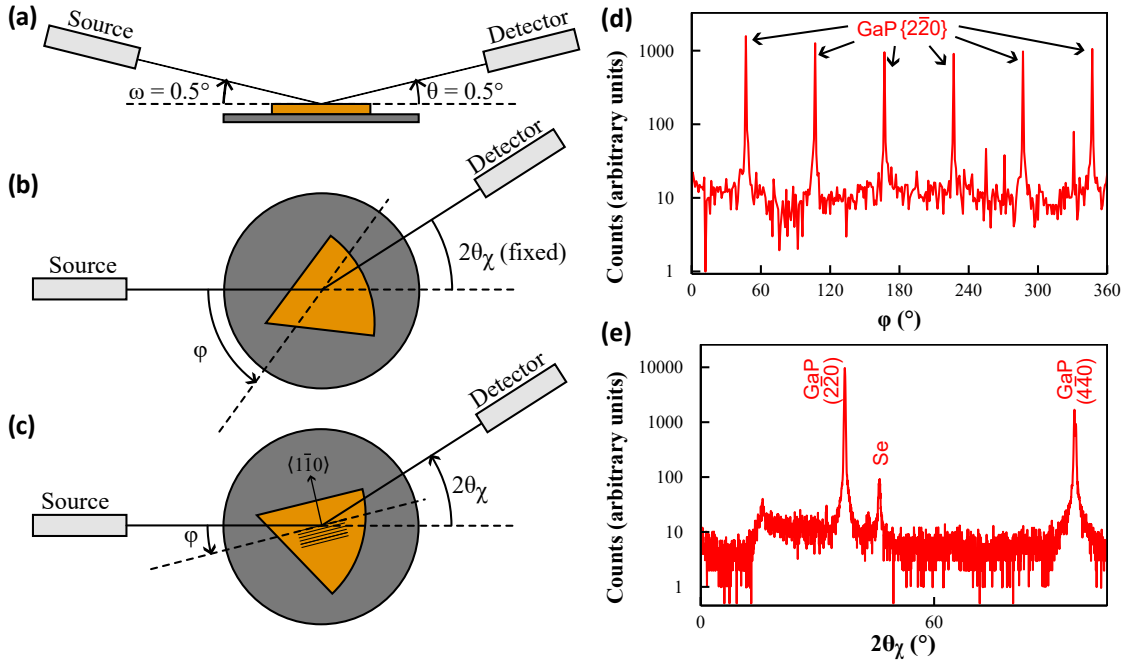


Figure 2.13: (a) Schematic of the grazing-incidence XRD measurement in side view. (b) Azimuthal scan in top view. (c) Radial scan in top view. (d-e) Diffractograms recorded on an oxidized TaSe₂ sample during (d) an azimuthal scan at $2\theta_\chi = 47.13^\circ$, and (e) a radial scan along the $\langle 1\bar{1}0 \rangle$ direction.

opposite directions such as $[2\bar{2}0]$ and $[\bar{2}20]$ despite of the 3-fold symmetry of the (111) surface. After alignment on the highest intensity peak, the diffraction pattern is recorded by making the detector and sample rotate simultaneously to keep the source and detector directions symmetric with respect to a substrate $\langle 1\bar{1}0 \rangle$ direction, as represented in Fig. 2.13 (c). These scans are refereed as $2\theta_\chi - \varphi$ and enable all planes perpendicular to that direction to be measured for $2\theta_\chi$ in the range 10° - 115° . In the example shown in Fig. 2.13 (e), the peak near 56° more likely corresponds to a $\{003\}$ or $\{2\bar{1}\bar{2}\}$ plane of the Se capping layer which is known to crystallize upon heating (See Table 20 in Appendix). A similar measurement is repeated after a 30° rotation along φ to measure the planes parallel to the substrate $\{11\bar{2}\}$ ones. Finally, for each identified compound, an azimuthal scan is performed on one of its characteristic peaks to determine its in-plane rotational distribution.

2.4.2 Electron diffraction

Compared to X-rays, electrons much strongly interact with matter, and therefore are suited for extreme surface analysis. The LEED and RHEED techniques are discussed in the following paragraphs.

2.4.2.a Low energy electron diffraction

The configuration used in LEED is illustrated in Fig. 2.14 (a). Electrons are focused onto a surface at normal incidence and those that are elastically scattered are detected on a surrounding fluorescent screen. The electron energy can be varied between 40 and 200 eV which enables one or few monolayers to be probed in the material as the attenuation length increases with kinetic energy over this range.³⁷⁶

Thanks to the hemispheric form of the screen, it unveils the intersection of the reciprocal surface lattice with the Ewald sphere. An example of diffraction pattern obtained on a Si(111)

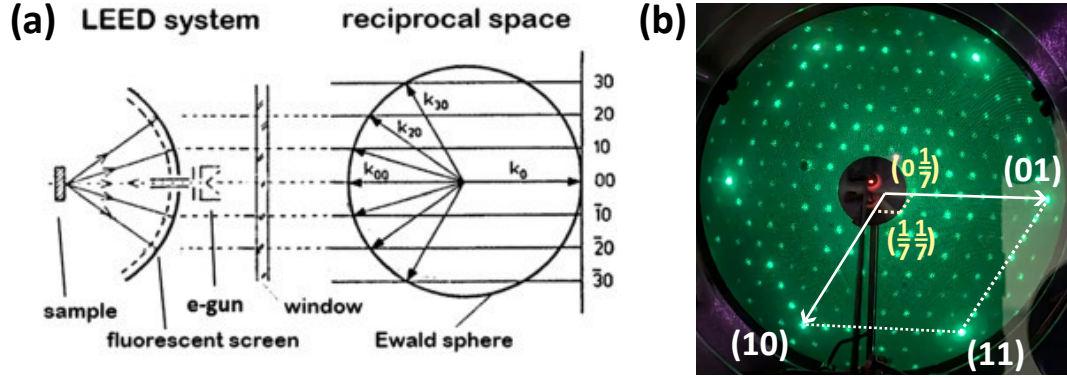


Figure 2.14: (a) Schematic of LEED, reproduced from Moritz *et al.*³⁷⁷. (b) LEED pattern of a deoxidized Si(111) wafer exhibiting a 7×7 surface reconstruction.

substrate is presented in Fig. 2.14. The brightest spots, noted (10) and (01), correspond to electrons diffracting on the cubic Si lattice. The others appear with a 7 times smaller spacing, indicating a 7 times larger period in the real space. This is a well-known surface reconstruction arising from the reorganization of the top layer of atoms to reduce the number of dangling bonds.³⁷⁸

2.4.2.b Reflection high energy electron diffraction

In RHEED, the electron energy is increased typically above 10 keV but they impinge at grazing incidence in order to probe the extreme surface. The main benefit of this configuration is the characterization of the sample during the growth in the MBE chamber because, in this case, the fluorescent screen lies on the side. It gives useful insights during the process as it not only reveals the crystallography, but is also very sensitive to the surface morphology. This is illustrated by archetypal examples in Fig. 2.15 (b-f).

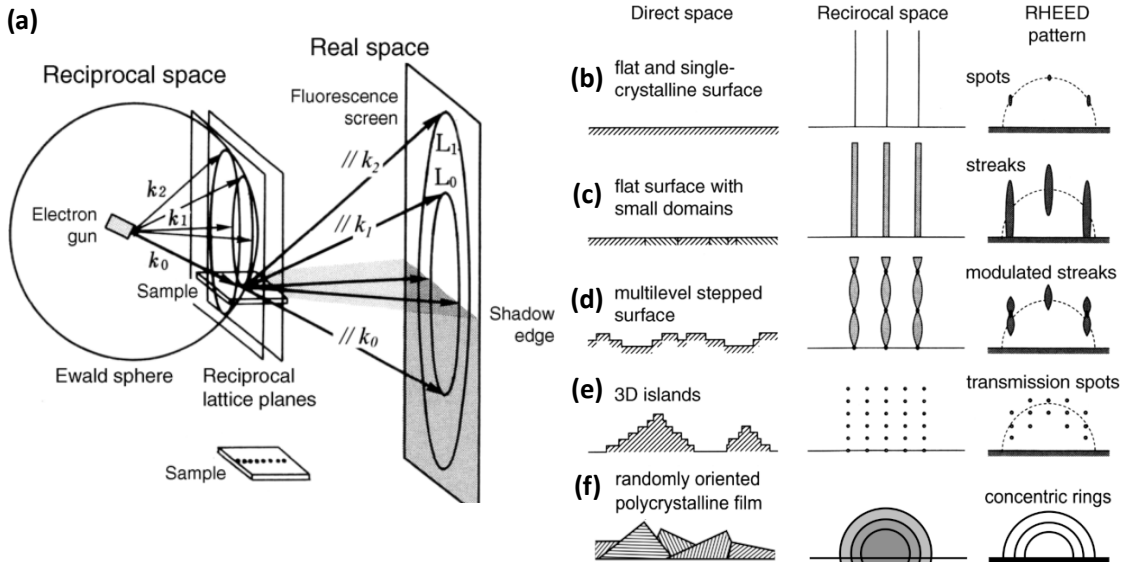


Figure 2.15: (a) Schematic of the RHEED, reproduced from Hasegawa *et al.*³⁷⁹. (b-f) Schematic of reciprocal space and RHEED patterns for various surfaces, adapted from Refs. 379, 380.

- In situation (b), the material is a flat single-crystal, which produces a ring of spots resulting from the intersection of the rods of the surface reciprocal lattice with the Ewald sphere represented in Fig. 2.15 (a). Similar to LEED, the spot spacing corresponds to the in-plane periodicity, measuring the reciprocal lattice parameter perpendicular to the beam direction and revealing possible superstructures.
- The coherence length for the electron beam used in RHEED is typically 50 to 200 nm.^{379,381} If the material is made of smaller domains, as represented in case (c), the rods widen in the reciprocal space which results in broader and elongated streaks on the RHEED pattern.
- These streaks appear modulated when the surface roughens, as seen in case (d), and ultimately becomes an array of spots when the electron beam is transmitted through the protruding islands in case (e).
- In the previous examples, the growth was still considered epitaxial. If the domains are no longer oriented in-plane, but remains oriented out-of-plane, the RHEED pattern is not expected to drastically change. It would only appear dimmer at a given position, and invariant by any rotation of the azimuth. If the domains are also misoriented out-of-plane, it would be completely isotropic and form rings as depicted in case (f).

2.5 Electron microscopy

The resolution of microscopes are ultimately restrained by the diffraction limit which is proportional to the wavelength.³⁸² A possible solution is found in the replacement of photons by massive particles such as electrons, that does not only interact more strongly with matter, but also have a wavelength below 1 Å for accelerating voltages above 1 kV,³⁸³ making the atomic resolution achievable in STEM.

2.5.1 Scanning transmission electron microscopy

The observation of transmitted electrons is possible for extremely thin samples. For this reason, cross section lamella were prepared perpendicular to a $[1\bar{1}0]$ GaP or Si direction using focus ion beam by David Troadec at IEMN using a *Crossbeam 550* instrument.

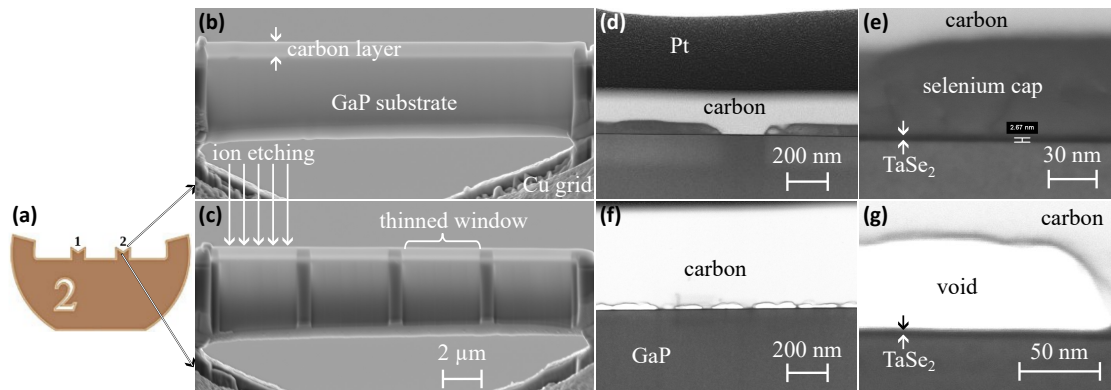


Figure 2.16: (a) Cu grid on which the slab is attached. (b) Sample lamella before and (c) after thinning using ion etching. (d-e) Lamella on which the Se capping was preserved at different magnifications. (f-g) Lamella on which the Se capping has been evaporated.

The layers are first covered by an amorphous carbon film and a small slab of the sample is placed on a Cu grid as seen in Fig. 2.16 (a) and (b). In some cases, an additional layer of Pt is evaporated for a better protection of the layers. Then, the edges are etched by Ga ions accelerated at 30 kV to reduce the thickness to 50 to 100 nm over small windows visible in Fig. 2.16 (c). During these steps, the observations with scanning electron microscopy (SEM) should be limited to 200 pA to avoid the evaporation of the Se capping layer. A sample for which it has been successfully preserved is presented in Fig. 2.16 (d,e) while in Fig. 2.16 (f,g) the presence of void indicates the evaporation of the selenium.

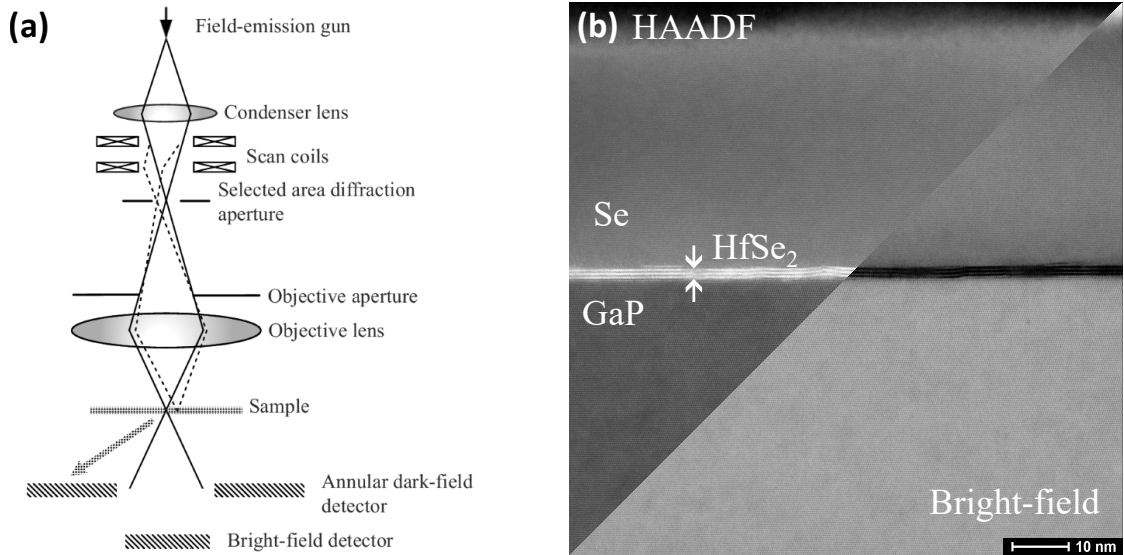


Figure 2.17: (a) Schematic of the STEM microscope, adapted from Nellist *et al.*³⁸⁴. (c) Comparison of STEM images acquired using high-angle annular dark-field (HAADF) and bright-field detectors.

The STEM investigation was performed by Gilles Patriarche at Centre de Nanosciences et de Nanotechnologies (C2N) using a *FEI Titan Themis 200* microscope equipped with a spherical aberration corrector and sketched in Fig. 2.17 (a). The electrons are emitted with a probe current of 40-45 pA and accelerated through a voltage of 200 kV. The electron beam is deflected by scanning coils and focused on the sample with a half-convergence angle of 17.6 mrad. Finally, the transmitted electrons are collected in the bright-field detector, while those scattered between 69 and 200 mrad are imaged on a HAADF detector. This mode is particularly sensitive to the atomic number, the heavy atoms appearing brighter as can be seen in Fig. 2.17 (b).

2.5.2 Energy dispersive X-ray spectroscopy

The high energy electron excitation in STEM is sufficient to eject electrons from the inner shells of the imaged atoms. When an electron from an outer shell fills this vacancy, a characteristic amount of energy is released through the emission of a X-ray-photon which is measured in energy-dispersive X-ray spectroscopy (EDX) allowing chemical identification and mapping. The *FEI Titan Themis 200* used in this study is fitted with a *super X* system with a 0.7 srad solid angle of collection.

2.6 Scanning probe microscopy

A more recent approach to overcome the diffraction limit is based on scanning probe techniques. It consists in scanning a surface with a tip maintained at a constant height, either by controlling the force in AFM or the tunneling current in STM. Then an image of the surface topography is reconstructed from the record of the tip position in space. These methods easily achieve the atomic resolution in the vertical direction while the lateral resolution usually depends on the tip apex.

2.6.1 Atomic force microscopy

The AFM offers the possibility to scan in air and the ability to scan insulating materials. The experiments were performed at IEMN using a *Dimension D3100* microscope and *NCHV-A* probes from *Bruker*. The measurement was made in the tapping mode illustrated in Fig. 2.18 (a). The small piezoelectric element makes the probe oscillate between a contact position, where the force is repulsive, and a non-contact position where the attractive interactions dominate as seen in Fig. 2.18 (b). This intermittent contact reduces the damage caused to the surface, and still enables the measurement to be made through a water film which may form in ambient conditions.³⁸⁵ The amplitude is typically few tens of nanometers,³⁸⁶ but is here recorded in volts. The probe is tuned for a target amplitude of 2 V, which gives a cantilever eigenfrequency around 350 kHz. The measurements are then performed with a slightly lower driving frequency, also corresponding to a lower amplitude setpoint. For TMDCs which are expected to be fragile, the tuning target amplitude is first reduced to 1 V, and then the measurement is preferentially done with the highest amplitude before losing contact. The smallest-scale images, down to $200 \times 200 \text{ nm}^2$, are recorded first, then the scan size is progressively increased up to $10 \times 10 \text{ }\mu\text{m}^2$, so that it can always be checked that the previous scan did not damage the sample.

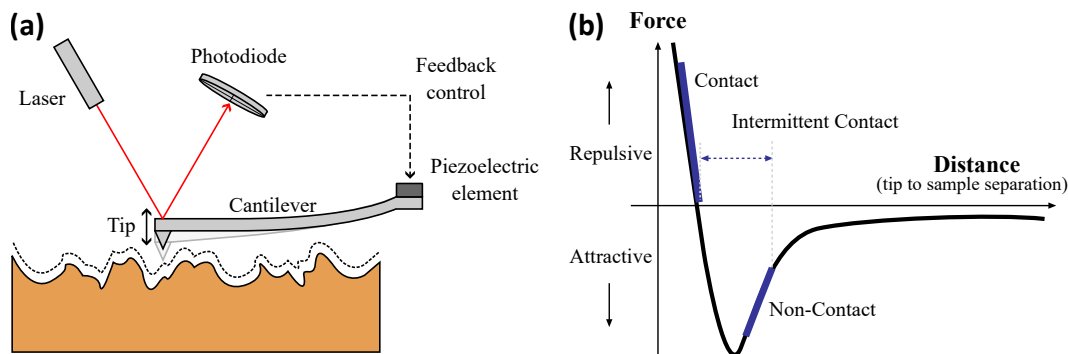


Figure 2.18: (a) Schematic of the AFM tapping mode. (b) Tip to surface interaction in the different AFM modes, reproduced from Maghsoudy-Louyeh *et al.*³⁸⁵.

The images were treated using the *Gwyddion* software.³⁸⁷ Notably, it allows the rows to be aligned to offset a possible vertical drift during the scan, using the median of heights method. In addition to the topographic mapping, the amplitude error and the phase are also recorded. The former is sensitive to height variations, and the latter is correlated to the local mechanical properties of the material.

2.6.2 Scanning tunneling microscopy

The STM technique is comparatively more demanding since it requires vacuum conditions. It can however image individual atoms and enable the local electronic properties to be investigated. Since the monitoring of the probe height is achieved through the measurement of an electrical current, a conductive tip is mandatory, as well as a conductive substrate. For this reason, the samples characterized by STM were grown on highly n-doped GaP and GaAs substrates.

These experiments were done by Houada Koussir and Yevheniia Chernukha at JUNIA-ISEN using a *Omicron* low-temperature STM operating at 77 K. The probes were made of tungsten wires electrochemically etched in a NaOH solution. Both the tips and the samples are outgassed in UHV prior to the measurements.

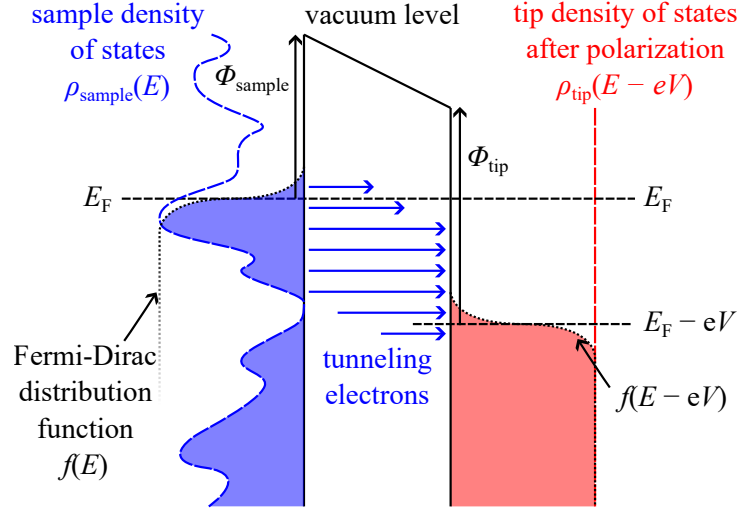


Figure 2.19: Schematic of the electronic states in a STM experiment.

Based on the schematic in Fig. 2.19, the tunneling current I between the sample and the tip polarized at a given voltage V is proportional to the number of filled states in the sample joint to an available state at the same energy E in the tip, which is expressed as

$$I_{\text{sample} \rightarrow \text{tip}}(z, V) \propto \int_{-\infty}^{+\infty} \rho_{\text{sample}}(E) f(E) T(z, E, V) \rho_{\text{tip}}(E - eV) (1 - f(E - eV)) dE \quad (2.23)$$

where ρ_{tip} and ρ_{sample} are the density of states in the tip and sample respectively, T is the transmission probability and f is the Fermi-Dirac distribution function

$$f(E) = \frac{1}{e^{\frac{E - E_F}{k_B T}} + 1}. \quad (2.24)$$

The total tunneling current is expressed as the difference between the electrons tunneling in both directions, which simplifies to

$$I(z, V) \propto \int_{-\infty}^{+\infty} \rho_{\text{sample}}(E) \rho_{\text{tip}}(E - eV) T(z, E, V) (f(E) - f(E - eV)) dE. \quad (2.25)$$

At low temperature, the electrons only occupy the lowest energy levels and f becomes a step function, which reduces the integral to

$$I(z, V) \propto \int_{E_F - eV}^{E_F} \rho_{\text{sample}}(E) \rho_{\text{tip}}(E - eV) T(z, E, V) dE. \quad (2.26)$$

The transmission probability T depends on the height of the tunneling barrier and exponentially decreases with respect to its width z , which is the sample to tip distance. Hence, it is possible to scan the surface without touching it by adjusting z to keep I constant. In this case, the movement of the probe reproduces more or less the surface topography, but is also sensitive to the local density of states since an increase of ρ_{sample} will as well be compensated by an increase of z . For this reason, regions with a high electron density also appear brighter in topographic STM images.

During the scans, the polarization V is normally constant. Nevertheless, different features may appear on the surface depending on the choice of V because the probe interacts with different energy bands in the sample. To further study the local density of states, the STS technique consists in measuring the dependence of I to the voltage at a given tip position.³⁸⁸ A convenient way to approximate the density of states is provided by the calculation of the current derivative³⁸⁹

$$\frac{\partial I}{\partial V}(z, V) \propto e\rho_{\text{sample}}(E_F - eV)T(z, E_F - eV, V) + \int_{E_F - eV}^{E_F} \rho_{\text{sample}}(E) \frac{\partial T}{\partial V}(z, E, V) dE \quad (2.27)$$

making the assumption that the density of states in the metallic tip is constant. Still, the variation of the barrier height with voltage makes the proportionality relation inexact.

2.7 Electrical characterizations

2.7.1 Four-point probe method

The four-point probe (4PP) technique enables the resistance of a material or device to be measured without a contribution of resistance between the probe and the contact. The calculation of the resistivity remains however not straightforward because of geometrical factors.

2.7.1.a Resistance of an infinite film

In the cases considered in this manuscript, the thickness of the layers will always be significantly smaller than the lateral distances. Therefore, even if the conductivity of two 2D materials is highly anisotropic, the current will reasonably be considered homogeneous over the vertical direction in a given material. This enables the sheet resistance to be defined as

$$R_{\square} = \frac{\rho}{t} \quad (2.28)$$

where ρ is the electrical resistivity and t the thickness.

The relationship between ρ and the measured I and V depends on the probe positioning and layer extent. In the case of a current spreading from a probe to an infinite plane, the integration of Ohm's law over concentric rings around the probe gives a potential difference

$$V(R) - V(R_{\text{probe}}) = \int_{R_{\text{probe}}}^R \frac{I\rho}{2\pi r t} dr = \frac{I\rho}{2\pi t} \ln\left(\frac{R}{R_{\text{probe}}}\right) \quad (2.29)$$

where R and r are the distances to the probe and R_{probe} the tip radius.

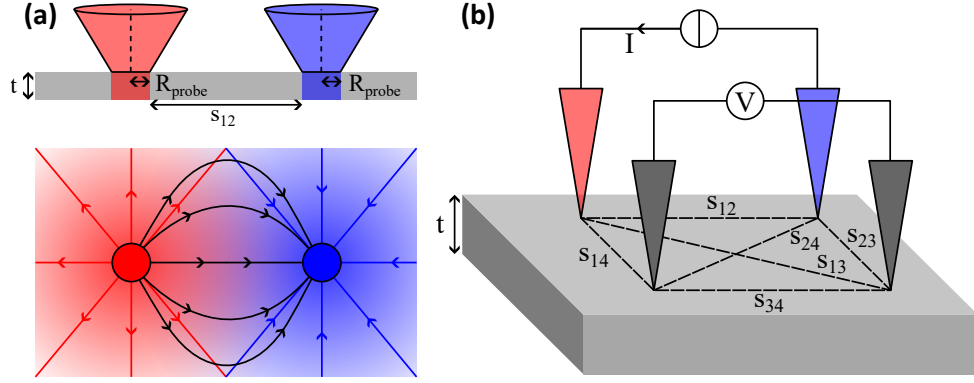


Figure 2.20: (a) Schematic of the potential in an infinite 2D layer in side view and top view. (b) Schematic of the four-point probe measurement in the square configuration.

The potential between two probes can be derived from this using the superposition theorem, noting that the current flowing from probe 1 to probe 2 can also be described as the current flowing from probe 1 to infinity and then to infinity to probe 2, as depicted Fig. 2.20 (a). The potential difference between the two probes becomes

$$V_{12} = \frac{I\rho}{2\pi t} \ln\left(\frac{s_{12}}{R_{\text{probe}}}\right) + \frac{-I\rho}{2\pi t} \ln\left(\frac{R_{\text{probe}}}{s_{12}}\right) = \frac{I\rho}{\pi t} \ln\left(\frac{s_{12}}{R_{\text{probe}}}\right) \quad (2.30)$$

where s_{12} is the distance between probe 1 and probe 2. It is clear that besides the contact resistance itself, this formula is impractical as it requires the contact dimensions to be known. Finally, the four-point probe method solves this issue by measuring the voltage between two other probes, which gives³⁹⁰

$$V_{34} = \frac{I\rho}{2\pi t} \ln\left(\frac{s_{13}s_{24}}{s_{23}s_{41}}\right). \quad (2.31)$$

This formula is valid for any probe arrangement provided that the tip radius is small behind the probe separation. If the probes are disposed in square as in Fig. 2.20 (b), $s_{12} = s_{23} = s_{34} = s_{41}$ and $s_{13} = s_{24} = \sqrt{2}s_{12}$ it reduces to

$$V = \frac{I\rho}{2\pi t} \ln 2 \quad (2.32)$$

which is independent of the tip separation.

2.7.1.b Limited sample size

Compared to an infinite plan, the proximity of the sample edge increases the resistance and leads to an over-estimation of the resistivity derived from Equation 2.32. A correction factor F can be introduced to take the sample size into account.

$$V = \frac{1}{F} \frac{I\rho}{2\pi t} \ln 2 \quad (2.33)$$

The expression of F for the square 4PP geometry on a circular sample was found to be³⁹⁰

$$F(s, d) = \frac{\ln 2}{\ln 2 + \ln\left(\frac{((d/s)^2 + 2)^2}{(d/s)^4 + 4}\right)} \quad (2.34)$$

where s is the probe spacing and d the sample diameter. In the worst case, in which the probes lie at the sample edges, $d = \sqrt{2}s$ and $F = 0.5$. Then, F increases with sample size and tends to 1 when the sample size becomes large compared to probe spacing. For a triangular sample, the

correction factor is not known but must be comprise between 0.5 and 1 as long as an imaginary circle containing all probes can be drawn in the triangle.

2.7.2 Instruments and usage

HfSe₂ layers and heterostructures were measured using a four-probe station equipped with *Keithley 2636B* and *Keyseith 34465A* multimeters. All measurements were performed with the microscope light turned off to avoid photo-induced effects and the sample chuck was left floating to prevent eventual parasitic currents. Four probe measurements were performed by measuring voltage during current sweeps whereas two probe measurements for diodes were realized through voltage sweeps to avoid electrical breakdown.

Temperature dependence measurements on TaSe₂ samples were recorded under vacuum in a *Janis VPF100* cryostat operating from 78 K thanks to nitrogen cooling to 500 K. The contact was mechanically maintained all over this range using tungsten probes screwed on a spring. Prior to the measurements, the ohmicity of all contact was verified through current-voltage curves measured for every permutation of the wires. The resistivity of TaSe₂ layers was deduced from the mean of these four measurements to average possible inhomogeneity of the layer and dissymmetry in the probe arrangement. Then, the temperature dependence of the resistivity was determined at constant current during heating at a rate between 5 to 10 °C/min.

To avoid oxidation, all layers were measured through the capping layer, the resistivity of which is above 500 Ω.m. The Se capping evaporates at high temperature in the cryostat but the unprotected TaSe₂ layers remain stable under 10⁻⁵ mbar whereas they sensibly oxidize in air.

Growth of TaSe₂ on GaP and GaAs substrates

In this chapter, the growth of TaSe₂ is studied with the aim of producing both metallic and Mott insulating phases. It is shown that they can be selectively grown in monolayer depending on the growth temperature, whereas the multilayers exhibit mostly H-polytypes. In addition to the phase, the morphology, crystallinity and in-plane orientation are systematically discussed in order to determine the optimal growth conditions.

These studies have mainly been performed on GaP substrates, which are expected to exhibit a better temperature stability, but more established GaAs substrates have also been used for comparison. The first section is thus dedicated to their preparation.

3.1 Surface preparation

GaP and GaAs substrates must be first deoxidized to remove a thin amorphous surface oxide. This is done in the MBE chamber dedicated to III-V compounds and equipped with a valve-cracker arsenic cell and a high-temperature injector producing P₂ species out of PH₃. Then, their surface must be passivated in order to remove the dangling bonds as required for 2D-material growth.

3.1.1 Preparation of Se-terminated GaP(111)B surfaces

The deoxidation, homoepitaxy and surface passivation of GaP have been studied by Niels Chapuis.³⁹¹ Here, the main conclusions of his work are succinctly presented as a starting point for the future experiments.

3.1.1.a Substrate deoxidation

One of the issues of a thermal deoxidation is the roughening caused by the oxide desorption.³⁹² It is well known that in GaAs, arsenic oxide is first converted to Ga₂O₃, which then evaporates as the more volatile Ga₂O molecule.³⁹³ Both stages require extra Ga atoms that are provided by the etching of the GaAs substrate.³⁹⁴ To prevent this, an alternative consists in using atomic H to enable the oxygen to be desorbed as H₂O instead. This technique has already shown to be effective on GaP, but at relatively high temperature, the preferential desorption of P atoms leads to the formation of Ga droplets.³⁹⁵ The addition of PH₃ is expected to stabilize the surface, preventing the formation of droplets and enabling the surface to be smoothened at high temperature.

Therefore, the recipe consists in an initial heating step from 250 °C to 430 °C under atomic H only, followed by a progressive PH₃ supply in addition to the atomic hydrogen while the substrate temperature is increased from 430 °C to 500 °C. Finally, the samples are annealed up to 530 °C under PH₃ only and the sample rapidly exhibits a 2×2 RHEED pattern shown in Fig. 3.1 (a). Finally, the PH₃ flux is progressively decreased as the sample is cooled.

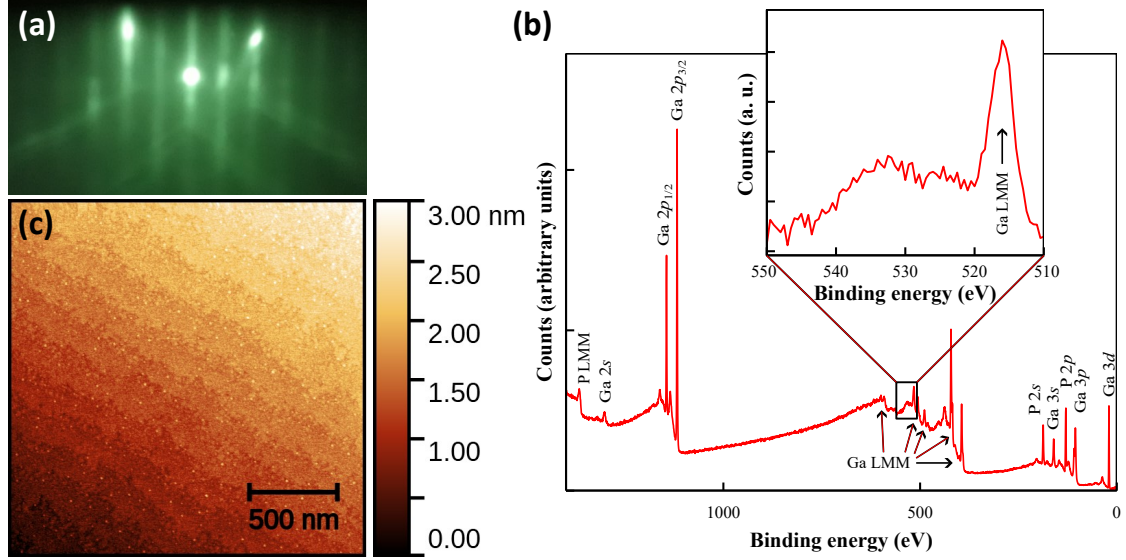


Figure 3.1: (a) RHEED pattern recorded on a deoxidized GaP substrate along a $\langle \bar{2}11 \rangle$ direction. (b) Full XPS spectrum, measured by Niels Chapuis on a deoxidized GaP substrate. The inset shows the region where the O 1s CL would be expected to appear. (c) AFM image of a deoxidized GaP substrate.

Fig. 3.1 (b) presents the XPS survey recorded on a deoxidized substrate. Every peak could be attributed to either Ga or P. The absence of O 1s signal confirms the successful deoxidation of the substrate. Besides, an AFM image reproduced in Fig. 3.1 (c) demonstrates the absence of large Ga droplets, even though tiny dots are observed. The 100 nm-wide terraces are separated by about 0.3 nm-high atomic steps, which matches the predicted value for GaP(111) interlayer distance. This is attributed to the wafer miscut since the corresponding angle is within the specification of $\pm 0.5^\circ$.

3.1.1.b Surface passivation by selenium

For selenium passivation, the deoxidized substrates are transferred under vacuum to the chamber dedicated to selenides, to be heated under vacuum up to 250 °C, and then exposed to a high ($\approx 4 \times 10^{-6}$ Torr) or a low ($\approx 4 \times 10^{-7}$ Torr) Se flux up to either 450 or 700 °C. The samples under consideration in the following are summarized in Table 3.1.

Sample #	Procedure (Temperature ranges under Se flux)	Se flux (Torr)	Exposure duration (min)	Characterizations
P1	as deoxidized	-	-	XPS
P2	250 °C to 700 °C + 3 min at 700 °C	4×10^{-6}	25.5	XPS
P3	250 °C to 450 °C + 3 min at 450 °C	4×10^{-6}	13	XPS
P4	250 °C to 700 °C + 3 min at 700 °C	3×10^{-7}	25.5	XPS
P5	250 °C to 450 °C + 3 min at 450 °C	5×10^{-7}	13	XPS

Table 3.1: Passivation procedures for GaP substrates.

The RHEED pattern immediately turns to a 1×1 one at 250 °C, as shown in Fig. 3.2 (a), which remains stable up to 700 °C under Se flux. An AFM image of the Se-terminated surface is presented in Fig. 3.2 (b). Compared to the deoxidized surface in Fig. 3.1 (b), the dots have vanished. However, the terraces still exhibit a small residual roughness and the edges remain saw-toothed.

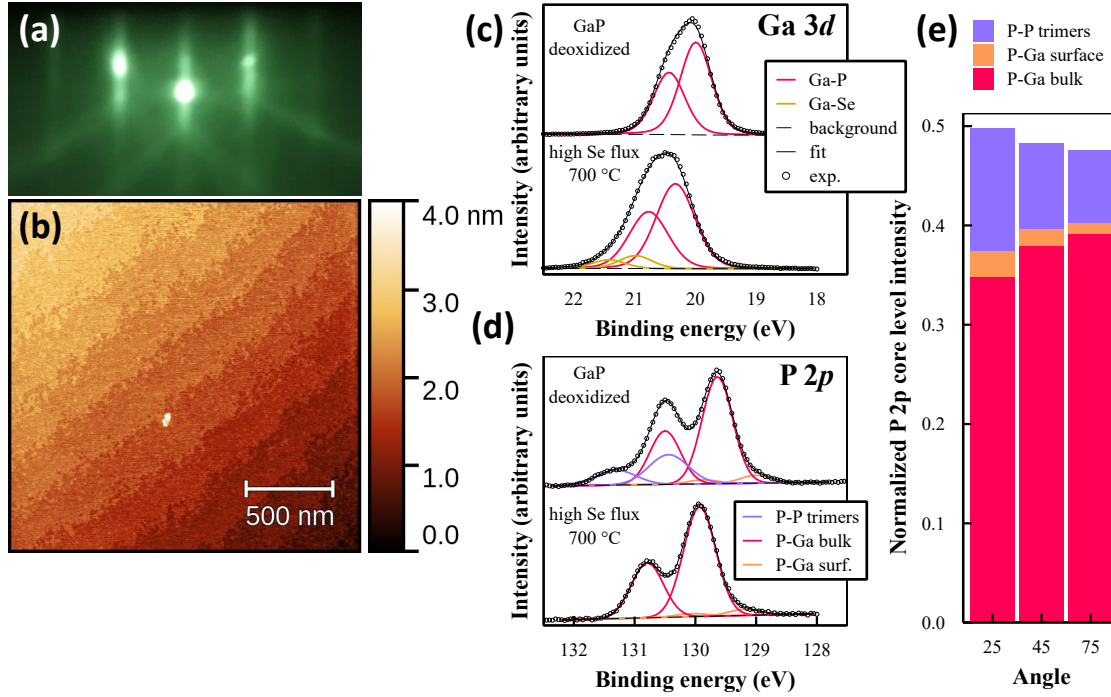


Figure 3.2: (a) RHEED pattern of the Se-passivated GaP substrate along a $\bar{2}11$ direction. (b) AFM image of a substrate after Se-passivation up to 700 °C. (c) Comparison of the Ga 3d CLs measured in XPS, as deoxidized and after exposure to Se (samples P1 and P2). (d) P 2p CL measured in XPS, as deoxidized and after exposure to Se (samples P1 and P2). All the XPS spectra were recorded at an emission angle of $\theta = 25^\circ$ to improve the surface sensitivity. The shift is mostly ascribed to the change of band bending upon Se-passivation, even though the two samples are measured on different substrates: both are n-type, but the as deoxidized one being slightly less doped. (e) Normalized intensity of the different components in the P 2p CL decomposition of the deoxidized sample as function of the electron take-off angle (sample P1). The intensity normalization is chosen so that $I_{P2p} + I_{Ga3d} = 1$ where the CL intensities I are corrected by their relative sensitivity factors.

The evolution of the Ga 3d and P 2p CLs measured in XPS upon selenium treatment is presented in Fig. 3.2 (c) and (d) respectively. If the Ga 3d CL of the as-deoxidized sample exhibits only one component, the P 2p one contains three visible doublets. This observation is compatible with the expectation of the 2×2 surface reconstruction being P-terminated on GaP(111)B,³⁹⁶ since the atoms lying on the surface can have different chemical environments than those in the bulk. To confirm this, the intensities of the components used to fit the P 2p CL of the deoxidized sample and their evolution with the electron take-off angle are presented in Fig. 3.2 (e). The vertical scale is normalized with respect to the total P 2p and Ga 3d CL intensities, corrected as described in Paragraph 2.2.4. The overall P 2p intensity decreases when the electron take-off angle is changed from 25 to 75°, hence when the analysis depth is increased, which is consistent with the surface being P-rich. Note that it should normally tend toward 0.5 in bulk, the remaining 0.5 being related to Ga, but here the proportion of P appears slightly less probably because the sensitivity factors are not totally accurate. Conversely, the relative intensity of the most intense doublet increases from 25 to 75°. It is thus attributed to Ga-P

bonds in the bulk. By contrast, the intensity of the two other doublets is more pronounced at 25°, when the measurement is more sensitive to the surface. They are thus identified as the surface components. The one lying at high binding energy could correspond to P-P bonds, in accordance with the observations of Kleinschmidt *et al.* who attributed it to the formation of P trimers on the 2×2 reconstructed GaP surface.³⁹⁶ This P 2*p* component is completely suppressed after exposition to selenium, which is consistent with the disappearance of the surface reconstruction. The second surface component, at the low binding energy side, is reduced upon Se-passivation but not entirely removed. It could correspond to the surface P atoms bonded to only 3 Ga atoms, as in Se-terminated GaAs, where only part of the As atoms at this position are replaced by Se atoms.³²⁶

Beyond the suppression of the surface reconstruction, which suggests the removal of the dangling bonds, the electronic surface passivation is seen through the evolution of the band bending. The bulk Ga-P component in both the Ga 3*d* and P 2*p* CLs are shifted toward higher binding energies upon Se passivation. This is explained by a displacement of the band position with respect to the Fermi level at the surface. In this case, the increase of the CLs binding energy indicates that the conduction band becomes closer to the Fermi level after Se-passivation. Since both substrates are n-type, this corresponds to a decrease of approximately 0.2 eV in the band bending, which is consistent with a reduction in Fermi level pinning and a partial passivation of the surface, similar to what has been reported on GaAs.³⁵⁹

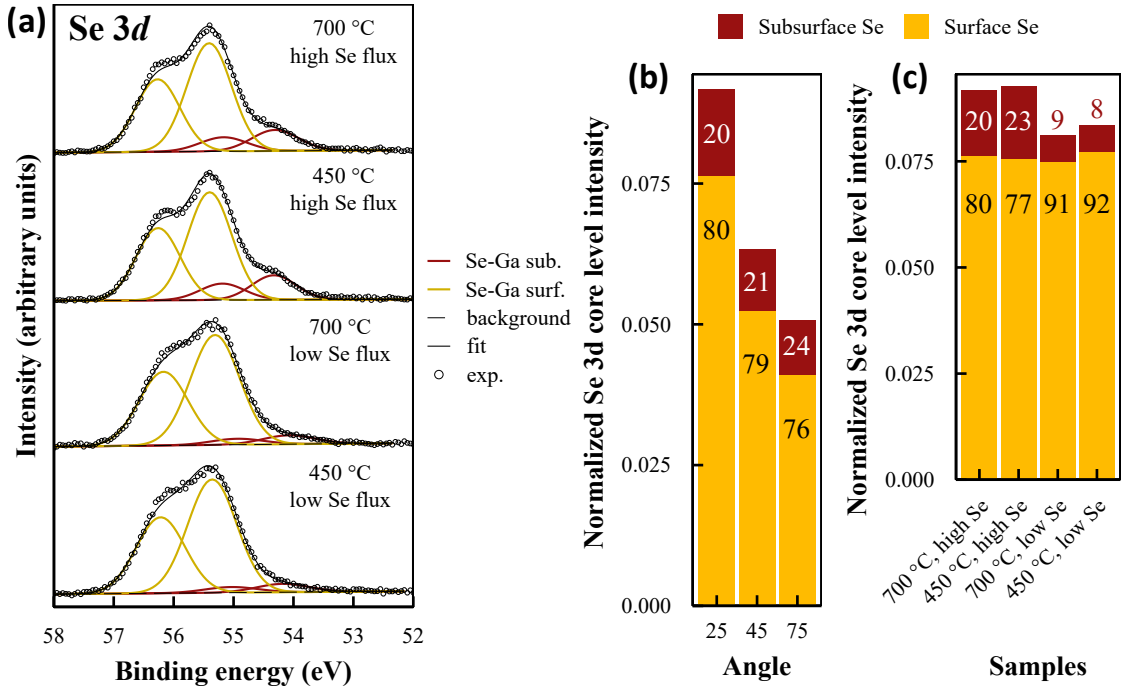


Figure 3.3: (a) Se 3*d* CL measured in XPS for different passivation conditions (samples P2–P5). (b) Variation of the Se 3*d* component intensities from the fit in (a) with respect to the electron take-off angle, measured on the sample prepared at 700 °C under a high Se flux (sample P2). (c) Comparison of the Se 3*d* component intensities from the four conditions presented in (a). All the XPS spectra were recorded at an emission angle of $\theta = 25^\circ$ to improve the surface sensitivity. The numbers on the columns are the percentages of the total Se intensity. The normalization is chosen so that $I_{P2p} + I_{Ga3d} + I_{Se3d} = 1$ where the CL intensities I are corrected by their relative sensitivity factors.

In Fig. 3.3 (a), the Se 3*d* CL is presented for different passivation conditions. It can be decomposed into a high and a low binding energy doublet which are attributed, by analogy with Se-treated GaAs,³²⁷ to Se at the surface and below the surface, respectively. To confirm the correct interpretation of these components, the evolution of their intensities as function of the electron take-off angle is presented in Fig. 3.3 (b) for the sample passivated at 700 °C and high Se flux. The proportion of Se signal decreases compared to the P and Ga ones as the probed depth is increased at high angles, in good agreement with the presence of Se mostly on the top surface, which was also confirmed by Niels Chapuis using photodiffraction.³⁹¹ However, if both Se components are reduced, one decreases more rapidly than the other as shown by their relative percentages. It confirms that the high binding energy component corresponds to the surface sites, whereas those related to the low binding energy doublet probably lie close below. Finally, the influence of the temperature and selenium flux is analyzed through the comparison of the Se 3*d* component intensities in Fig. 3.3 (c). Both remains quantitatively similar at 450 and 700 °C, whereas a decrease of the Se flux by one order of magnitude effectively reduces the sub-surface component. Remarkably, the surface one stays unchanged among the four samples which indicates that the surface is saturated by Se atoms and suggests that the passivation is achieved in every condition. Even if the process is largely self-limiting, the too large excess of Se atoms at high flux seems responsible for the subsurface component. Therefore, a low Se flux may be preferable to reduce the diffusion below the surface, whereas the temperature does not play a visible role.

3.1.1.c Growth of a GaP buffer layer

In the previous section, the GaP substrates have been successfully deoxidized and passivated by Se atoms. However, the terraces on the resulting surfaces were not atomically smooth. To prevent the extra atomic steps to act as nucleation sites, the use of a buffer layer is proposed.

Right after the deoxidation process previously established, the substrate is brought to the growth temperature under continuous PH₃ flux of 8 sccm. Around 600 °C, the surface reconstruction changes to a $\sqrt{19} \times \sqrt{19}$ one. For the sample grown at the highest temperature, the RHEED pattern becomes spotty at 670 °C, but immediately recovers as the Ga shutter opens without changing the PH₃ flux.

The AFM scan presented in Fig. 3.4 (a) reveals a very high roughness for the sample grown at the lowest temperature. The surface is very disordered, but triangular pyramids are clearly observed. Some of them are oriented in opposite directions, suggesting the presence of mirror twins which are known to occur at low temperature on GaAs(111)B.^{397,398} On this sample, the optical microscope image (Fig. 3.4 (i)) appears featureless, indicating an absence of large-scale structures. A much lower roughness is found at higher growth temperatures. On the sample grown at 650 °C, in Fig. 3.4 (b) and (f), a smooth stepped surface is revealed over two different regions. Interestingly, in region A, some parallel arrangements are observed which exhibit sudden 120° rotations, while in region B, the steps are slightly disordered but they keep the same orientation overall. The corresponding optical microscope image (Fig. 3.4 (j)) reveals elongated pyramids that cover only a small fraction of the surface. It is hence possible that the parallel steps in region A belong to a pyramid much larger than the scan size. Such a variation of morphology is more clearly evidenced in Fig. 3.4 (c) and (g) for the sample grown at 660 °C. The 2×2 μm scan reveals very large terraces with triangular shapes, but a high density of parallel atomic steps attributed to a pyramid is found next to it in the 10×10 μm image. On this sample, the pyramids occupy a large proportion of the surface according to optical microscopy (Fig. 3.4 (k)), and appear very similar to some observed on GaAs(111)B substrates.³⁹⁹ Finally, in Fig. 3.4 (d) recorded on the sample grown at the highest temperature, the terraces are not perfectly straight and resembles more to those of Fig. 3.4 (f), probably originating from the substrate miscut. It seems that no pyramids have been found in AFM on this sample, which is consistent with the optical microscope image in Fig. 3.4 (l) revealing a small density of very faint structures.

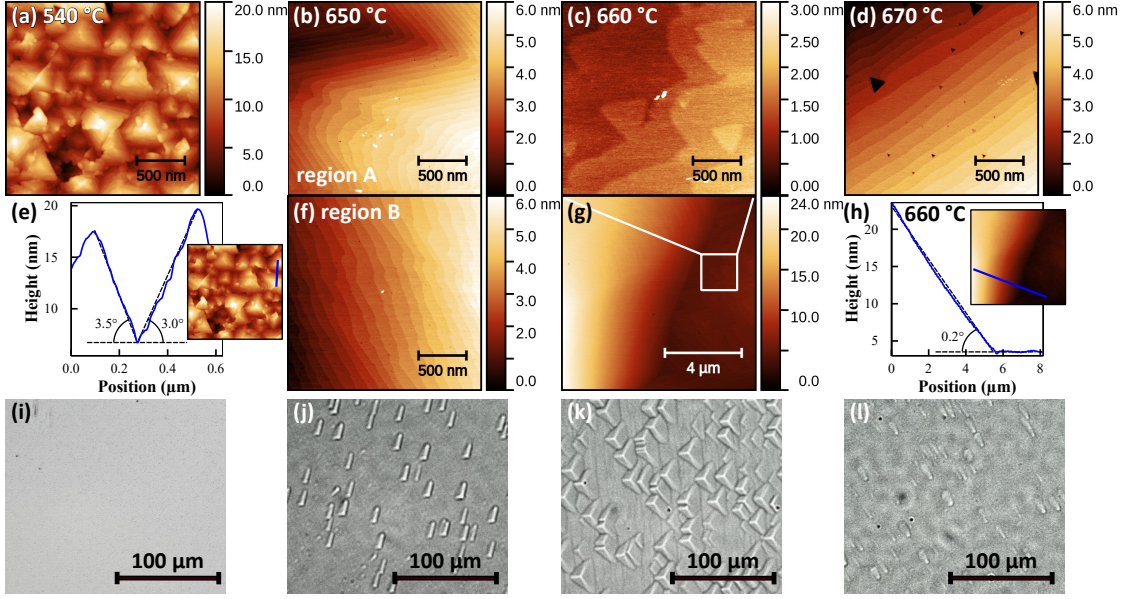


Figure 3.4: (a-d,f) $2 \times 2 \mu\text{m}^2$ AFM images of 53-nm thick homoepitaxial buffer layers grown on GaP(111)B using a Ga flux of 0.16 ML/s and 8 sccm of PH₃ at a substrate temperature of (a) 540 °C, (b, f) 650 °C, (c) 660 °C, and (d) 670 °C. (e) Height profile measured perpendicular to two pyramid facets oriented in opposite directions. (g) $10 \times 10 \mu\text{m}^2$ AFM image measured at the same position as image (c). (h) Height profile measured perpendicular to the pyramid facet in image (g). (i-l) Optical microscope images corresponding to the samples in (a-d), in which the contrast was greatly enhanced to reveal the pyramids.

However, in this case the AFM image also reveals deep triangular holes. Some have also been observed on the samples grown at 650 and 660 °C (not shown), but they were much smaller and scarcer. Hence, it is believed that they are caused by a too high growth temperature. The formation of multilayer holes on GaAs(100) surface at high temperature has been explained by the presence of sites where the growth is inhibited.⁴⁰⁰ The origin of those was not clearly identified but Ga droplets were suspected to be the growth inhibitors. On GaP(111)B, droplets are known to be easily formed at 750 °C and vanish below 650 °C.³⁹⁵

Overall, it appears that the growth temperature has a significant impact on the morphology since a lower density of much larger pyramids is observed as the temperature is increased, in accordance to a larger adatom diffusion. It also seems that the pyramids flatten, in a similar way to what was reported on GaAs(111)B.⁴⁰¹ In Fig. 3.4 (e), an angle of $3 \pm 0.5^\circ$ is measured on two opposite pyramid facets from the sample grown at 540 °C, whereas in the region A of the sample grown at 650 °C Fig. 3.4 (b) the average terrace width of 60 ± 15 nm corresponds to an angle of $0.3 \pm 0.1^\circ$. It is only 0.2° on the 660 °C sample as shown in Fig. 3.4 (h). Even though the pyramid coverage does not exhibit a monotonous trend from 650 °C to 670 °C, it suggests that pyramids could completely vanish at higher growth temperature. However, the apparition of the triangular holes indicates that the temperature stability limit has been reached.

The influence of the Ga and P flux have been discussed by Niels Chapuis in his thesis.³³⁵ These parameters did not seem to have a significant influence on the pyramid and hole formation, even though a slightly better morphology was remarked at low growth rates. It contrasts with a recent report of a flat GaP(111)B surface achieved in homoepitaxy using much higher Ga flux.⁴⁰² In this study, a 1×1 surface reconstruction appearing at high temperature was believed to promote a step-flow growth, preventing the formation of pyramids. Since the $\sqrt{19} \times \sqrt{19}$ surface reconstruction is a mixed Ga and P termination, its disappearance may be related to Ga rich conditions, but the authors also hypothesize a role of the atomic H from the cracked PH₃.

In any case, the temperature range for the 1×1 RHEED pattern before it degrades is reported to be very narrow, and slightly shifts toward lower temperatures when the PH_3 flux is decreased. Using a higher Ga/P flux ratio, it is possible that the authors have found this range at a lower temperature. In addition, the use of a high growth rate, up to 1.5 ML/s in their optimal recipe, introduces more adatoms, which may favor the suppression of the surface reconstruction. By contrast, our results show a complete overlap of the $\sqrt{19} \times \sqrt{19}$ surface reconstruction and the degradation characterized by the formation of holes.

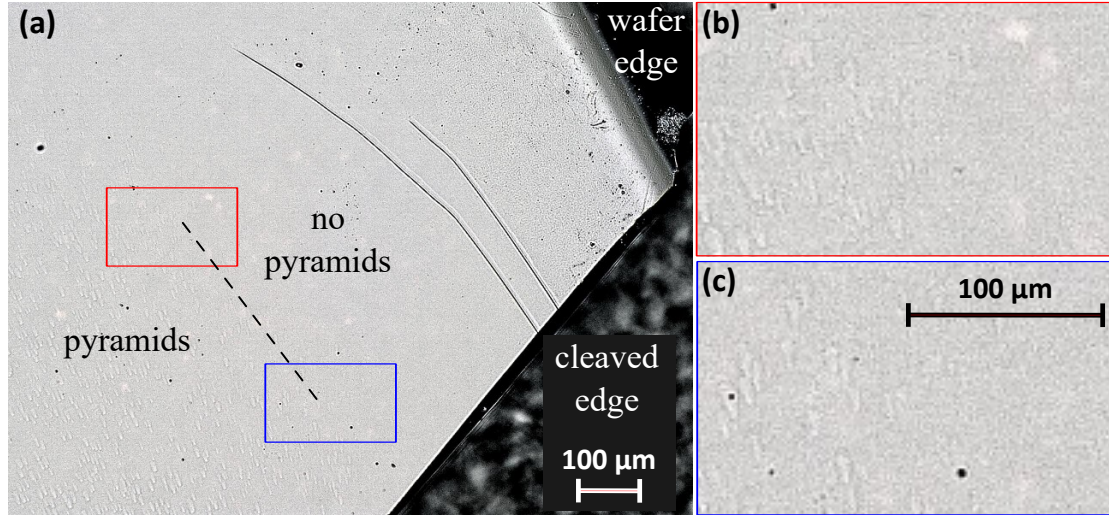


Figure 3.5: Optical microscope image of the GaP(111)B buffer grown at 670 °C near the sample edges. (b, c) Same image magnified over two different regions to reveal the limit of the pyramids.

Still, if the growth conditions may not have been optimal, the absence of clear trends among about 20 samples must be discussed. As shown in optical microscope images in Fig. 3.4 (f-h), the pyramids exhibit different shapes. It is explained by the substrate miscut which varies in angle and orientation. The larger terraces away from the pyramids in Fig. 3.4 (c) effectively suggest a smaller tilt angle, which results in well-formed pyramids in (k) compared to case (j) and (l). Interestingly, it seems that the pyramid density is reduced on more tilted surfaces, on which the pyramids are elongated. In addition, images taken near the sample edge, in Fig. 3.5, show an absence of pyramids close to the wafer edge, whereas the cleaved edges do not exhibit such an effect. This has already been observed on other substrates, and was explained by the local variation of the miscut near the wafer edges resulting from the polishing process.^{403–405} In GaAs(111)B homoepitaxy, the pyramids have been reported to become very rare on a 1° vicinal substrate and totally absent with a tilt of 2° .⁴⁰⁶ Hence, if the size and angle of the pyramids is clearly correlated to the temperature, their density is probably not relevant since it depends on the miscut angle. Finally, the use of vicinal GaP substrates could be helpful, but they cannot be easily purchased.

3.1.2 Preparation of Se-terminated GaAs(111)B surfaces

Following the difficulty to get a smooth GaP(111)B surface, it is proposed to investigate GaAs instead since it is a more widespread and less expensive substrate. In addition, the GaAs homoepitaxy was comparatively more studied in the literature, and several successful growths of a buffer layer on (111) surfaces have been reported,^{397,407} although mostly on vicinal substrates.^{406,408} Here, the growth of GaAs buffer layer on a $\pm 0.5^\circ$ GaAs(111)B is first presented, followed by a study of its passivation by Se atoms.

3.1.2.a Growth of a GaAs buffer layer

The deoxidation process used for GaAs substrate is similar to GaP. A 1×1 RHEED pattern is rapidly observed during the initial heating step under atomic hydrogen. From 450 °C to 530 °C, an As₄ flux of 0.9 ML/s on GaAs(111) is supplied in addition to the atomic hydrogen, and a 2×2 surface reconstruction appears around 490 °C. The sample is further heated under As₄ only and the surface reconstruction turns to a $\sqrt{19} \times \sqrt{19}$ one around 540 °C, which vanishes above 635 °C as the RHEED becomes spotty. Finally, the growth occurs at 630 °C near the temperature stability limit. Similar to the GaP case, the RHEED rapidly recovers and exhibits the $\sqrt{19} \times \sqrt{19}$ reconstruction during the growth at a Ga deposition rate of 0.35 ML/s and under an As flux of 0.9 ML/s.

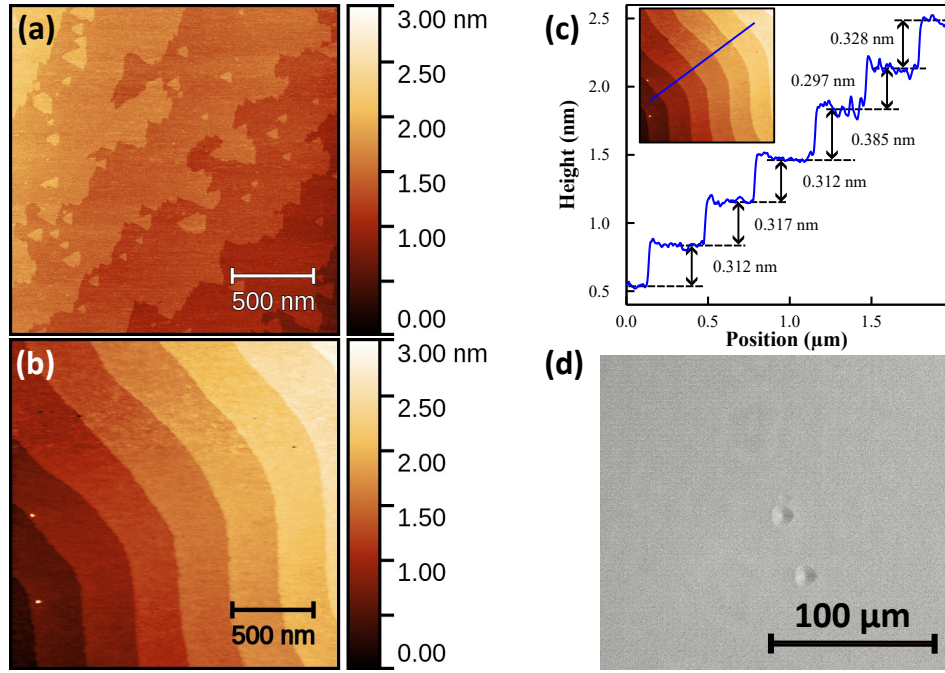


Figure 3.6: (a) $2 \times 2 \mu\text{m}^2$ AFM image of a deoxidized GaAs(111)B substrate. (b) $2 \times 2 \mu\text{m}^2$ AFM image of the GaAs(111)B buffer grown at 630 °C. (c) Height profile measured on image (b) along the line drawn on the inset. (d) Optical microscope image of the GaAs buffer layer.

The morphology of the buffer layer is compared to a reference deoxidized GaAs substrate in Fig. 3.6. The latter exhibits serrated atomic steps (Fig. 3.6 (a)), similar to those observed on the deoxidized GaP surfaces, with small triangular islands on the terraces. By contrast, the buffer layer (Fig. 3.6 (b)) is characterized by smooth terraces separated by parallel curved atomic steps. The measured step height on the profile Fig. 3.6 (c) is 0.33 ± 0.05 nm, perfectly matching the expected height for monoatomic steps.³²⁴ Besides very few pyramids were observed by optical microscopy, as revealed in Fig. 3.6 (d), which means that the buffer layer is also rather smooth at macroscopic scale. The reason why the growth was successful on GaAs and not on GaP is not clear. Especially, the terraces width being above 300 nm on GaAs, the influence of the substrate miscut can be ruled out here. Hence, it is believed that the optimal growth conditions have been found near the end of the $\sqrt{19} \times \sqrt{19}$ stability domain, as recommended by some authors,³⁹⁷ even though the high temperature 1×1 reported elsewhere^{408,409} was not attained.

3.1.2.b Surface passivation of GaAs

New GaAs buffer layers have been prepared using the same recipe to study the Se passivation on this surface. In a similar way as for GaP, the GaAs substrates are heated under vacuum up to 250 °C. At this temperature the Se shutter opens and the RHEED pattern turns to a 1×1 . Various annealing temperatures, Se fluxes and durations have been tested and are summarized in Table 3.2. Overall, the temperatures have been limited to 550 °C considering the thermal stability of GaAs, and the selenium flux was lowered to reduce the Se uptake. Samples A2 and A3 have been prepared using the same method as for GaP substrates, with a continuous Se supply from 250 °C to the annealing temperature, leading to a long exposure to Se. To limit this latter, samples A4 and A5 have been prepared without Se supply during the heating step.

Sample #	Procedure (Temperature ranges under Se flux)	Se (Torr)	Exposure duration (min)	Characterizations
A1	as deoxidized	-	-	XPS
A2	250 °C to 550 °C + 3 min at 550 °C	5×10^{-7}	18	XPS
A3	250 °C to 500 °C + 3 min at 500 °C	2×10^{-7}	15.5	XPS
A4	1 min at 500 °C	4×10^{-7}	1	XPS
A5	5 min at 250 °C	4×10^{-8}	5	XPS

Table 3.2: Passivation procedures for GaAs substrates.

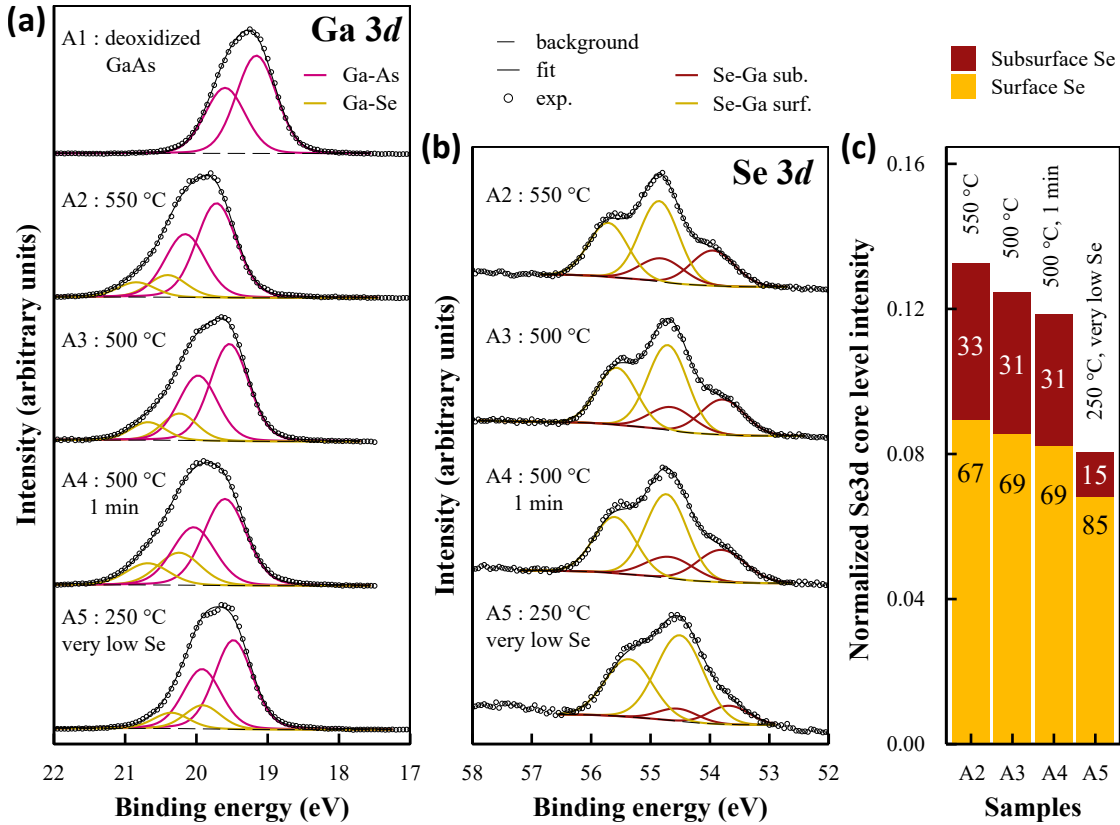


Figure 3.7: (a) Ga 3d and (b) Se 3d CLs measured in XPS at 25° from the surface and their decomposition. (c) Surface and subsurface component intensities in the Se 3d CLs in (b), normalized with respect to all elements with the appropriate sensitivity factors, so that $I_{As3d} + I_{Ga3d} + I_{Se3d} = 1$. The numbers on the columns are the percentages of the total Se intensity.

The evolution of the Ga 3*d* CL is presented in Fig. 3.7 (a). The Se-passivated GaAs samples exhibit a tail at high binding energy which is more prominent than in GaP-Se ones, suggesting a large Se incorporation. This is, however, less pronounced in sample A5. The fit of the Se 3*d* CLs shown in Fig. 3.7 (b) indeed reveals a non-negligible subsurface component at the low binding energy side. To quantitatively study this, the proportion of surface and subsurface Se with respect to the total amount of Ga, As and Se is presented in Fig. 3.7 (c). Both the surface and subsurface Se 3*d* intensities decrease from sample A2 to A5, following the reduction of the deposited Se. Nevertheless, the overall quantity of Se does only slightly decrease from sample A2 to A4, despite of a drastic decrease of the exposition time. Notably, it remains much larger than in Se-terminated GaP. The excess Se appears mostly in the subsurface component, as observed in GaP, but on GaAs the surface Se also varies, indicating that the process is not completely self-limiting. This is worrying since the Se passivation was only achieved in 1 minute on sample A4, which is much shorter than a standard growth duration for a monolayer TMDC, indicating that the Se uptake would also continue during a growth under these conditions. For this reason, sample A5 was prepared at a lower temperature and using a much lower Se flux so that the duration could be increased. It exhibits a significantly lower Se content, comparable to the one in GaP-Se samples. Again, both components are decreased, but the subsurface Se represents 15 % of the total Se intensity in this sample whereas it ranges from 31 to 33 % in the other GaAs-Se ones. Hence, the subsurface component is proportionally more reduced than the surface one.

Overall, it is clear that Se is more easily incorporated into GaAs than in GaP as larger Se contents have been obtained for a similar amount of deposited Se, comparing for instance samples A3 and P5. This could be explained by the lower temperature stability of GaAs, related to weaker III-V bonds, and a larger lattice parameter, Se atoms having a radius closer to the As one.⁴¹⁰ The subsurface component has been significantly reduced from sample A2 to A5, however the fact that the surface Se content does also vary raises the question of whether it efficiently suppresses the dangling bonds.

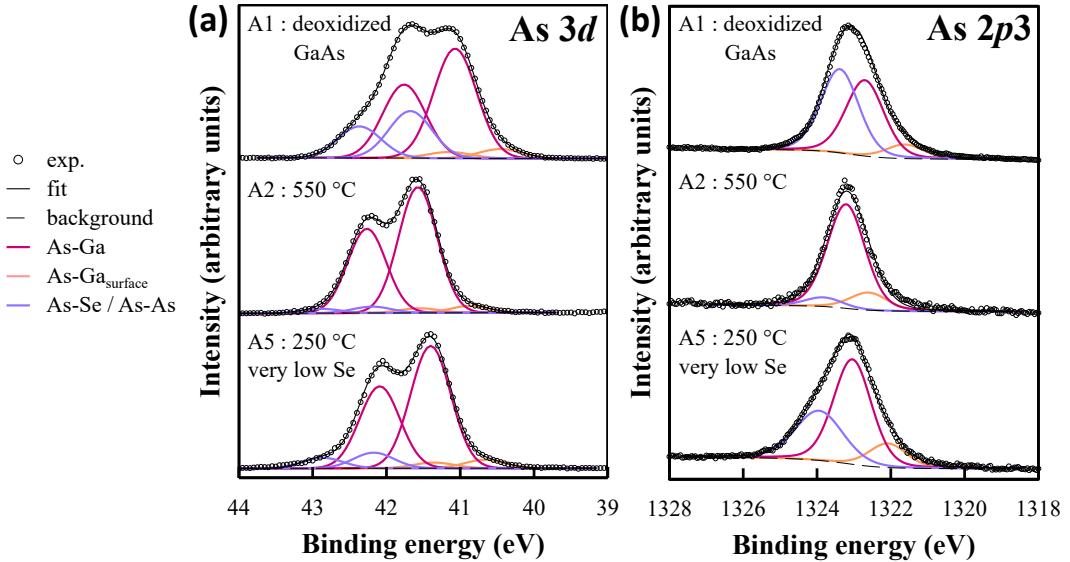


Figure 3.8: (a) As 3*d* and (b) As 2*p*_{3/2} CLs measured in XPS at 25° from the surface on two Se-passivated GaAs buffer layers (samples A2 and A5) and a deoxidized substrate (sample A1).

To answer this, the surface passivation is studied through the As CLs. Based on the As 3*d* one, presented in Fig. 3.8 (a), the surface components are clearly evidenced on the bare substrate, which are interpreted in the same way as P 2*p* ones. They are almost entirely removed in sample A2, in accordance to an efficient passivation, while they remain non-negligible in sample A5

meaning that the passivation is incomplete in this case. This is more clearly observed on the As $2p_{3/2}$ CL, presented in Fig. 3.8 (b), which is extremely surface sensitive because of the low kinetic energy of the photoelectrons. However, to ensure the uniqueness of the fit, additional constraints are required in this case. The energy separation between the As $3d_{5/2}$ and As $2p_{3/2}$ CLs is measured to be 1281.6 eV on sample A2, which is almost correctly fitted by a single chemical environment. Then, the positions of the bulk As-Ga components in the other samples are set relatively to their respective As $3d$ counterpart. On the bare GaAs substrate, the surface component at high binding energy, attributed to As trimers, is particularly prominent, and is almost completely suppressed on the Se-passivated sample A2. Concerning the low binding energy one, it is only slightly reduced compared to the bulk As-Ga upon Se passivation at 550 °C and increases back for the sample prepared at 250 °C, which suggests an insufficient passivation on the latter. This can also be deduced from the shift of the bulk GaAs component in the Ga $3d$ CL in Fig. 3.7 (a) as well as in the As CLs in Fig. 3.8. If both CLs are significantly moved toward larger binding energies on sample A2, indicating a good surface passivation, the shift is effectively less important on sample A5. On the As $2p_{3/2}$ CL, though, it is not obvious because a large component lies at high binding energy on this sample. Its position is not far from the As-As peak, but it spreads even further on the high binding energy side, hence it could be attributed to As-Se bonds as already observed on GaAs(100) prepared at the same temperature.³²⁷ Finally, it seems that some Se atoms cannot replace the surface As atoms at 250 °C and are adsorbed onto them, explaining why the Ga-Se component is less pronounced in this case in Fig. 3.7 (a). Hence, a higher temperature would be preferable for an efficient Se passivation.

Besides, it is noteworthy that the total amount of Se evaporated on samples A4 and A5 is only 1.8×10^{15} and 1.1×10^{15} at.cm⁻², respectively, whereas the ideal passivation with 75 % of the surface As atoms replaced by Se³²⁶ would require at least 5.4×10^{14} at.cm⁻². This means that the optimal quantity of Se atom to ensure a passivation without excess incorporation lies in a narrow range since for a value of 1.8×10^{15} at.cm⁻², Se is strongly incorporated below the surface.

Summary

The buffer layer growth and surface passivation of GaP and GaAs have been compared. If the GaAs homoepitaxy was more successful, this substrate reacts more easily with Se which leads to an important incorporation below the surface. As we expect this to impose severe restrictions on the usable temperatures and Se flux for the subsequent TMDC growth, GaP substrates are preferred for the following studies, and GaAs ones are only used for the sake of comparison. Because the formation of pyramids could not be avoided on the GaP buffer layers, GaP substrates are directly Se-passivated after deoxidation.

3.2 TaSe₂ monolayers

The substrate being characterized, the growth of TaSe₂ is now explored. In this section, monolayers are discussed first because they were more studied in the literature, and only two different phases, namely the 1T and 1H ones, are expected. XPS and UPS characterizations confirm the successful growth of both phases, which are completed by the study of the layer morphology and electrical properties.

Except if otherwise stated, all growths are performed on GaP substrates which are deoxidized according to the process described in Section 3.1.1.a. The Se passivation is achieved at various temperatures ranging between 450 and 700 °C, with Se flux varying from 3×10^{-7} to 5×10^{-6} Torr which are the limits explored Section 3.1.1.b. Apart from the amount of subsurface Se, the substrates prepared under these conditions are relatively similar according to the XPS characterization.

3.2.1 Phase control in TaSe₂ monolayer

According to previous studies on graphene substrates, the 1T phase appears at high temperature and the 1H at low temperature.^{238,239} This is why the influence of the growth temperature is discussed first. Then, a post-growth annealing is considered to improve the film morphology. Finally, the growth on GaP and GaAs are compared.

3.2.1.a Influence of growth temperature

The Ta and Se fluxes are measured before the substrate preparation. A TaSe₂ growth rate in the 0.004–0.007 Å range is chosen to promote surface diffusion and the growth duration is calculated accordingly to get the targeted thickness. Se is provided in large excess, with typically a Se flux of few 10^{-6} Torr, corresponding to 0.5–1.5 Å/s, in order to avoid metallic cluster formation. The growth is monitored by RHEED, and the layers are then characterized by XPS before any further characterization to control the purity and the thickness.

Table 3.3 summarizes the sample growth conditions and presents the thickness estimation derived from XPS measurements using the method described in Section 2.2.5. These estimated thicknesses are consistently below the target ones, leading to fractions of monolayers. Therefore, the incomplete monolayer model is systematically applied in this section, which means that the presented values correspond in fact to the surface coverage. This improved model slightly increases the estimated thickness when it is strictly less than 1 ML, but it will still be shown to underestimate the thickness. Though, some variations are observed among the samples, probably arising from the difficulty to precisely measure a very low Ta deposition rate. Hence, the control using XPS remains valuable in order to compare the different samples. As much as possible, samples with a similar thickness will be presented to discuss the influence of other parameters.

Sample #	Growth T. (°C)	Annealing T. (°C)	Targeted thick. (ML)	Measured thick. (ML)	Characterizations
T1	250	-	1	0.84	RHEED, AFM, XPS, UPS
T2	450	-	1	0.99	RHEED, XPS, UPS
T3	550	-	1	0.55	RHEED, XPS, UPS
T4	600	-	1	0.91	RHEED
T5	600	-	1	0.70	XPS, UPS

Table 3.3: Monolayer TaSe₂ samples grown at various temperatures.

After few minutes of TaSe₂ growth, additional faint streaks appear on the RHEED pattern, which are slightly away from the GaP ones. This is because the TaSe₂ lattice parameter is about 10 % smaller than the GaP one along the $[2\bar{1}\bar{1}]$ direction. This observation demonstrates

that the growth is epitaxial, even if the TaSe₂ layer grows with its own lattice, as expected in vdW epitaxy. After the calculated growth duration, typically about 20 min, the GaP spots are barely visible, and the obtained RHEED pattern are presented in Fig. 3.9 (a-d). Broad streaks are observed on the sample grown at 250 °C. These streaks become progressively thinner and brighter at higher growth temperature. However, at 450 °C and above, extra spots are observed on the RHEED pattern, suggesting a surface roughening. The AFM image in Fig. 3.9 (e) reveals the morphology of the sample grown at 250 °C. Despite the surface appears largely disordered, the GaP steps remain barely visible and are evidenced by the height distribution plotted in Fig. 3.9 (f). The fit effectively reveals terraces separated by 0.37 nm, which is not far from the GaP(111) interplanar distance.⁴¹¹ The terraces are decorated with numerous islands and holes less than 10 nm wide. Since some of them are higher than a single GaP step, they are attributed to the TaSe₂ layer. Based on the expected thickness and the estimation from XPS measurements, it is believed that most of the substrate is covered by a TaSe₂ monolayer, and only the brighter islands correspond to bilayers. Finally, the dim RHEED pattern in Fig. 3.9 (a) is consistent with the presence of grains having a smaller lateral size than the coherence length of the electron beam.

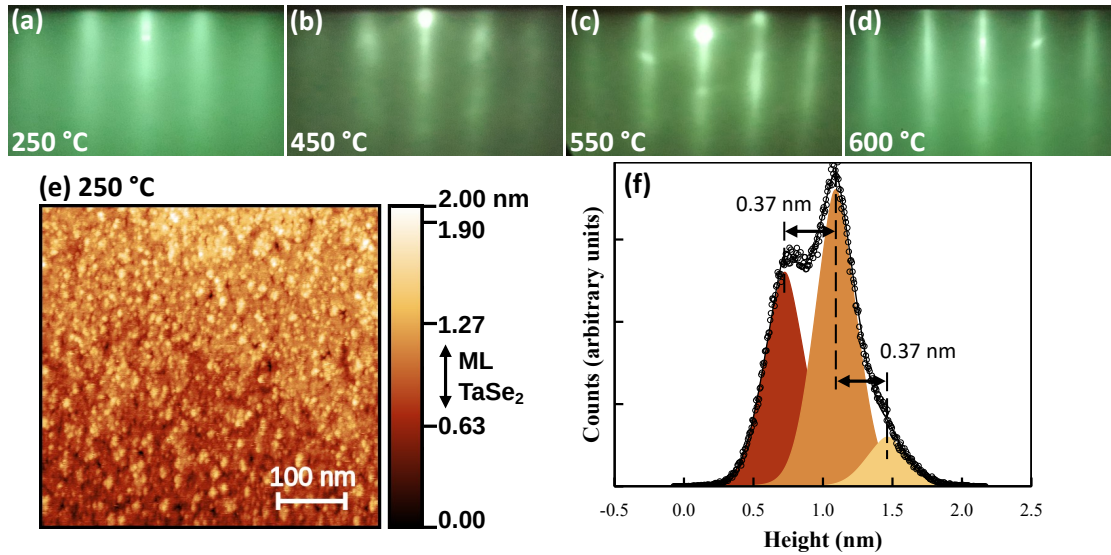


Figure 3.9: (a-d) RHEED pattern recorded along a $\langle 10\bar{1}0 \rangle$ direction of the TaSe₂ monolayer grown at (a) 250 °C (sample T1), (b) 450 °C (sample T2), (c) 550 °C (sample T3), (d) 600 °C (sample T4). (e) $500 \times 470 \text{ nm}^2$ AFM of a TaSe₂ monolayer grown at 250 °C (sample T1). (f) Histogram of the heights measured on image (e).

The layers are characterized by XPS through the Se 3*d* and Ta 4*f* CLs presented in Fig. 3.10 (a,b). Both are asymmetric as expected for a metallic material.

The Se 3*d* CL exhibits a prominent doublet on the samples grown at 250, 550 and 600 °C whereas it is more indistinct on the sample grown 450 °C. In addition, a shift of the peak maxima is observed after careful alignment of the spectra to offset the photovoltage. The Se 3*d*_{5/2} maximum is positioned at 53.5 eV from the Fermi level for the sample grown at 250 °C and at 53.8 eV in the one grown at 600 °C. This is in very good agreement with the positions reported for the 1H and 1T phases respectively.²³⁹ However, in this case the maximum intensity is reached for the Se 3*d*_{3/2} peak even though its integrated area should be 2/3 of the Se 3*d*_{5/2} one. To explain this, a fit of Se 3*d* CL recorded on the sample grown at 600 °C is presented in Fig. 3.10 (d). The experimental data is perfectly reproduced when taking into account the asymmetry of the Ta-Se peaks together with the presence of another doublet at high binding energy evidenced by the shoulder around 55.5 eV. The latter is attributed to Ga-Se bonds in the Se-terminated GaP

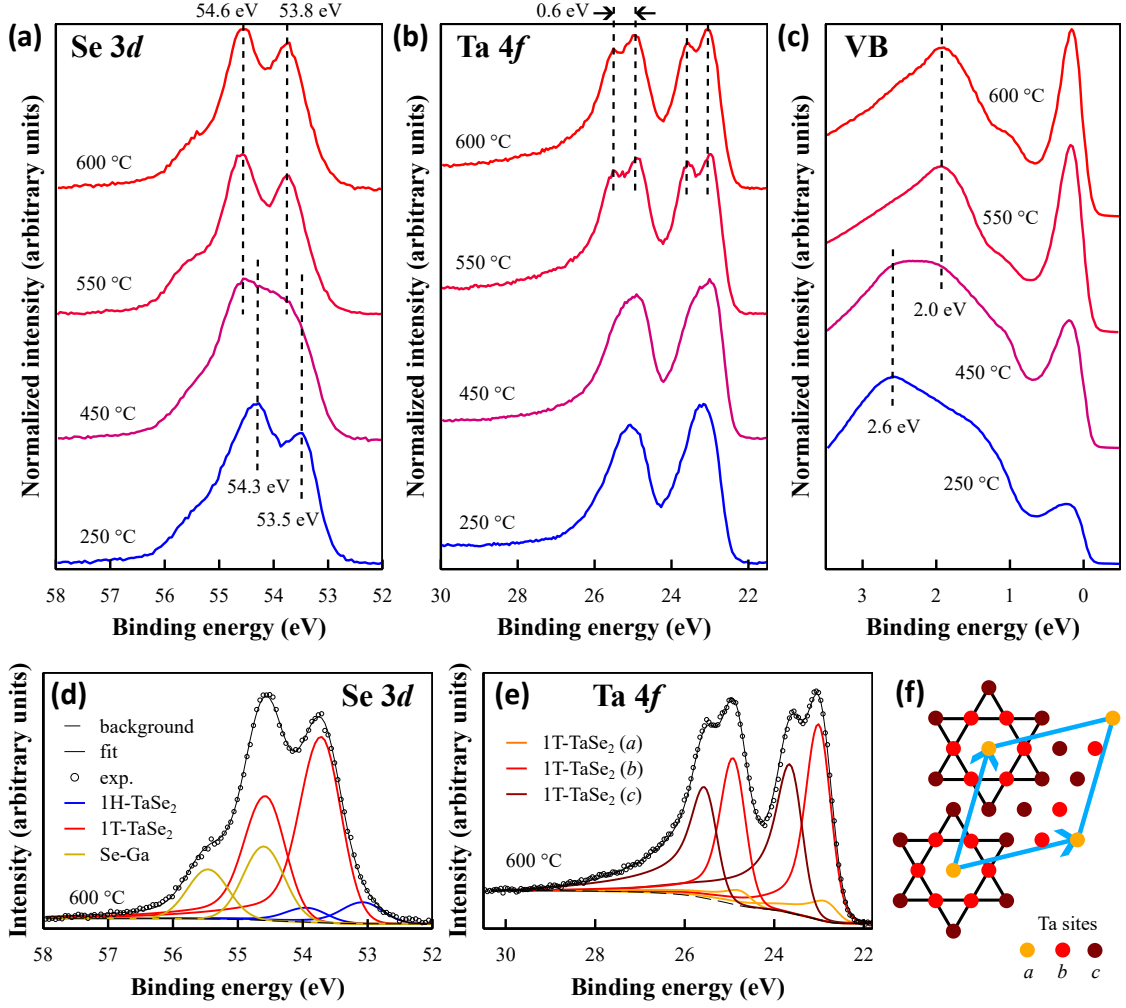


Figure 3.10: (a) Ta 4*f* and (b) Se 3*d* CLs measured in XPS on TaSe₂ monolayers grown at various temperature (samples T1, T2, T3 and T5). All the spectra are acquired at 45°. (c) Valence band of the same samples, measured around Γ using UPS. (d,e) Decomposition of the (d) Ta 4*f* and (e) Se 3*d* CLs of the TaSe₂ monolayers grown at 600 °C (sample T5). (f) Schematics of the inequivalent Ta sites in 1T-TaSe₂ in the presence of the CDW.

substrate, Ga atoms being more electronegative than Ta ones. In addition, a small component of at low binding energy is added considering an eventual contribution of 1H phase. Here, the best fit is achieved with 10 % of 1H phase, confirming that the 1T phase is largely dominant. However, the asymmetry and the presence of 3 doublets makes the decomposition not unique and therefore, the determination of phase proportion is rather uncertain.

Regarding the Ta 4*f* CL, it exhibits a large doublet for the samples grown at low temperature, which is split into two doublets at 550 and 600 °C. The large width of the CL for the sample grown at 250 °C could be due to the poor crystallinity of this layer. However, it seems even wider for the one grown at 450 °C, suggesting the presence of more than one component. The splitting of the Ta 4*f* CL on the layers grown at 550 and 600 °C is in agreement with the presence of the CDW at room temperature in the 1T phase and the observed peak separation of 0.6 eV perfectly matches previous measurements.⁴¹² It originates from the presence 3 inequivalent Ta sites in the star-of-David pattern, denoted *a*, *b* and *c*, which are in the proportion 1:6:6 as shown in the schematic in Fig. 3.10 (f). The state *a*, corresponding to the central atom, is not resolved

in the spectra but is revealed through a CL decomposition in Fig. 3.10 (e) for the sample grown at 600 °C. For this, the energy separation between states *a* and *b* is set to 0.23 eV based on the work of Horiba *et al.*⁴¹². No 1H phase is considered in this case because its shape cannot be described by standard functions, and the addition of more components would be detrimental to the fit uniqueness. However, the position of the peak for the sample grown at 250 °C, which does not exhibit the CDW splitting and rather corresponds to the 1H phase according to the Se 3*d* CL, is aligned on the low binding energy one from the samples grown at high temperature (1T-TaSe₂ (b)). Therefore, the presence of the high binding energy peak (1T-TaSe₂ (c)) is a characteristic feature of the 1T phase.

The valence band presented in Fig. 3.10 (c) also exhibits a clear evolution with growth temperature. The sample attributed to the 1H phase is found to have a maximum around 2.6 eV whereas the nearest local maximum is at 2.0 eV in those assigned to 1T phase. In addition, the 1T phase exhibits a large density of state approximately 0.2 eV below the Fermi level, which has been attributed to the lower Hubbard band.⁵⁵ Finally, the XPS and UPS results indicate the growth of the 1H phase at low temperature and the 1T one at high growth temperature, in agreement with the literature.^{238–240} The spectra obtained on the sample grown at 450 °C can be explained by the presence of both phases in substantial proportion, whereas the 1T phase seems already largely dominant at 550 °C since no significant difference are noticed compared to the sample grown at 600 °C. Hence, the transition occurs around 450 °C, which is comparable to the transition at 490 °C reported by Nakata *et al.*²³⁸ and less than the one at 600 °C found by Lee *et al.*²³⁹.

3.2.1.b Annealing of TaSe₂ monolayer

The TaSe₂ monolayers grown at high temperature exhibit surface roughness according to the RHEED pattern whereas a poor crystallinity with small grains is obtained for the one grown at low temperature. To improve the morphology and crystallinity, some samples have been annealed 3 minutes at 700 °C. Those discussed in this section are presented in Table 3.4. The new samples have been attributed a new sample number, while the notation T4' signifies that it corresponds to the former sample T4 after annealing. It is seen that the thickness does not appreciably change in this case, which suggests a good reproducibility of the measurement even though the calculated thickness may not be completely accurate.

Sample #	Growth T. (°C)	Annealing T. (°C)	Targeted thick. (ML)	Measured thick. (ML)	Characterizations
T6	250	700	1	0.97	AFM, XPS, RHEED
T7	450	700	1.2	0.78	XPS
T4'	600	700	1	0.91	AFM, RHEED
T8	600	700	1	0.70	XPS, STM

Table 3.4: Monolayer TaSe₂ samples grown at different temperatures and annealed at 700 °C.

The evolution of the sample morphology is first studied thanks to the RHEED and AFM characterizations presented in Fig. 3.11. For the sample grown at 250 °C, the RHEED pattern progressively brightens and thin streaks are obtained as shown in Fig. 3.11 (a). The corresponding AFM image (Fig. 3.11 (c)) reveals a very smooth layer with clear atomic steps, and very few holes and islands. The large terraces correspond to the substrate according to the height histogram in Fig. 3.11 (e). Again, the thickness being rather close to a monolayer, it seems that the layer has largely coalesced to uniformly cover the substrate except for the few holes and bilayers islands. Individual grains cannot be discerned in the monolayer but the improvement of the RHEED pattern suggests an increase of the crystallinity. On the other hand, on the layers grown at 600 °C, the tiny dots progressively vanish above 650 °C and a 2D RHEED pattern very similar to the low-temperature grown sample is obtained as shown in Fig. 3.11 (b).

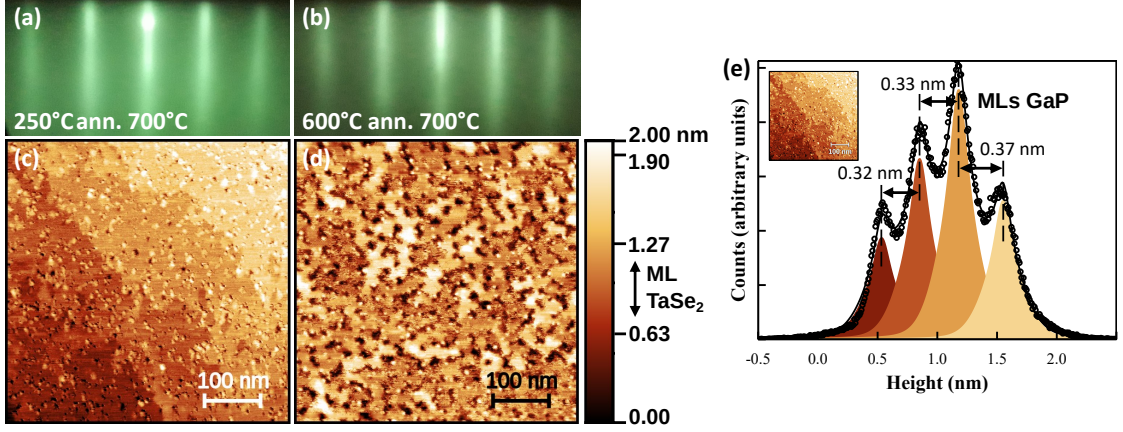


Figure 3.11: (a,b) RHEED pattern recorded along a $\langle 10\bar{1}0 \rangle$ direction of TaSe₂ monolayer grown at (a) 250 °C (sample T6) and (b) 600 °C (sample T4') after a 3 minutes annealing at 700 °C under a few 10^{-6} T of Se. (c,d) Corresponding 500×500 nm² AFM images: (c) sample T6 and (d) sample T4'. (e) Histogram of the heights measured on image (c).

However, the morphology is completely different according to the AFM image in Fig. 3.11 (d). The sample is made of many terraces of various heights, and the steps are usually much larger than the GaP ones. Therefore, it corresponds more likely to the layer itself, forming mostly one and two monolayer islands of tortuous shapes, similar to previous observations of MoSe₂ grown on GaAs,³²⁴ which have not completely coalesced. Finally, it appears that the substrate is not entirely covered by the layer in this case, even if the thickness is estimated to be almost identical to the sample grown at 250 °C.

To better understand this morphology, an STM image recorded by Houada Koussir⁴¹³ on another sample (sample T8) prepared under similar conditions is analyzed in Fig. 3.12. A single terrace is found to cover most of the surface, though higher and lower terraces are also observed. The profile along the blue line, presented in Fig. 3.12 (b), shows that the terraces numbered 1 to 4 are separated by 0.3 nm, matching the GaP(111) interplanar distance. By contrast, the deeper pit lies 0.6 nm below terrace 1, which corresponds well to the TaSe₂ monolayer height. However, this is not completely conclusive since two GaP steps would have almost the same height.

Looking closely to the terrace 3, a periodic modulation is observed as better revealed by the magnified square area in Fig. 3.12 (c), even if the pattern does not seem to repeat itself identically. The FFT of this region, shown in Fig. 3.12 (d), exhibits two sets of 6 spots, indicating that there are two different periodicities. In this case, the two main frequencies are 0.30 and 0.88 nm⁻¹, corresponding to periods of 3.4 and 1.14 nm respectively. The former matches very well a moiré of the TaSe₂ and GaP lattices, whose size can be calculated from the relative mismatch as

$$a_{\text{moiré}} = \frac{a_{\text{GaP}[11\bar{2}]} \times a_{\text{TaSe}_2[10\bar{1}0]}}{a_{\text{GaP}[11\bar{2}]} - a_{\text{TaSe}_2[10\bar{1}0]}}. \quad (3.1)$$

Here, the STM measurements are in better agreement with the moiré of 3.5 nm predicted for the 1T phase, rather than a moiré of 3.2 nm calculated for the 1H phase. Besides, the periodicity of 1.14 nm is attributed to the CDW. Even though it is slightly below the value of 1.25 nm expected for the 1T phase, a more precise estimation by Houada Koussir was found slightly above instead.⁴¹⁴ The moiré and CDW patterns are revealed in Fig. 3.12 (e) and (f) by filtering the low and high frequencies, respectively. The two lattices are not perfectly aligned as expected for the 1T phase, the $\sqrt{13} \times \sqrt{13}$ CDW being rotated by 13.9° with respect to the TaSe₂ lattice.⁵⁵ Finally, the distorted pattern in Fig. 3.12 (c) is understood as the superposition of both the moiré and the CDW. The same pattern is observed on the terraces at height 1, 2 and 4 as revealed by the magnified round areas.

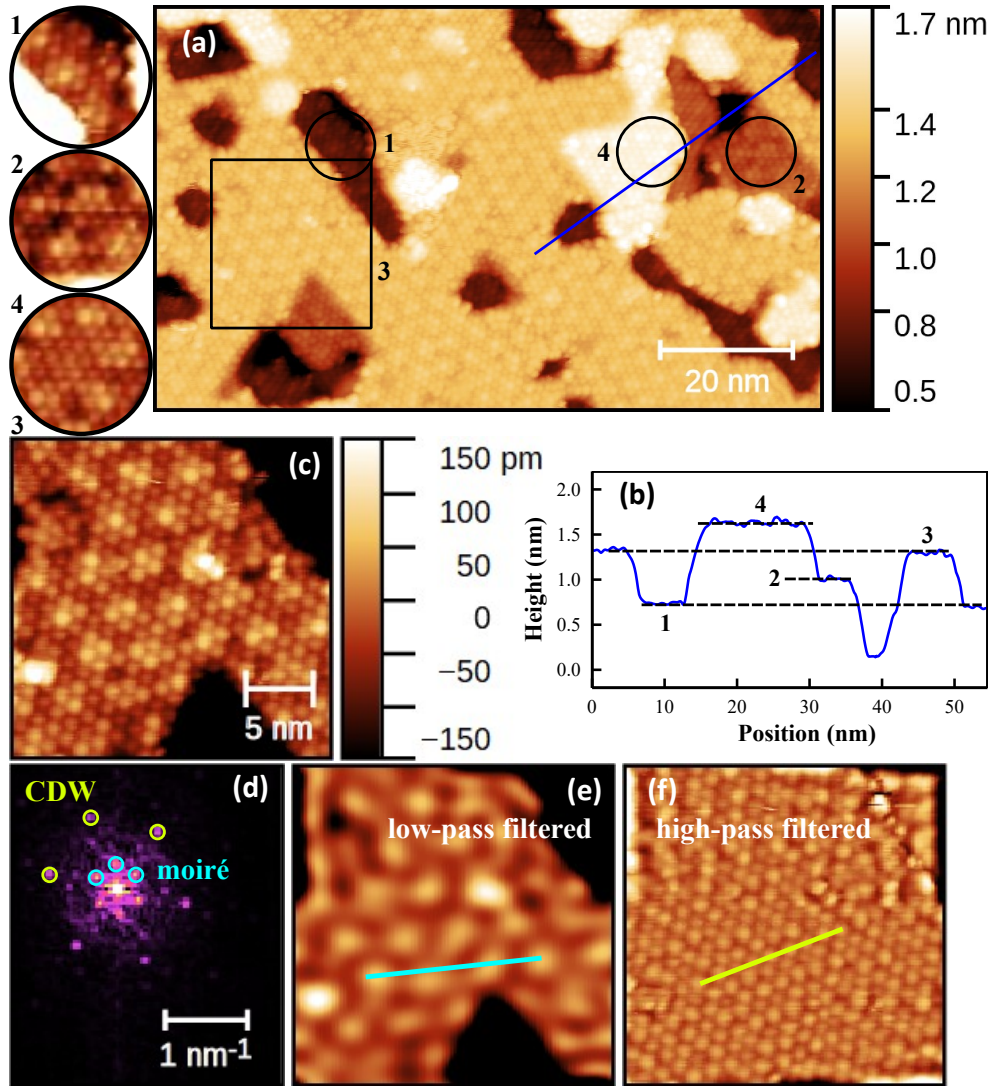


Figure 3.12: (a) $60 \times 100 \text{ nm}^2$ STM image of a TaSe₂ monolayer grown at 600 °C and annealed at 700 °C (sample T8) recorded at 77 K. (b) Height profile along the blue line on image (a). (c) Magnification of image (a) in framed area labeled 3 with a different height scale. The round pictures above show other areas (numbered 1, 2 and 4) at the same magnification but different heights (same color scale with the 0 being shifted by -600, -300 and 300 pm respectively) (d) fast-Fourier transform (FFT) of image (c). (e-f) Copies of image (c) in which low and high spatial frequencies have been filtered, respectively. The cutoff frequency is comprised between the CDW and moiré ones.

The observation of a CDW indicates the presence of TaSe₂, whereas the moiré suggests that it is only one monolayer, as the interaction with the substrate is expected to rapidly vanish with the number of layers. Although the samples grown at 600 °C and annealed at 700 °C exhibited a high density of steps, the observation of the combined CDW and moiré pattern over most of the surface in STM confirms that the TaSe₂ coverage is rather uniform, and therefore most of these steps originate from the GaP substrate. It also proves that the targeted thickness near 1 ML is effectively achieved even though the estimation derived from the XPS measurements indicates less. Since it is the thinner sample for which at least 90 % of coverage was demonstrated, the sample T8 is considered as the reference for a monolayer thickness, and it is therefore concluded that the thickness of TaSe₂ monolayers is underestimated in XPS.

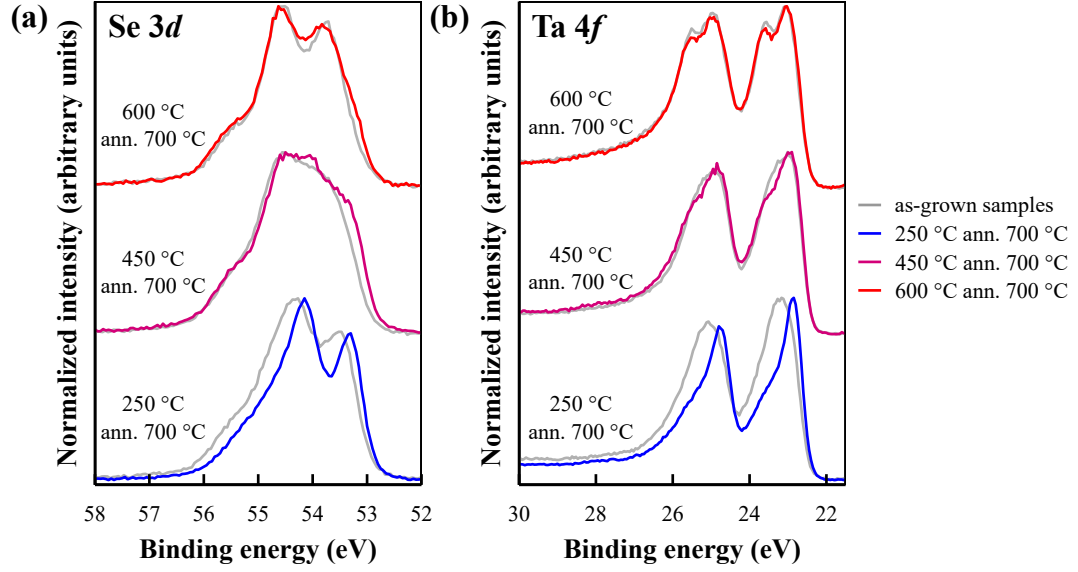


Figure 3.13: (a) Ta 4*f* and (b) Se 3*d* CLs measured in XPS on TaSe₂ monolayers grown at various temperature before and after annealing at 700 °C (samples T6, T7 and T8). All the spectra are acquired at 45°. The gray curves correspond to the as-grown samples (T1, T2 and T5). The photovoltage is corrected based on the Fermi level position measured in XPS for all spectra except for the spectra of sample T7 after annealing which is shifted by −0.2 eV to align the Se-Ga compound at the high binding energy edge of the Se 3*d* CL.

The phase of the annealed samples is now analyzed through the XPS measurements presented in Fig. 3.13 (a,b). The as-grown spectra discussed in Fig. 3.10 (a,b) are reproduced in gray to help the comparison. For each growth temperature, a small evolution of both the Ta 4*f* and Se 3*d* CLs is observed. The sample grown at 250 °C, which was already attributed to the 1H phase seems further shifted toward lower binding energies. It exhibits much thinner peaks after annealing, which is consistent with the improvement of the crystal quality, even though it could also be due to a better phase purity. The shoulder observed on the Ta 4*f* CLs is not necessarily due to a minor fraction of 1T phase but may also be an intrinsic feature of the 1H phase as a very similar shape has been observed on cleaved 2H-TaSe₂ single crystals.⁴¹⁵ Conversely, the characteristics of the 1T phase in a sample grown at 600 °C are slightly less pronounced. It is thus suggested that a small amount of 1T phase is transformed into the 1H one. This is more clearly seen on the sample grown at 450 °C for which the 1H doublet seems to slightly emerge around 54.1 eV after annealing, even though the spectra still resemble a combination of both phases. Overall, it seems that the 1H phase is favored by the annealing as expected for the stable phase, but the changes remain modest.

3.2.1.c Influence of thickness and coverage

In order to improve the coverage, an average thickness slightly above 1 ML has been targeted in some samples grown at high temperature. In addition, the instability of the Ta flux has led to a reduced thickness in some experiments, as shown for instance for sample T9 in Table 3.5. The latter is estimated about 50 % thinner than the previously characterized sample T8, and will therefore be refereed as a 0.5 ML sample. The influence of these thickness variations must be studied to determine how it can affect the results.

The phase is first discussed based on the Se 3*d* and Ta 4*f* CLs in Fig. 3.14 (a) and (b). The doublet of the Se 3*d* is more clearly separated on the 0.5 ML-thick sample, whereas the CL shape is flattened as the thickness is increased, suggesting the apparition of the 1H doublet.

Sample #	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Measured th. (ML)	Characterizations
T9	600	700	1	0.38	XPS
T8	600	700	1	0.70	XPS, STM
T10	600	700	1.4	0.90	XPS, STM, STEM

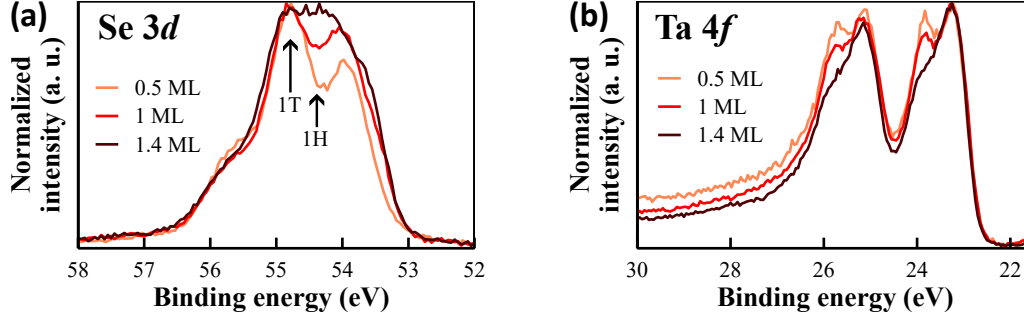
Table 3.5: Monolayer TaSe₂ samples grown at 600 °C and annealed at 700 °C having different thicknesses.

Figure 3.14: (a) Ta 4f and (b) Se 3d CLs measured in XPS on TaSe₂ layers grown 600 °C and annealed at 700 °C with different thicknesses (sample T8, T9 and T10). All the spectra are acquired at 45°. The photovoltage is corrected based on the Fermi level position measured in XPS on samples T8 and T9, while the spectra of sample T10 is shifted by -0.32 eV to align the Se-Ga compound at the high binding energy edge of the Se 3d CL.

This is also confirmed by the reduction of the high-binding energy component of the 1T-phase in the Ta 4f CL. Hence, it is clear that a high nominal thickness favors the more stable 1H-phase. However, since a phase change is also observed between the sample T9 and T8, corresponding to 0.5 and 1 ML respectively, and for which very few bi-layers are expected, it could rather be related to the surface coverage. Shimada *et al.* suggested that the formation of the metastable 1T phase could be kinetically favored because the octahedral coordination is generally more stable in molecules.²⁴⁵ Recently, a much faster growth rate for the 1T phase has effectively been demonstrated in TaS₂.⁴¹⁶ In this latter study, the stable 1H phase was believed to originate from the random conversion of 1T islands after a certain time. However, the authors argued that the 1T phase lifetime only depends on temperature, whereas here the growth durations are very similar for the three samples (24, 25 and 30 min for T8, T9 and T10 respectively), suggesting the phase transition is driven by something else. In MoS₂, a lower edge energy has been calculated for the 1T' phase compared to the 1H one, hence small clusters of 1T' phase could be stable despite the 1H one is stable in bulk in this material,⁴¹⁷ and a similar conclusion was reached for the 1T phase.⁴¹⁸ Hence, it is believed that the grain size increases with the surface coverage and stabilizes the 1H phase. Alternatively, in TaS₂, the 1H phase has been suggested to emerge from the grain boundaries during the film coalescence because its smaller in-plane lattice parameter enables to release strain.⁴¹⁹

According to the STM images presented in Fig. 3.15 (a,b), the morphology of the two thickest samples is very similar. The TaSe₂ layer covers at least 90 % of the surface for both samples, and the root mean square (RMS) of height differences is only slightly larger on the thicker one. However, at the nanometer scale, a large part of the surface of the thicker sample appears disordered as shown in Fig. 3.15 (d) whereas disordered areas are rather rare on the 1 ML sample (Fig. 3.15 (c)). In average, these disordered regions are only 0.1 ± 0.1 nm thicker than those where the moiré and CDW are visible. Hence, they unlikely correspond to TaSe₂ bilayers. However, the disorder might be caused by adsorbed atoms or defects, that could eventually disturb the CDW order. Especially, according to the XPS results, it might be the 1H phase. The latter would be expected to exhibit a 3×3 CDW,²⁴¹ but as it takes place at 122 K and becomes commensurate only below 90 K, it may not be perfectly ordered at 77 K.

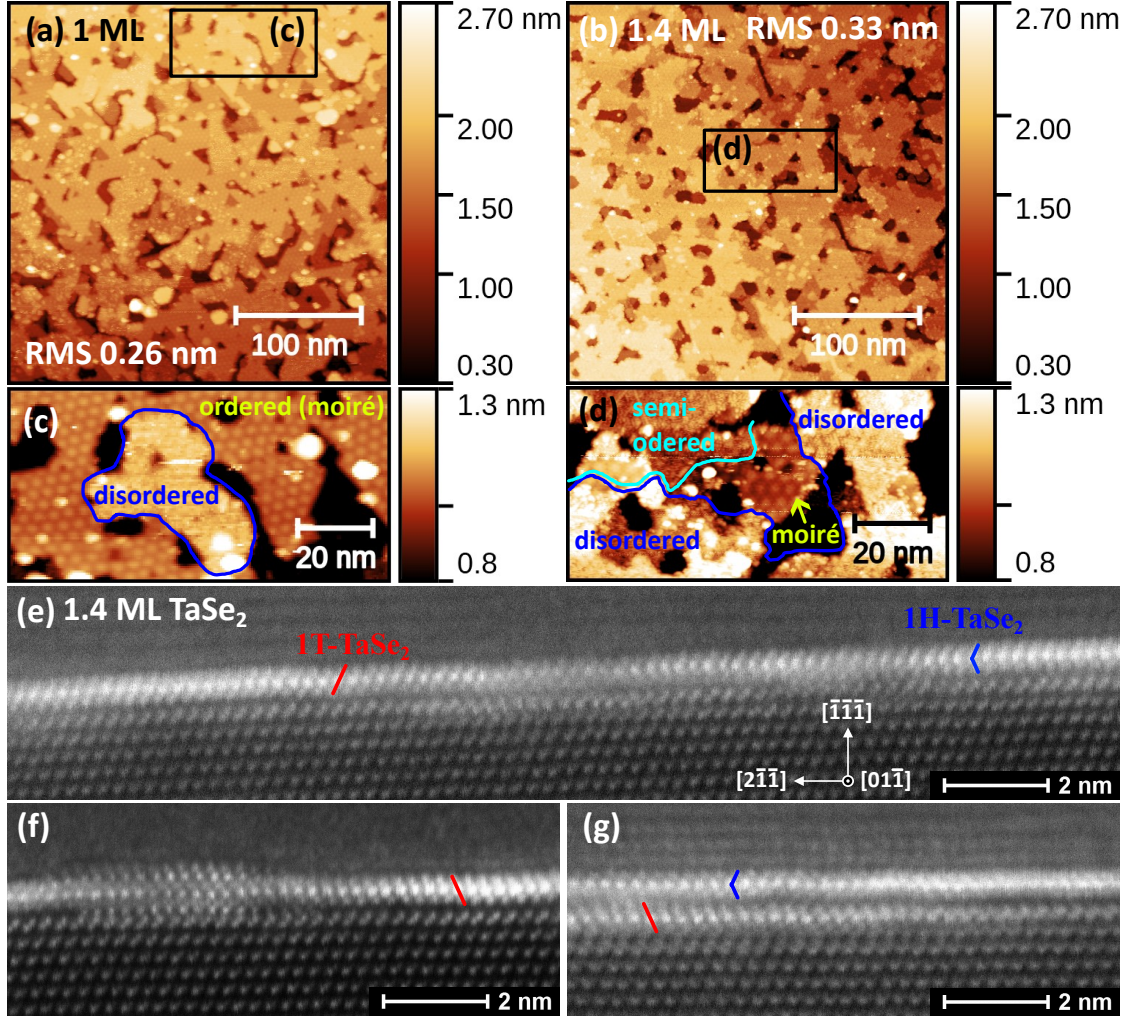


Figure 3.15: (a,b) $300 \times 300 \text{ nm}^2$ STM images at 77 K of the (a) 1 ML-thick (sample T8) and (b) 1.4 ML-thick (sample T10) TaSe₂ layers. (c,d) Magnified $100 \times 50 \text{ nm}^2$ STM images of the framed areas in images (a,b). The STM measurements were made by Houada Kousir and Yevheniia Chernukha. (e-g) STEM images of the 1.4 ML-thick TaSe₂ layer (sample T10), observed along the $[0 \ 1 \ \bar{1}]$ zone axis.

To get further insights on what it could be, the 1.4 ML sample is further analyzed using STEM in Fig. 3.15 (e-g). Right below the TMDC monolayer, the top layer of the GaP substrate appears brighter with the two atoms being clearly visible, confirming the presence of Se replacing lighter P atoms. The spacing between the bottom Se in TaSe₂ and the top ones on the GaP substrate is about 3 Å which is more or less what could be expected for a vdW gap. The image in Fig. 3.15 (e), reveals both the 1T phase, whose projection along the $[0 \ \bar{1} \ 1]$ direction appears as oblique lines (" $///$ "), and the 1H phase, which is shaped as inequality symbols (" $>>>$ "). In several regions, the images are blurry probably because of the phase mixture, in good accordance with the XPS results for this sample. In addition, other types of defects are regularly found. The most frequent is the intercalation of Ta atoms in the vdW gap, which results in the growth of non-layered island as shown in Fig. 3.15 (f). A similar observation is made near some step edges as presented in Fig. 3.15 (g), in contrast with previous observation of other TMDCs climbing over GaAs steps.^{237,420} These defects may be the explanation for the greater disorder observed on this sample in STM.

In conclusion, the surface coverage of the sample grown at high temperature could not be conclusively enhanced by increasing the nominal thickness to 1.4 ML. Instead, a phase mixture is obtained exhibiting a large disorder and many defects. Finally, the thickness appears to be a determining parameter for the 1T into 1H phase transformation.

3.2.1.d TaSe₂ monolayer grown on GaAs

The use of a more conductive substrate would be beneficial for STM characterization. In addition, the smoother initial surface of GaAs buffer layer could reduce the density of steps, making it appealing for TaSe₂ growth. Because the temperature stability of GaAs is a concern, the growth is performed at 550 °C as it is the lowest temperature at which pure 1T phase has been obtained. The Se-treated GaAs sample A2 presented in Section 3.1.2.b, which has been passivated at this temperature, is chosen for the GaAs one, since the Se uptake will be unavoidable during the growth. The Se flux is even increased to circa 3×10^{-6} Torr to meet the conditions previously used for GaP substrates.

Then, another sample is prepared under similar conditions on GaP to compare the two substrates. The measured thickness is very comparable for both samples, as shown in Table 3.6, even though it is still believed to be underestimated. In fact, both samples seem slightly thicker than the monolayer reference (sample T8) in accordance with the targeted thickness.

Sample #	Substrate	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Thickness th. (ML)	Characterizations
T11	GaP	550	650	1.2	0.79	XPS, LEED, STM
T12	GaAs	550	650	1.2	0.75	RHEED, XPS, LEED, STM

Table 3.6: TaSe₂ monolayer samples grown at 550 °C and annealed at 650 °C on GaAs or GaP substrates.

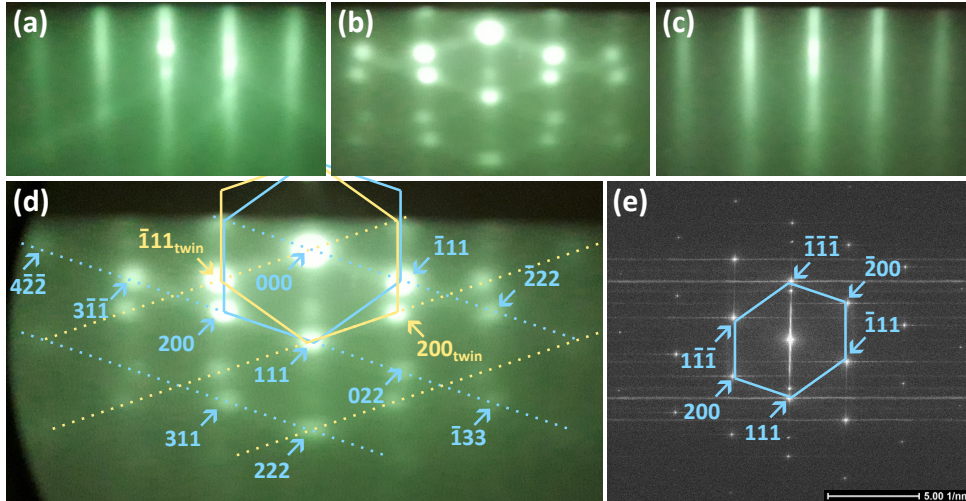


Figure 3.16: (a) RHEED pattern recorded along a GaAs $\langle \bar{2}11 \rangle$ (TaSe₂ $\langle 10\bar{1}0 \rangle$) direction of the sample T12 at different stages of the growth: (a) the initial Se-terminated GaAs substrate, (b) as-grown TaSe₂ monolayer, and (c) after annealing at 650 °C. (d) Spot indexation on the RHEED pattern (b). (e) Fast-Fourier transform of a STEM image of sample T10. The main spots attributed to the GaP reciprocal lattice are indexed. The tiny spot below the $(\bar{1}\bar{1}\bar{1})$ one is attributed to the Se capping layer.

The initial RHEED pattern recorded on the Se-terminated GaAs substrate (Fig. 3.16 (a)) is very similar to the GaP one. During the first half of the growth, the TaSe₂ streaks progressively strengthen. Then, once 0.6 ML have been grown, few spots suddenly appear on the RHEED

pattern and within one minute they completely cover the streaks as shown in Fig. 3.16 (b). Although the spot positions are similar to those on GaP, the degradation is far more pronounced on GaAs. Interestingly, the diffraction pattern corresponds rather well to a twinned zinc-blende structure,^{421,422} whose proposed peak indexation is shown in Fig. 3.16 (d). It can be compared to the GaP diffraction pattern in Fig. 3.16 (e) obtained through a FFT of a STEM image of sample T10. A reasonable match is found between the two lattices, as highlighted by the blue lines, but a mirrored array of spots, sketched in yellow on the RHEED pattern in Fig. 3.16 (d), indicates the presence of twins. Here, this diffraction pattern could therefore correspond to GaAs, but it could also be any FCC structure with a similar lattice. The fact a stronger degradation is observed on GaAs compared to GaP indicates that the substrate is involved in the surface roughening at high temperature, but it must still be triggered by the growth since, so far, no degradation has been noticed during annealing under Se only.

The layers are then annealed at 650 °C since the RHEED pattern of the samples grown on GaP improves at this temperature. Effectively, the RHEED pattern immediately recovers once this temperature is reached as shown in Fig. 3.16 (c).

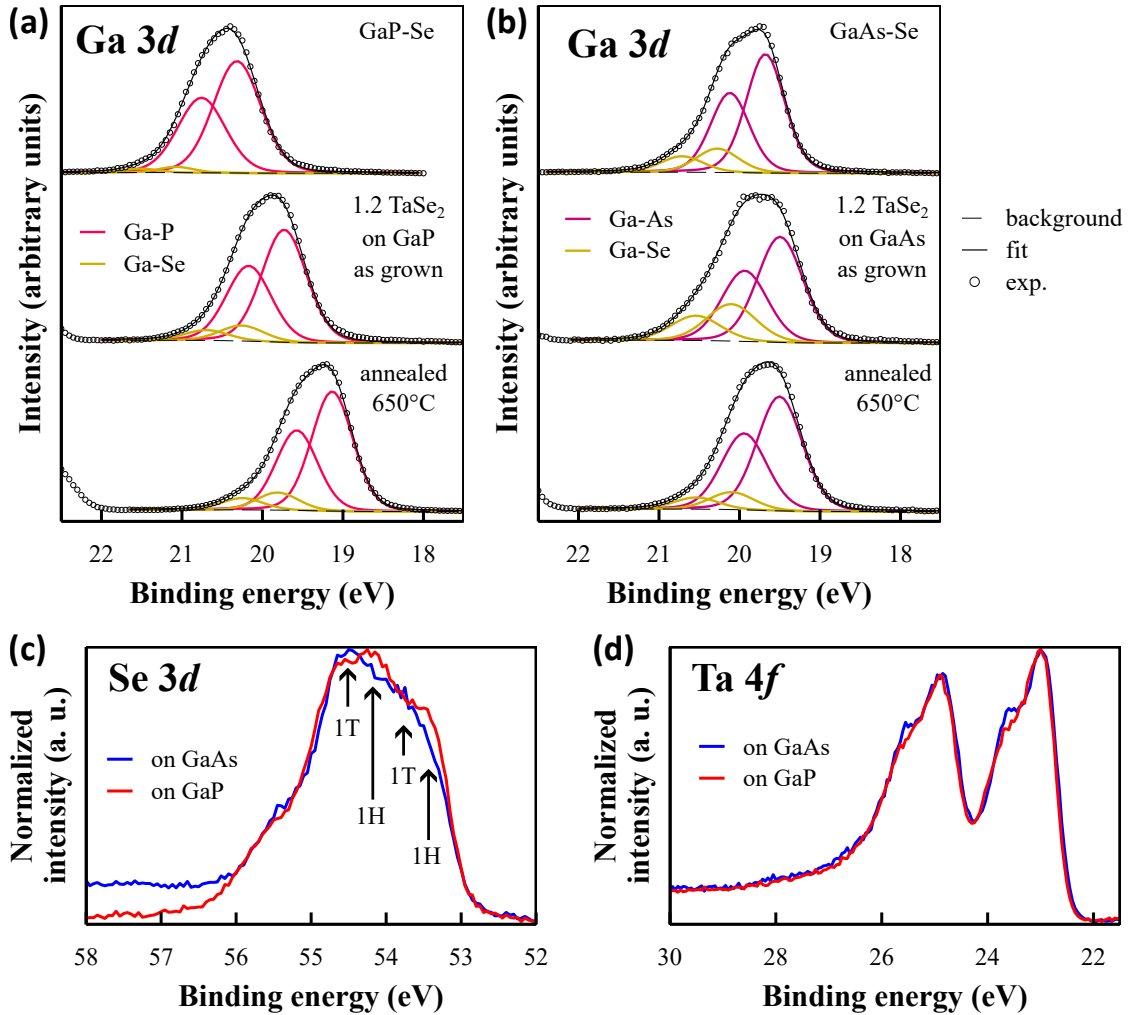


Figure 3.17: (a,b) Ga 3d CLs measured in XPS at 45° on TaSe₂ monolayers grown at 550 °C on (a) GaP (samples T3 and T11) and (b) GaAs (sample T12). The Ga 3d CLs of the Se-terminated GaP substrate prepared at 450 °C under high Se flux (sample P3) and GaAs prepared at 550 °C under low Se flux (sample A2) are presented as reference. (c,d) Comparison of the (c) Se 3d and (d) Ta 4f CLs of the TaSe₂ monolayers grown on GaP (sample T11) and GaAs (sample T12) measured in XPS at 45°.

To explain the evolution of the RHEED pattern, the Se incorporation in the substrate at different stages of the growth is studied through the Ga 3*d* CL presented in Fig. 3.17 (a) and (b) for GaP and GaAs, respectively. In the as-grown TaSe₂ on GaAs sample, a very large component is observed at the high binding energy side, which is attributed to Ga-Se bonds, in perfect agreement with the large Se uptake expected for this substrate. Interestingly, most of the Ga-Se content vanishes after the annealing. It is known that layered GaSe evaporates around 650 °C,²⁵¹ whereas the Se-termination of GaAs may be more stable under Se flux, in the same manner that GaP-Se is stable up to 700 °C. Hence it is believed that the annealing removes the excess Ga_xSe_y compounds formed during the growth. Because, their apparition and evaporation perfectly coincide with the degradation and recovering of the RHEED pattern, these compounds are suspected to be the cause of the surface roughening. Especially, Ga₂Se₃ exhibits a defective FCC structure with a lattice parameter very close to the GaP one,³⁷ and a similar twinned RHEED pattern has been reported for the isostructural (In,Ga)₂Se₃.⁴²³ It has already been formed on GaAs(111) at 330 °C using a much higher Se flux,⁴²⁴ but given the significant subsurface Se incorporation at 10⁻⁷ Torr, it may be progressively formed in the present growth conditions at 10⁻⁶ Torr. Besides, the Ga₂Se₃ lattice contains one third of Ga less than the GaAs one. This means that when As atoms are substituted by Se in the bulk to form Ga₂Se₃, extra Ga atoms will be released enabling more Ga₂Se₃ to be grown. It is possible that the competition between 2D TaSe₂ and 3D Ga₂Se₃ triggers a vertical growth mode when the substrate coverage increases, explaining the sudden RHEED transition. By contrast, the Ga 3*d* CL presents very little evolution in GaP during the growth and annealing, showing that such an effect cannot be expected to a significant extent on this substrate. This is consistent with the much smaller spots observed on the RHEED patterns in Fig. 3.9.

The influence of the substrate on the phase formation is examined through the Se 3*d* and Ta 4*f* CLs measured on the annealed layers and compared in Fig. 3.17 (c) and (d), respectively. Overall, both CLs resemble those of the 1.4 ML-thick TaSe₂ sample (Fig. 3.14), suggesting a mixture of 1T and 1H phases, probably as a result of the annealing and of the thickness being slightly above the monolayer reference. However, despite the very similar thickness and growth conditions, the 1T phase seems more predominant in the sample grown on GaAs according to the maximum shifted toward the 1T position on the Se 3*d* CL, and the more pronounced shoulder on the Ta 4*f* CL. At this stage, it is not clear whether the 1T phase is indeed favored by the GaAs substrate itself, or indirectly induced by a different morphology.

The structure of the layers is now compared through their LEED patterns presented in Fig. 3.18. Both patterns exhibit a six-fold symmetry, in accordance with the good alignment of the layer, but noticeable differences are noted. For the monolayer grown on GaP, each of the 6 main spots, attributed to the TaSe₂ layer, is surrounded by 6 extra spots. The distance between these secondary spots is about 10 times smaller than the separation of the main ones. This corresponds to a 10 times larger lattice in the real space, which perfectly fits the moiré observed in STM in Fig. 3.12. By contrast, the LEED pattern (b) recorded on the sample grown on GaAs exhibits two bright spots repeated 6 times. The outer spots appear slightly more diffuse than the inner spots. The GaAs lattice being larger than the TaSe₂ one, the sharp inner spots are attributed to the substrate. The diffuse spots, therefore ascribed to the TaSe₂ layer, are surrounded by a very faint superstructure similar to the moiré observed on GaP. Its observation is also expected on GaAs given the lattice mismatch of about 15 % in this case. However, this superstructure is not as bright as on GaP despite the very similar thickness of the two samples. The GaP-related spots are not as narrow as the GaAs-related ones, probably because the GaP substrate is largely covered and these spots are only observed through the moiré. Conversely, the bright GaAs spots indicate that the corresponding sample contains some uncovered areas, whereas the low intensity of the moiré suggests that single layer TaSe₂ regions are relatively scarce on GaAs.

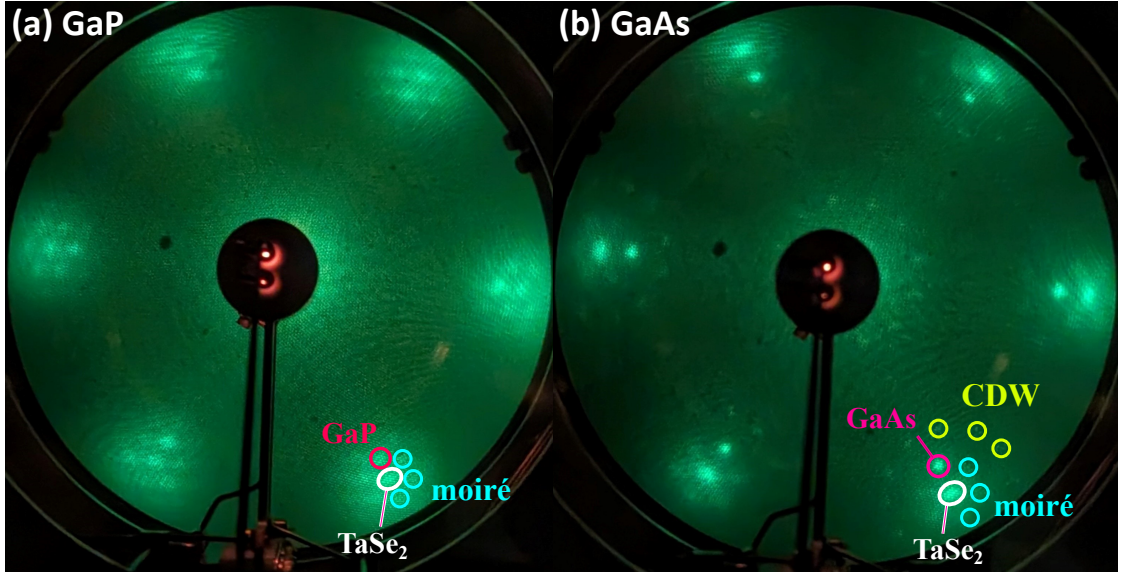


Figure 3.18: (a,b) LEED pattern observed on the 1.2 ML TaSe₂ samples grown on (a) GaP (sample T11) and (b) GaAs (sample T12) after annealing.

Still on this substrate, another faint superstructure, consisting of 12 spots arranged in a circle, is also observed around the TaSe₂ spots. The measurement of its radius leads to the calculation of a lattice about 3.5 times larger than the TaSe₂ one, which better matches the 1T-TaSe₂ CDW. The presence of 12 spots has already been reported in the literature and will be discussed later.⁴²⁵ Still, the observation of the CDW only on the GaAs sample is surprising given the rather small difference in 1T/1H phase proportion observed in XPS between both samples. This may be related to the fact the moiré is much less visible on this substrate, probably because of a different morphology.

Effectively, the STM comparison of the two samples presented in Fig. 3.19 reveals a rougher surface on GaAs. The coverage is estimated to be 77 % on this substrate, whereas it reaches 91 % on the GaP one, in good accordance to the previous 1 ML and 1.4 ML samples. The most frequent steps on the GaP substrate are 0.7 ± 0.1 Å high according to the profile in Fig 3.19 (c), in agreement with the presence of a TaSe₂ monolayer. By contrast, the profile measured on the GaAs one (Fig 3.19 (d)) reveals mostly step heights above 1 nm. It suggests that the film is largely composed of few-layers, which explains the lower surface coverage for a similar amount of deposited TaSe₂ compared to the sample grown on GaP, although the presence of Ga_xSe_y under the TaSe₂ layer cannot be excluded. Looking closely to the GaAs sample, it appears that a large proportion of the layer is disordered, similar to the previously characterized 1.4 ML sample on GaP. Still, some areas exhibit a periodic ordering, as in Fig. 3.19 (f). The profile in Fig. 3.19 (g) reveals a period of 1.3 nm which corresponds to the CDW. However, the pattern is perfectly periodic in this case, in stark contrast to the samples grown on GaP. This is attributed to the absence of the moiré on GaAs substrate, in agreement with LEED observations, which might be explained by the fact that the TaSe₂ consists mostly of few-layers or the possible presence of Ga_xSe_y underneath. Concerning the different morphology, it is probably related to a reorganization of the layer monitored by the sudden RHEED pattern changes observed during the growth and annealing on the GaAs sample. Finally, the choice of the substrate is found to have significant consequences, and it is clear that a uniform surface coverage would be difficult to achieve on GaAs in these conditions.

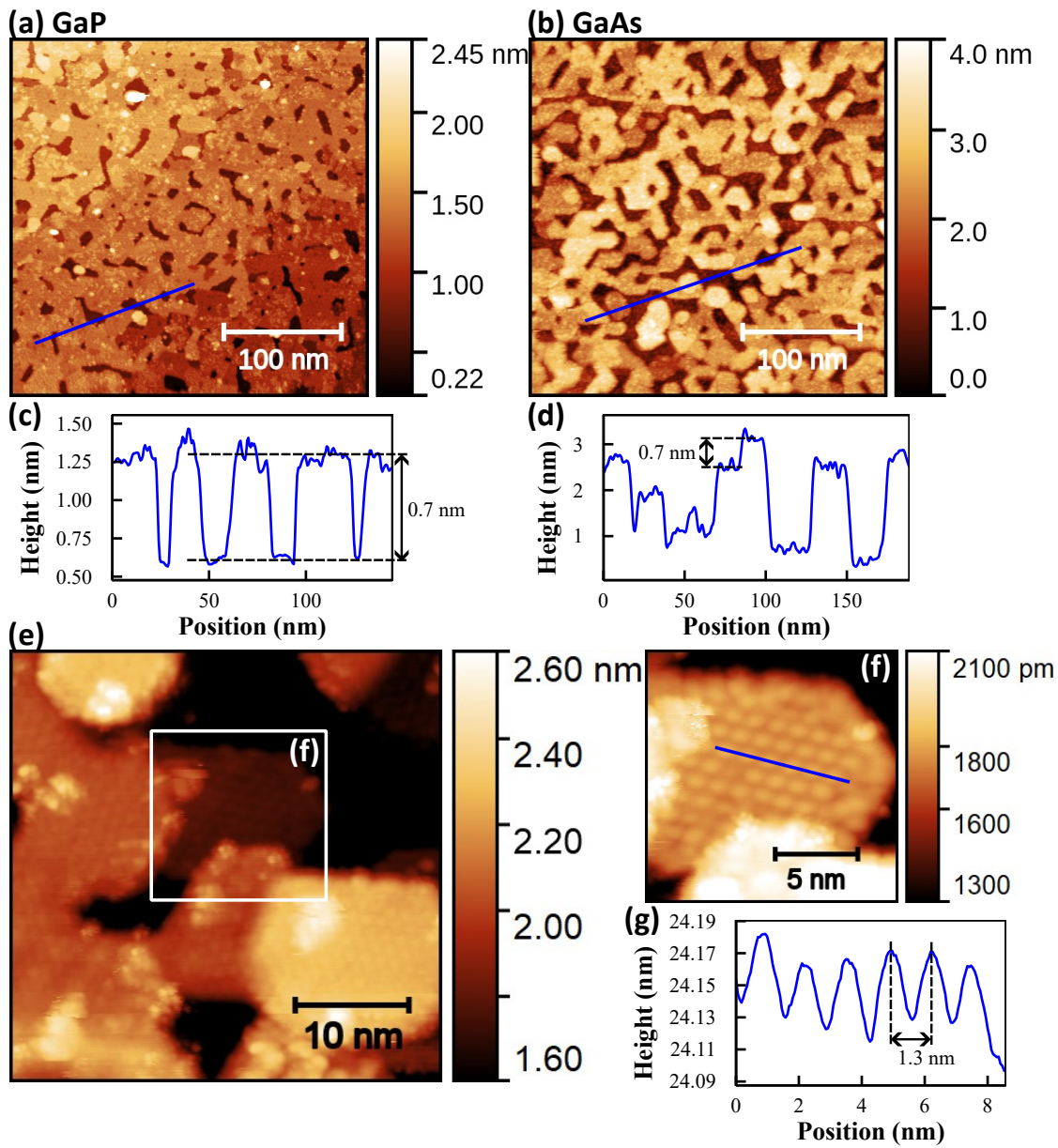


Figure 3.19: (a,b) 300 × 300 nm² STM image observed on the 1.2 ML TaSe₂ layers grown on (a) GaP (sample T11) and (b) GaAs (sample T12). (c,d) Height profile along the lines drawn on the images above. (e) 38 × 38 nm² STM image of layer grown on GaAs. (f) 20 × 20 nm² STM image in the area outlined in (e). (g) Height profile along the periodic reconstruction observed in (f). All measurements were made by Yevheniia Chernukha. .

3.2.2 In-plane orientation of TaSe₂ monolayers

In the previous section, the film has been observed to be formed of domains of rather small size, as expected in MBE. In 3D-material epitaxy, this is balanced by the fact that each individual island grows on the same lattice which allows them to merge coherently. This is however rarely achieved in 2D-material growth because the weak vdW interaction hardly enables a sufficient in-plane alignment to the substrate lattice. To determine if this is the case for TaSe₂ grown on GaP or GaAs, the orientation of the different domains is studied in this section. For this, only samples exhibiting good phase purity are considered, since a phase mixture would obviously be detrimental to any long-range ordering.

3.2.2.a Relative alignment of the substrate, TaSe₂ and CDW lattices

Sample #	Substrate	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Thickness th. (ML)	Characterizations
T6	GaP	250	700	1	0.97	LEED
T4'	GaP	600	700	1	0.91	LEED
T8	GaP	600	700	1	0.70	STM
T12	GaAs	550	650	1.2	0.75	LEED

Table 3.7: TaSe₂ monolayer samples grown at various temperature on GaAs or GaP substrates.

In the previous section, the six-fold symmetry of the LEED patterns have already proved the rotational alignment of the TaSe₂ layers grown at 550 °C with respect to their respective substrate. Here, different samples from the previous sections, reported in Table 3.7, are compared to study the rotational domains in the layers. Their corresponding LEED patterns are reproduced in Fig. 3.20 (a-c). The moiré observed in patterns (a) and (b) is aligned on the TaSe₂ lattice, as expected from the good alignment of the GaP and TaSe₂ lattices. However, the TaSe₂ spots on LEED pattern (b) from the layer grown at 250 °C seem distorted. They are in fact elongated along the azimuthal direction, indicating a non-negligible residual misorientation.

In the LEED (c), recorded on the sample grown on GaAs, the CDW exhibits 12 spots and neither are aligned along the TaSe₂ and GaAs direction. This is similar to previous reports⁴²⁵ while some others have found only 6 spots.⁴¹² An angle of $13 \pm 1^\circ$ is measured with respect to the TaSe₂ lattice, which is in good accordance with the expectation of the $\sqrt{13} \times \sqrt{13}$ CDW to be rotated by 13.9° . However, it should be highlighted that there are two possible ways for a $\sqrt{13} \times \sqrt{13}$ superstructure to be formed on a hexagonal lattice as illustrated in the schematics in Fig. 3.20 (h). Finally, the 12 spots can be explained by the presence of two sets of 6 spots, one being rotated by $+13.9^\circ$ and the other one by -13.9° , since there is no reason for one of the two symmetrical orientations to be preferred.

This is however not specific to the GaAs substrate as the CDW domains have also been observed during the STM characterization of sample T8 grown on GaP. The already analyzed image is reproduced in Fig. 3.20 (d). Contrary to the previous FFT over a reduced area (Fig. 3.12 (d)), the FFT of the whole image presented in Fig. 3.20 (e) reveals 12 spots similar to the LEED pattern. This indicates the presence of both CDW orientations in this image. Indeed, in Fig. 3.20 (f), two orientations of the CDW periodic modulation are observed. Interestingly, the star-of-David pattern looks like triangles that are not perfectly aligned along the CDW direction. This is better observed at the atomic resolution in the image Fig. 3.20 (g). The triangular shape is explained by the fact that the CDW pattern is centered on a Ta atom whereas in this case, the tip mostly interacts with the top Se atoms. As a results, the 6 top Se atoms inside the star-of-David appear much brighter than the outer ones. Therefore, the triangles indicate the true orientation of the TaSe₂ lattice, whereas the two possible CDW orientations result from the arrangement of these triangles as shown in the schematics in Fig. 3.20 (h). In the image

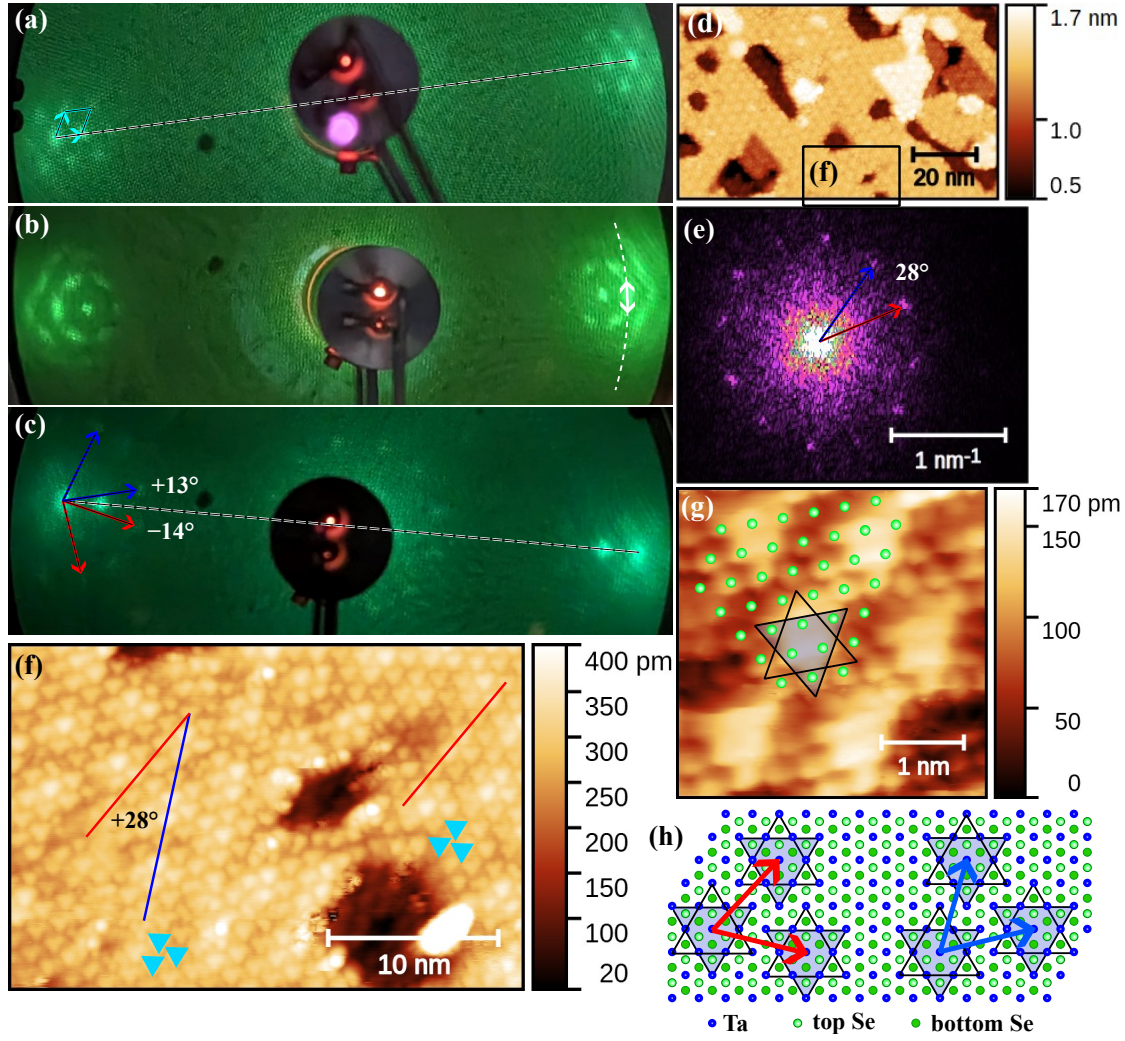


Figure 3.20: (a-c) LEED patterns of the TaSe₂ monolayer grown on GaP at (a) 600 °C and annealed at 700 °C, (b) 250 °C and annealed at 700 °C, and (c) on GaAs at 550 °C and annealed at 650 °C. (d) 100 × 60 nm² STM image of a sample grown at 600 °C and annealed at 700 °C on GaP. (e) FFT of image (d). (f) STM image of the framed area in image (d). (g) Atomic resolution STM image of the same sample. The green dots indicate the top Se atoms positions. The STM measurements have been performed by Houada Koussir. (h) Schematics of the two possible orientations of the 1T-TaSe₂ CDW.

Fig. 3.20 (f), the triangles are effectively all facing in the same direction, but they are arranged differently. Finally, despite the two CDW domains, the layer seems uniformly oriented and rather continuous in this image. The few defects in between probably explain this change of CDW orientation by contrast to high quality crystals which have been shown to exhibit single rotational CDW domains.⁴²⁶

In Fig. 3.20 (f), no evidence of a grain boundary has been found, whereas on the same sample, two domain boundaries are clearly observed in Fig. 3.21 (a) between the white arrows. In this latter image, the periodic modulation corresponds to the moiré according to its larger lattice. Interestingly, significant variations of its orientation are observed as highlighted by the blue lines. To explain their origin, a similar moiré effect has been reproduced with two hexagonal lattices in the schematics presented Fig. 3.21 (c-e). The blue one is 10 % smaller than the red one, as is the TaSe₂ monolayer compared to GaP. In case (c), a hexagonal moiré lattice is obtained, perfectly

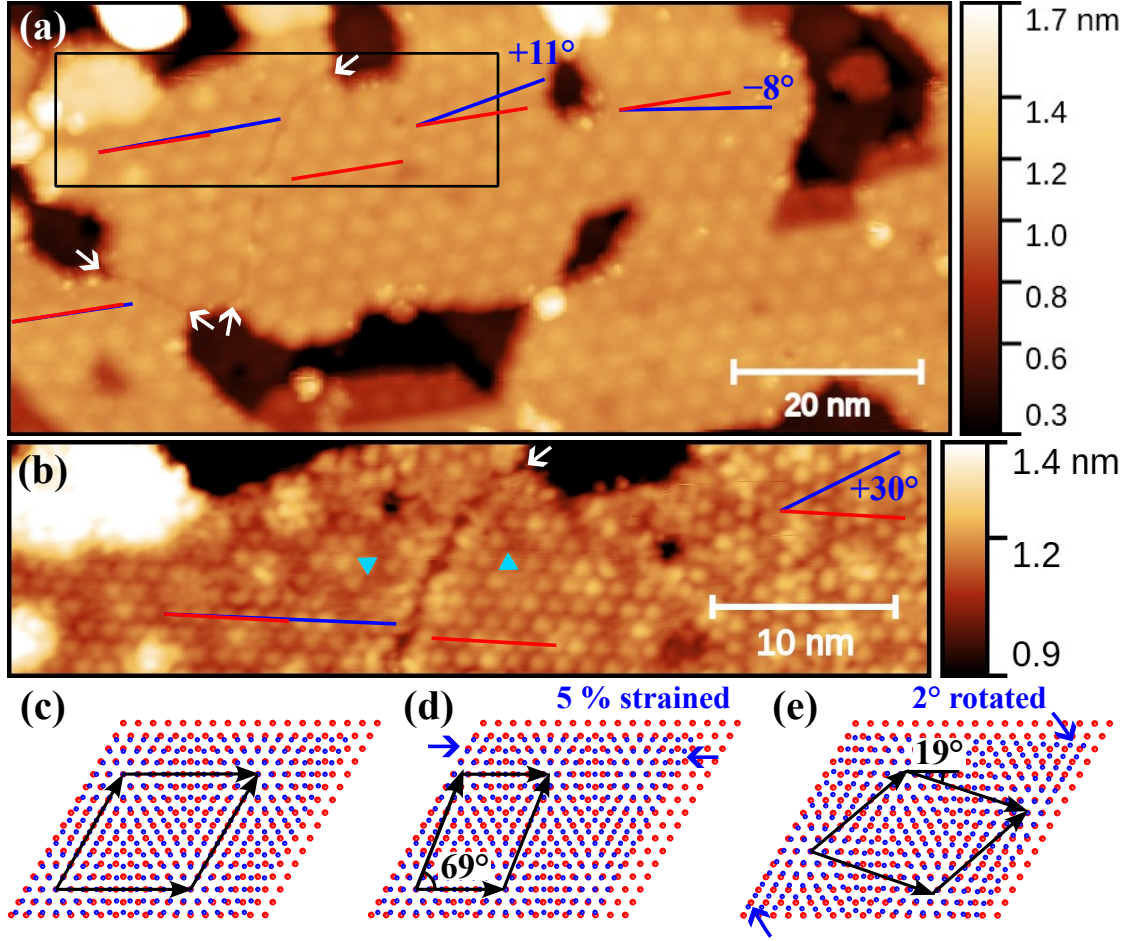


Figure 3.21: (a) STM The white arrows show the extremities of two boundaries. The blue lines highlight the local orientation of the moiré whereas the red one was reported at the different positions to serve as a reference. (b) STM of the framed area in (a). The blue lines highlight the local orientation of the CDW. The two triangles indicate the orientation of the triangular CDW pattern. The STM measurements have been performed by Houđa Koussir. (c-e) Schematics of the moiré between two lattices having 10 % of mismatch. In (d), the blue lattice size is further reduced by 5 % along the horizontal axis. In (e), the blue lattice is rotated by 2°.

aligned on the two other lattices and 10 times larger than the blue one, as could be expected. Since strain is known to strongly affect moiré patterns,⁴²⁷ 5 % of uniaxial compressive strain is added on the blue lattice in case (d). It results in a large distortion of the moiré lattice. Even though one of the two moiré vectors is now rotated by 9°, this essentially changes the lattice size. In case (e), the blue lattice is rotated by 2° which makes the whole moiré rotate by 19° while its shape and dimensions are largely preserved. Finally, the large rotations of the moiré pattern can be explained by very small misalignments of the TaSe₂ lattice as previously observed on Au(111) substrates.²³² This is typically illustrated by the LEED pattern of the sample grown at 250 °C in Fig. 3.20 (b), for which the few degrees-large TaSe₂ spot width corresponds to rotations of several tens of degrees for the moiré. Conversely, on the sample grown at 600 °C, the moiré rotations up to 11° observed in STM are compatible with the small spot width in the corresponding LEED pattern in Fig. 3.20 (a). The absence of discernible grain boundaries between these rotational domains in Fig. 3.21 (a) shows that the layer can probably accommodate these lattice rotations with a reasonable strain.

The framed area is more precisely analyzed in Fig. 3.21 (b). The boundary is more clearly seen and the CDW is now observed. The latter has the same orientation on either side of the boundary, whereas it is rotated by $30\pm 1^\circ$ on the top right, which corresponds rather well to the expected 27.8° between the chiral CDW domains plus a $1.4\pm 0.2^\circ$ TaSe₂ lattice rotation deduced from the $11\pm 1^\circ$ moiré rotation. Concerning the grain boundary marked with the white arrows, for which no moiré or CDW rotation is discerned, an explanation still needs to be found. It can be observed that the individual stars-of-David exhibit triangular shapes facing in opposite directions on either side of the boundary. Since this pattern originates from the 6 top Se atoms, this means that they are placed in the opposite way with respect to the Ta atoms. This corresponds to complete inversion of the layer lattice, signifying that one of the two sides is a mirror twin. Finally, this is not surprising that a grain boundary is observed at this position.

In conclusion, three types of domains have been identified in STM, which were either attributed to the chirality of the CDW, small angle misalignment of the TaSe₂ layer or mirror twins. However, only the third type leads to a clear grain boundary. Overall, they seemed rather rare on the few analyzed images but this needs to be confirmed at larger scale. The LEED observations have proved a good rotational alignment with respect the TaSe₂ lattice, especially for the sample grown at high temperature. However, this technique can hardly distinguish mirrors twins because of the symmetry, at the first order, of the diffraction patterns as stipulated by Friedel's law.⁴²⁸

3.2.2.b Large-scale grain alignment revealed by X-ray photoelectron diffraction

To better understand the TaSe₂ growth and illustrate the importance of the grain alignment, the TaSe₂ nucleation is studied. For this purpose, 0.3 ML-thick samples have been grown at either 250 or 600 °C. The thickness estimated from XPS measurements is reported in Table 3.8.

Sample #	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Measured th. (ML)	Characterizations
T13	250	-	0.3	0.20	XPD
T13'	250	650	0.3	0.21	XPD
T14	600	-	0.3	0.17	XPD, AFM

Table 3.8: Sub-monolayer TaSe₂ samples grown on GaP substrate to study the grain alignment.

The AFM characterization of the layer grown at 600 °C is presented in Fig. 3.22 (a). The TaSe₂ is observed to form small islands of indistinct shapes. The terraces of the GaP substrates are barely distinguished underneath. Approximately 29 % of the substrate seems covered by the TaSe₂ islands, confirming that the XPS measurements slightly underestimate the thickness. The nucleation density is about $3500 \pm 500 \mu\text{m}^2$, which means that the grains are expected to reach an average diameter of circa 20 nm before coalescence. This is consistent with the typical width of the coherent domains observed in STM, even though up to 100 nm-long elongated ones have also been observed. These larger domains are believed to originate from the merging of several nuclei, which explains their tortuous shapes. However, this can be made possible only if the grains have the same orientation. Otherwise, a grain boundary similar to the one observed in the previous section would be expected to form.

To determine the orientation of the grain at macroscopic scale, the XPD technique is used. It consists in measuring the variation of a CL intensity measured in XPS as function of the take-off angle to determine the positions of the neighboring atoms. Usually, this technique requires heavy calculations for the results to be interpreted, but it can be made straightforward when the studied system is relatively simple. The 0.3 ML samples fulfill this condition because no bilayers are expected at such an early stage of the growth, as confirmed by the AFM characterization. Hence, there is only one layer of transition metal atoms surrounded by Se ones. It has been shown that electrons having a large kinetic energy are mostly forward scattered.³⁶³ Therefore,

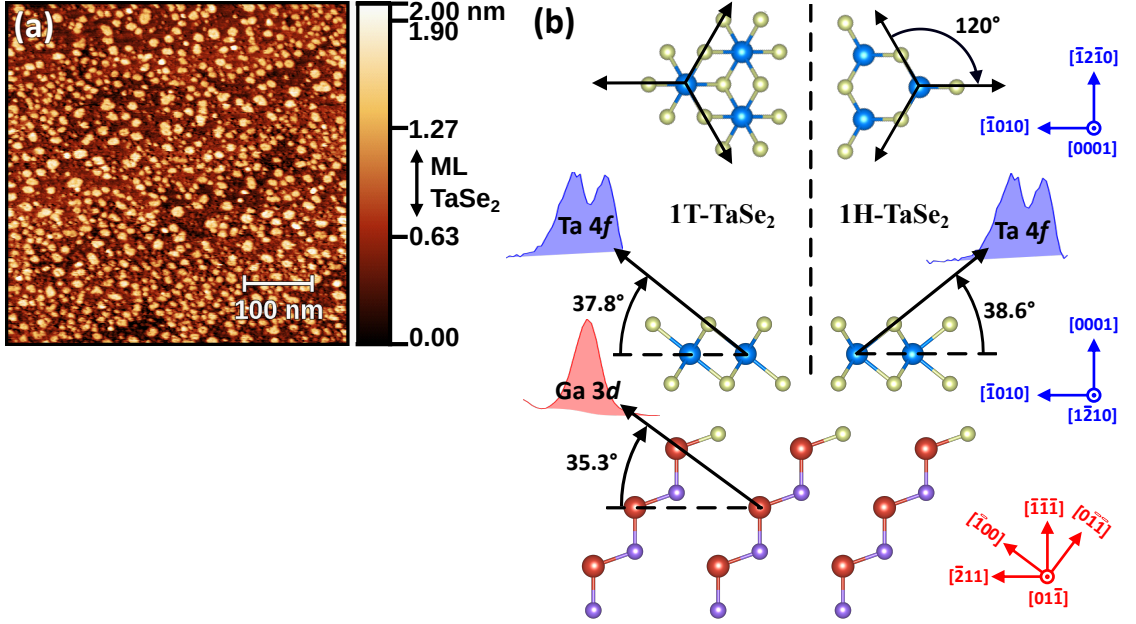


Figure 3.22: (a) $500 \times 500 \text{ nm}^2$ AFM image of a 0.3 ML-thick TaSe₂ sample grown at 600 °C (sample T14). (b) Schematics of the photo diffraction angles considered in the XPD experiments for the two TaSe₂ phases and the GaP substrate.

neglecting any back-scattering, the Ta 4*f* electrons are expected to be only scattered by the top Se atoms before reaching the analyzer. By this mean, the orientation of the top Ta-Se bond can be determined, and then the orientation of the layer can be deduced provided that the phase is known. This last point has an importance because the orientation of the Ta-Se bonds is different in the two phases as illustrated in the schematics in Fig. 3.22 (b). The two phases have their Ta-Se bond at relatively similar azimuthal angle, but the top and bottom bonds are facing in the same direction in the 1H phase whereas they are 180° rotated in the 1T one. Hence if the two phases have their bottom Ta-Se bond oriented in the same direction with respect to the GaP substrate, the top Ta-Se bond will be measured 180° apart, as it would be the case for a mirror twin. Therefore, an enhancement of the Ta 4*f* intensity would be expected along 3 directions only if the TaSe₂ layer contains only one phase and no mirror twins. In any other cases, the XPD spectrum would reveal 6 peaks separated by 60°.

For the present experiment, the detector is set at a polar angle of 37.8°, which corresponds to the 1T phase but also enables the 1H one to be detected thanks to the 2° half-aperture of the analyzer. Each sample had their azimuth first aligned along a $\langle \bar{2}11 \rangle$ direction of the substrate. Then, the Ta 4*f* and Ga 3*d* CL intensities were measured every 2.5°. The results are presented in Fig. 3.23.

In each measurement, the Ga 3*d* CL intensity is strongly enhanced at three angles separated by 120° as expected from the 3-fold symmetry. They are attributed to the $\langle \bar{1}00 \rangle$ directions represented in Fig. 3.22 (b). This confirms that the substrates were oriented in equivalent direction in the three experiments. Concerning the Ta 4*f* CL, 6 peaks of comparable intensities are observed in the sample grown at 250 °C before annealing. As discussed earlier, this could be either due to the presence of mirror twins or both phases. The 1H phase is expected to be predominant at this growth temperature in monolayers, but it is not excluded that the 1T phase could be present in significant amount since it was suspected to be favored for small nuclei. After annealing at 650 °C, however, the 6 peaks remain visible but 3 of them are clearly more pronounced. Hence, there is one dominant phase, for which one orientation is also preferred. This could be understood by the fact that the annealing favors the stable phase as well as the

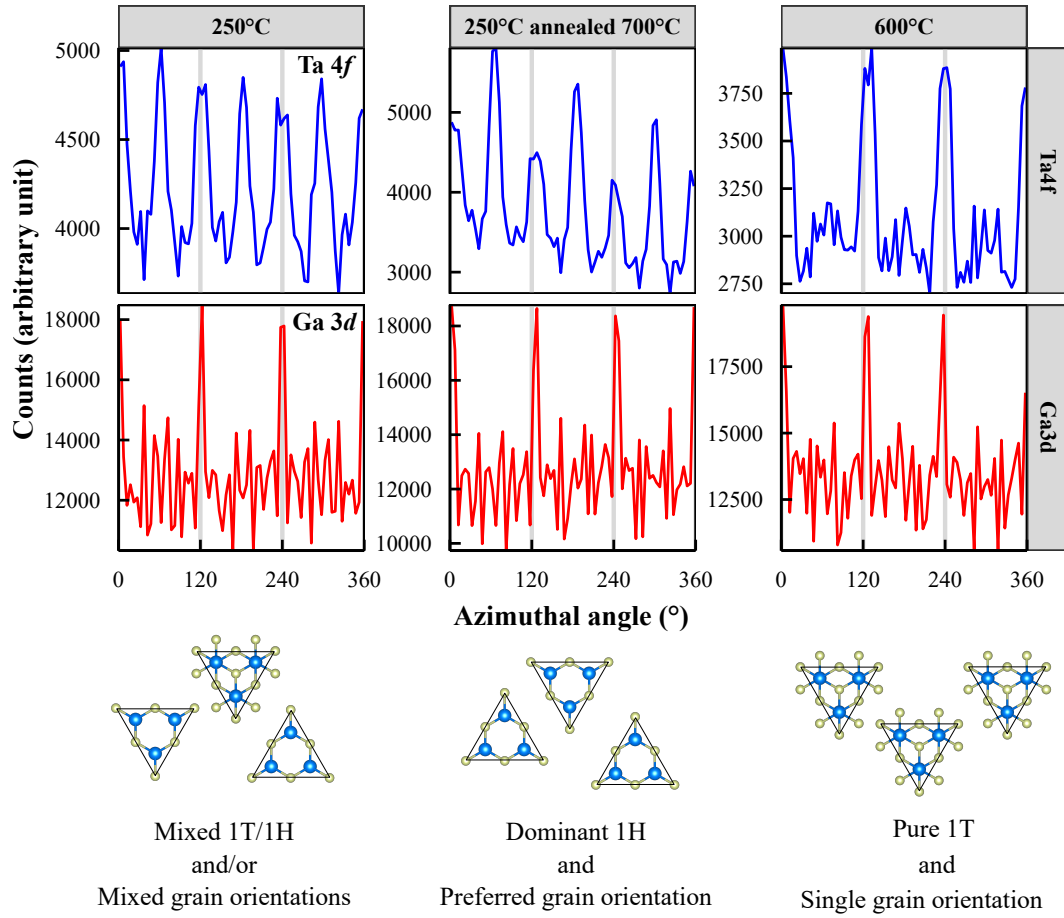


Figure 3.23: Records of the Ta 4*f* and Ga 3*d* measured in XPS at a take-off angle of 37.8° and various azimuths.

grain orientation having the lowest energy on GaP. Finally, for the sample grown at 600 °C, only 3 peaks are obtained for the Ta 4*f* CL, proving the absence of mirror twins and the phase purity at this stage of the growth. In this case, the 1T phase is expected to be favored by both the growth temperature and the small size of the nuclei. It is interesting to note that the peaks are 60° apart from the most intense ones on the previous sample. This is consistent with the 1T and 1H phase having opposite upper bond direction, since it seems rather intuitive that both phases would have the same orientation for their lower bonds. Concerning the absence of mirror twins, it is line with the observation of few mirror twin boundaries during the STM characterization of the monolayer grown at this temperature.

Finally, the structural characterization of the layers has revealed important differences between those grown at 250 and 600 °C. At low temperature, it is not possible to control both the phase and the grain orientation during the growth, which means that many grain boundaries would be expected after coalescence of the nuclei. An intermediate annealing at 650 °C could be beneficial since an improvement is noticed, but it remains insufficient to achieve a single phase and grain orientation. The growth of 1T phase at high temperature seems however promising, with no 1H phase nor mirror twins being detected at the nucleation stage, and very few in the monolayer. Still, the XPS, STM and STEM characterizations of the thicker layer in the previous section suggest that this is only the true up to the monolayer limit.

3.2.3 Electrical characterization of TaSe₂ monolayers

The selective growth of the 1T and 1H phases has been demonstrated in monolayer, and the crystalline quality of the samples has been discussed. In this paragraph, their electrical characterization is presented to determine if the properties of each phase are obtained in spite of the observed defects.

3.2.3.a Investigation of the TaSe₂ band structure

Sample #	Substrate	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Measured th. (ML)	Characterizations
T6	GaP p	250	700	1	0.96	UPS
T8	GaP n+	600	700	1	0.66	UPS, STS

Table 3.9: monolayer TaSe₂ samples for band structures characterizations.

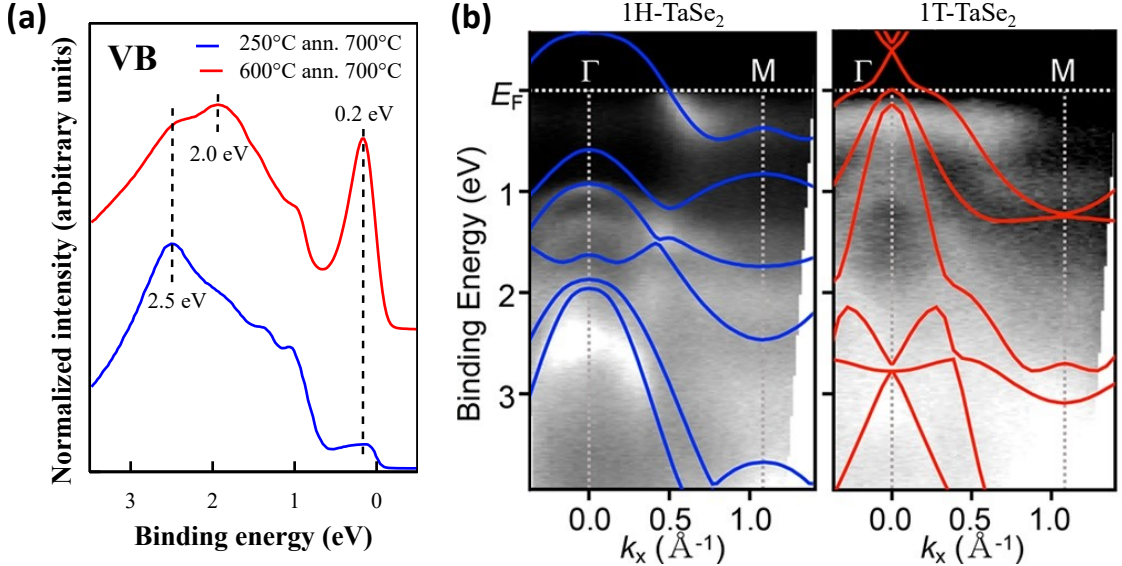


Figure 3.24: (a) Valence band measured in UPS on two annealed layers grown at different temperatures. (b) ARPES measurements of 1H and 1T-TaSe₂ monolayers grown by MBE on graphene and band structure calculations, reproduced from Nakata *et al.*²³⁸.

To highlight the striking difference between the 1H and 1T phases, the band structure is first discussed. In Fig. 3.24 (a), the valence band measured around Γ in UPS is presented for the monolayers grown at 250 or 600 °C after annealing. A maximum at 2.6 eV previously attributed to the 1H phase (Fig. 3.10 (c)) is clearly visible on the sample grown at 250 °C. On the sample grown at 600 °C, a maximum is reached at 2.0 eV as expected for the 1T phase. However, a shoulder is also observed at 2.5 eV which suggests that a small fraction of 1H phase has been formed in agreement with the minor phase transformation observed during the annealing process. A large difference of electron density near the Fermi energy is observed between the two phases, in accordance with previous ARPES measurements and band structure calculations from Nakata *et al.* which have been reproduced in Fig. 3.24 (b).²³⁸ In the 1H phase, the metallic Ta 5d band is predicted to be above E_F in Γ , which explains that it is not detected by photoemission. Instead, the largest density of states is found between 1 and 2.5 eV in UPS with minor peaks at 1 and 1.3 eV that correspond very well to the bands observed in ARPES. The residual electron density

below 1 eV could be either due to the detection of the metallic band at the edge of the acceptance cone, or the presence of a minor fraction of 1T phase. Indeed, an intense and narrow peak is observed in the UPS spectra at 0.2 eV in the sample grown at 600 °C and attributed to the lower Hubbard band in this Mott insulating compound, in accordance with the large flat band revealed in ARPES at this position. A small bandgap would normally be expected in the Mott insulating phase, but it is smaller than the experimental resolution of the UPS measurement and the magnitude of the photovoltage effects.

Therefore, the presence of the Mott gap is investigated through STS measurements at 77 K performed by Houda Koussir. The first derivative of the current intensity is plotted as function of the voltage in Fig. 3.25 (a). It reveals a large density of states below -1.0 V and above 1.4 V, which is attributed to the GaP substrate as the inner interval match rather well its band gap.⁴²⁹ The signal is much lower in this range, but it remains different from zero because the carriers can be evacuated through the layer. The inset shows a spectrum acquired from -0.5 to 0.5 eV. In this case, a negligible signal is observed in a very small interval of circa 0.13 ± 0.02 eV around E_F which is attributed to the TaSe₂ band gap. It is surrounded by two peaks which are ascribed to the lower and upper Hubbard bands.

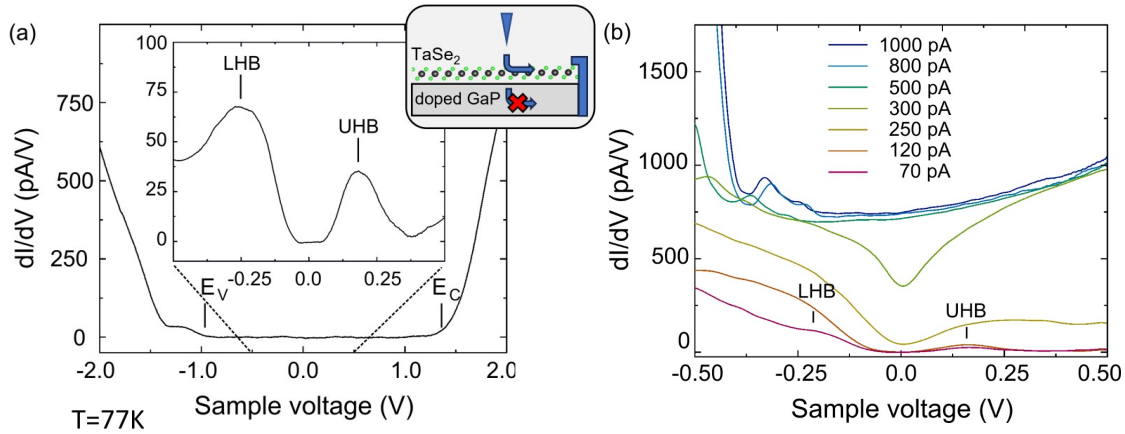


Figure 3.25: (a) STS spectra acquired at 77 K using $V = -2.0$ V and $I = 200$ pA as feedback parameters for the main plot and $V = -0.5$ V and $I = 20$ pA for the inset. (b) STS spectra acquired at 77 K using various current setpoints. The figures and measurements are from Houda Koussir.⁴¹⁴

To determine if the Mott state can be controlled, the current intensity is varied among the different STS spectra presented in Fig. 3.25 (b). At 250 and 300 pA, the Mott gap is still visible, but the density of state does no longer reach zero. For a current of 500 pA and above, the Mott gap has completely vanished. This shows that an insulator to metal transition can be triggered in STM. Because the tip moves closer to the surface when the current setpoint is increased, it does not necessarily mean that this metallic state is induced by the increase of the electric field,⁴³⁰ but it may also be due to the proximity of the tip which modifies the electrons screening.⁴¹⁴

3.2.3.b Large-scale electrical resistivity measurement

The Mott insulating phase has been evidenced at microscopic scale using STS. However, it remains necessary to confirm its existence all over the surface to ensure a good homogeneity of the electrical behavior. For this, a TaSe₂ monolayer has been grown at 600 °C, to favor the 1T phase, on a semi-insulating GaP substrate which enables electrical measurements to be made. Its thickness is comparable to the preceding sample according to the XPS estimation reported in Table 3.10.

Sample #	Substrate	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Measured th. (ML)	Characterizations
T15	GaP (s.i.)	600	660	1.1	0.80	4PP

Table 3.10: Sample grown for the electrical characterization. "s. i." stands for semi-insulating.

The sample is measured under vacuum in a liquid nitrogen-cooled cryostat. To get rid of the contact resistances, four probes are directly placed onto the layer in the square configuration. The measurement is performed through a 20 nm-thick Se capping layer to prevent the oxidation during the sample transfer. At room temperature, the Se capping layer is largely more resistive, and it should be evaporated as the temperature is increased.

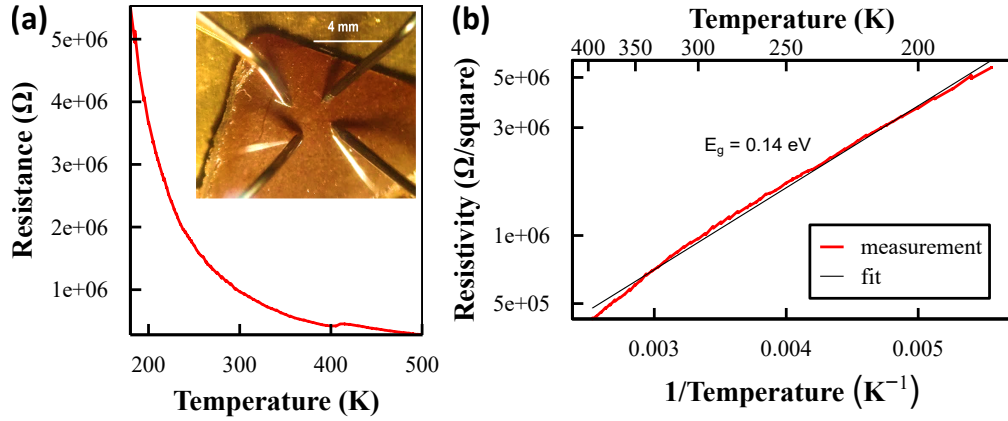


Figure 3.26: (a) Sheet-resistance measured as function on temperature on the sample grown at 600 °C and annealed at 700 °C (sample T15). The measurement was performed by Yevheniia Chernukha. A picture of the sample is presented in inset. (b) Exponential part of the curve in (a) in logarithmic scale.

The result, presented in Fig. 3.26 (a), reveals an exponentially decreasing resistance when the temperature is varied from 180 to 500 K, suggesting a semiconducting behavior as expected for the Mott-insulating 1T phase. The little increase around 405 K is possibly a measurement artifact. The linear fit of the region between 180 to 400 K in logarithmic scale is shown in Fig. 3.26 (b). The band gap, calculated as twice the activation energy, is 0.14 ± 0.01 eV in perfect agreement with the STS results. This result proves the predominance of the Mott insulating phase at microscopic scale and the continuity of the film.

Summary

TaSe₂ monolayers have been grown on both GaP and GaAs substrates, but the GaP one appeared more suitable given the degraded morphology caused by the low stability of GaAs at high temperature and large Se flux. The metastable 1T phase is grown at high temperature whereas the 1H phase is favored at low growth temperature, by a subsequent annealing and when the average thickness approach one monolayer. Still, the electrical measurements confirms that a continuous monolayer of dominant 1T phase can be grown with a sufficiently low defect density for the Mott insulating phase to be present in most of the sample.

3.3 TaSe₂ few-layers

In the previous section, small variations of thickness have been observed to play a non-negligible role on the phase formation. In this section, the thickness is increased to about 3 to 6 MLs to determine if this can be further confirmed. The influence of the growth parameters is first investigated on GaP substrate, before considering the growth on GaAs for comparison. Finally, the electrical properties of the few-layers are explored to determine their suitability as electrical contacts.

3.3.1 Growth on GaP

As in the monolayer case, the effect of the growth temperature is discussed first. Similar growth parameters are used, including a Se flux in the $2\text{--}4 \times 10^{-6}$ Torr range and a growth rate of 0.005-0.007 Å/s (3-4 ML/hour), except for the growth duration which is increased to target a thickness of 6 MLs. The as-grown and annealed samples are summarized in Table 3.11.

Sample #	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Measured th. (ML)	Characterizations
T16	250	-	6	5.23	RHEED, XPS, UPS
T17	250	650	6	4.04	XPS
T18	250	650	6	5.52	UPS STEM
T19	250	650	6	3.86	RHEED, AFM
T20	250	650	6	-	XRD
T21	400	-	6	3.79	RHEED, XPS, UPS
T21'	400	650	6	5.43	RHEED, XPS, UPS, AFM, XRD
T22	500	-	6	3.42	RHEED, XPS, UPS
T22'	500	650	6	4.83	RHEED, XPS, UPS, AFM, XRD, STEM
T23	550	-	6	3.49	RHEED, XPS, UPS
T23'	550	700	6	3.7	RHEED, XPS, UPS, AFM
T24	550	700	6	4.61	XRD, STEM
T25	600	-	6	4.08	RHEED, XPS, UPS
T25'	600	700	6	4.3	RHEED, XPS, UPS, STEM
T26	600	700	6	4.49	AFM, XRD
T27	650	-	6	4.33	XPS, UPS
T27'	650	750	6	4.26	XPS, XRD

Table 3.11: 6 ML-thick TaSe₂ samples considered to study the influence of the growth temperature.

Even though a variability is observed, the XPS measurements indicate an average thickness slightly below the target, as already noticed in the case of monolayers. Nevertheless, after annealing, the samples generally appear thicker than their as-grown counterparts. This could be related to an evolution of the morphology as discussed next.

3.3.1.a Morphology

As revealed by the RHEED monitoring, the as-grown layers exhibit a rather poor morphology. Similar to the monolayer case but clearly worse as the thickness increases, the diffraction pattern is diffuse at low temperature, as seen in Fig. 3.27 (a), whereas it entirely consists of spots in Fig. 3.27 (b-d) for growth temperatures between 400 and 550 °C. This spotty pattern is slightly different from the twinned FCC diffraction one observed on GaAs substrate in Section 3.2.1.d. Especially in the pattern (d), extra spots are observed, which could not be definitely attributed

to either a Ga_xSe_y or TaSe₂ polytype. Interestingly, even though small spots are visible, bright streaks are maintained for the growths at 600 °C (Fig. 3.27 (e)) and 650 °C (not shown).

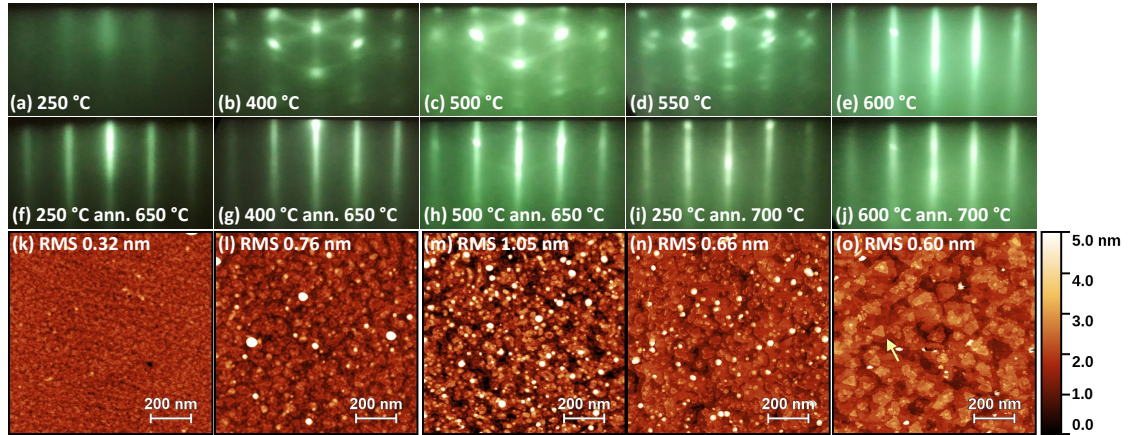


Figure 3.27: (a-e) RHEED patterns observed along the $\langle 010\bar{1} \rangle$ direction of the 6 ML-thick TaSe₂ layers grown at 250, 400, 500, 550, and 600 °C. (samples T16, T21, T22, T23 and T25) (f-j) RHEED patterns of the corresponding layers after annealing at 650 °C (samples T19, T21', T22') or 700 °C (T23' and T25'). (k-o) $1 \times 1 \mu\text{m}^2$ AFM images of the corresponding layers after annealing (samples T19, T21', T22', T23', T26). All images share the same color scale.

After annealing, most of the spots are removed from the RHEED pattern around 650 °C, as previously observed in the monolayer case, indicating an improvement of the morphology. However, a distinction should be made between the sample grown at 400 °C, for which the spots entirely vanish (Fig. 3.27 (g)), and the samples grown at 550 °C and above, for which some of them remain in spite of the higher annealing temperature (Fig. 3.27 (i-j)).

The morphology of the annealed layers is further revealed by the AFM images in Fig. 3.27 (k-o). The sample grown at 250 °C exhibits the lowest RMS roughness. In this case a grainy texture is observed but the heights remain in a narrow range, indicating a very uniform coverage. When the growth temperature is increased to 500 °C, the roughness progressively increases as a consequence of the larger spread of terrace levels and few bright spots indicate the presence of high islands. The roughness is maximum on the sample grown at 500 °C, in agreement with the as-grown RHEED patterns being worse for intermediate growth temperatures. This confirms that the morphology cannot completely recover during the post growth annealing. The sample grown at 550 °C still exhibits islands and few pits, but larger and smoother terraces are observed. The sample grown at 600 °C confirms this trend. Interestingly, the terraces are round-shaped on the sample grown at 550 °C whereas many islands exhibit hexagonal and triangular shapes (as pointed by the arrow) on the sample grown at 600 °C, suggesting a larger adatom diffusion length and a more thermodynamically controlled growth on the latter.²³⁶

3.3.1.b Phase and composition

The phase formed before and after annealing is then investigated through XPS and UPS measurements. The Se 3d CLs presented in Fig. 3.28 (a) are surprisingly similar for the samples grown at low and high temperatures, both before and after annealing. Only the samples grown at intermediate temperature are slightly different, with the two peaks of the doublet being less separated, suggesting a phase mixture, and shifted toward the high binding energies. This could be either due to the presence of the 1T phase, or to a larger Ga_xSe_y component. For any other sample, the peak positions correspond very well to the 1H layers, and especially after annealing, the very narrow doublets suggest a good phase purity. Still, it must be mentioned that the different polytypes made of 1H layers are not likely to be distinguished in XPS and

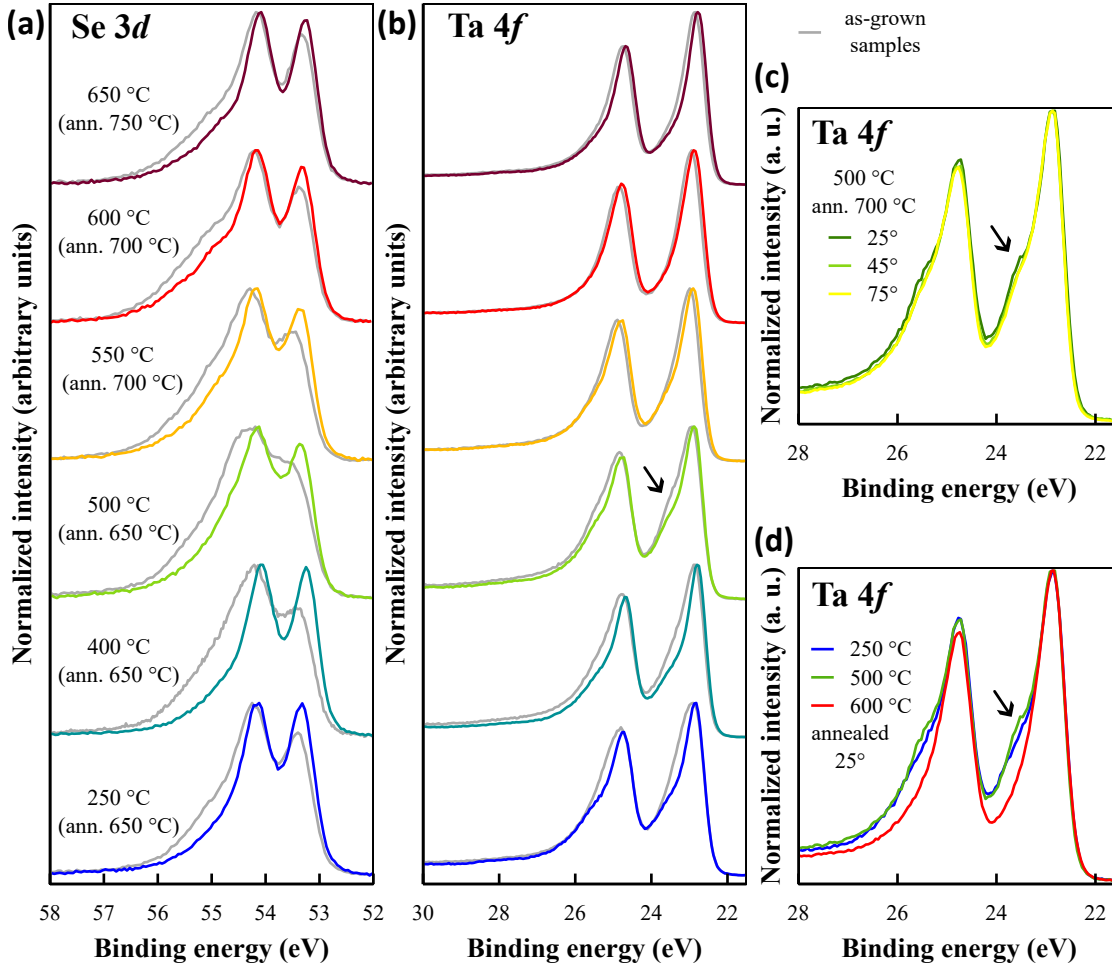


Figure 3.28: (a) Se 3d CLs and (b) Ta 4f CLs of 6 ML-thick TaSe₂ layers grown on GaP at various temperatures before and after annealing (samples T16, T17, T21, T22, T23, T25, and T27). The CLs are recorded in XPS at a take-off angle of 45°. (c) Ta 4f CL of the 6 ML-thick TaSe₂ layers grown at 500 °C after annealing (sample T22') measured at different take-off angles. (d) Comparison of the Ta 4f CL of the 6 ML-thick TaSe₂ layers grown at 250, 500, and 600 °C after annealing (samples T17, T22' and T25') measured at 25°.

will be referred as H phases, independently of them being 2H_a or 3R or any other stacking. The observation of more H phase in few-layers is in line with the thickness dependence observed in the section dedicated to monolayers, but it may appear surprising that the 1T phase remains only at intermediate temperatures. This is however rather consistent with the study of Shimada *et al.* who found mixed T and H layers in a sample grown at 410 °C while only H phases were detected at 495 or 590 °C.²⁴⁵ Even if the 1T phase is not predominantly formed at low temperature, they explained that the kinetically formed 1T layers are more likely to survive at low temperature, as demonstrated in TaS₂.⁴¹⁶ Conversely, a long growth at high temperature favors the phase conversion as does an annealing. Indeed, the annealing is shown here to shift further the peaks toward the H phase position, in accordance to the monolayer case. The analysis of the Se 3d CL is however not straightforward because of the asymmetry of the peaks and the possible presence of a Se-Ga bonds at high binding energy. Beyond a possible transformation of 1T to H phases upon annealing, the reduction of the high binding energy tail effectively suggests the evaporation of some Ga_xSe_y component as previously observed in monolayers.

The preceding conclusions are further confirmed by the Ta 4f CLs presented in Fig. 3.28 (b).

The fact that none of the samples distinctly exhibit the characteristic doublet splitting of the 1T phase CDW is consistent with its absence in large proportion in every sample. Similar to the monolayer case, the samples grown at low temperature exhibit a broad tail at high binding energy, which is then replaced by a smaller shoulder characteristic of the H phases after annealing. This shoulder is slightly more prominent on the sample grown at 500 °C. This can be observed as-grown (arrow on Fig. 3.28 (b)) but also after annealing when the electron take-off angle is reduced to 25° to improve the surface sensitivity in Fig. 3.28 (c). In this case, the shoulder is attributed to a small fraction of residual 1T phase among the predominant 1H phase and the fact it is more visible at low take-off angle suggests that it mostly lies in the upper layers. By contrast, this shoulder is neither visible on the samples grown at 600 and 650 °C as-grown nor after annealing, as shown by the comparison in Fig. 3.28 (d). This does not only rule out the possibility of a small fraction of 1T phase at high growth temperature, but also questions the nature of the presumed H phase grown at high temperature.

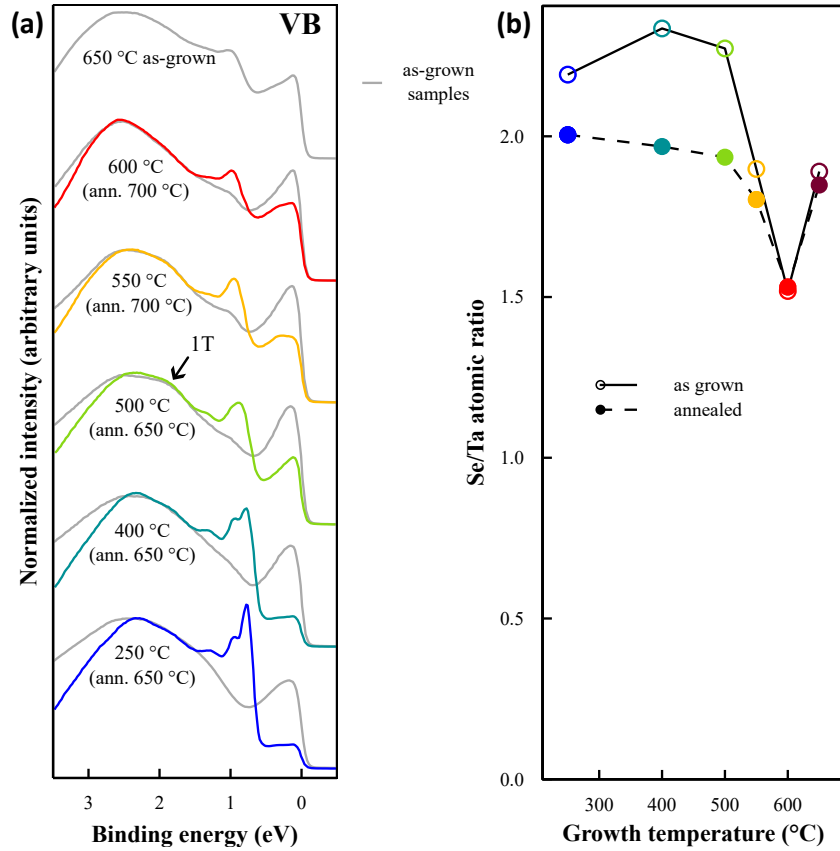


Figure 3.29: (a) Valence band of 6 ML-thick TaSe₂ layers grown at various temperatures before and after annealing (samples T16, T18, T21, T22, T23, T25, and T27) measured in UPS around Γ using 21.2 eV photons. (b) Se/Ta ratio in the layer based on XPS measurements at 25°.

A similar conclusion can be derived from the analysis of the corresponding valence bands presented in Fig. 3.29 (a). Even though the band structure is slightly modified with the number of layers,²⁹ some characteristics of the 1H and 1T phase are preserved. At low growth temperature, the valence band resembles the one previously attributed to the 1H phase in Section 3.2.3.a. Especially after annealing, it is characterized by a low electron density near E_F , consistent with the metallic band still being expected to be above the Fermi level around Γ in the bulk 2H phase. The peaks at 1.0 and 1.3 eV are better resolved in the annealed few-layers compared to the 1H monolayers, and a narrow one appears at 0.8 eV. When the growth temperature is increased to

500 °C, the increase of the density of states near E_F also correlates with apparition of a very faint shoulder at 2.0 eV (pointed by an arrow) and the shrinking of the peaks around 1 eV. This could be related to a substantial fraction of 1T phase as already detected on this sample through the Se 3*d* and Ta 4*f* CLs. The fact it appears more clearly in UPS is consistent with the 1T phase lying mostly in the upper layers, this technique being more surface sensitive than XPS. Finally, when the growth temperature is increased to 600 or 650 °C, the electron density near E_F remains high but the shoulder at 2.0 eV attributed to the 1T phase vanishes. At the same time, the narrow bands near 1 eV attributed to the H phases are further decreased. Hence, these samples cannot conclusively be attributed to either phase.

To determine what has been formed on samples grown at high temperature, the composition of the layers is investigated through quantitative XPS measurements. The atomic Se/Ta ratio in the layers, obtained through the integration of the Ta 4*f* and Se 3*d* CL intensities above a Shirley background and after correction of their respective sensitivities, is plotted in Fig. 3.29 (b). Reducing the electron take-off angle to 25° to be more surface sensitive, the signal from the Se-termination of the GaP substrate is supposed to be negligible, and therefore a ratio of 2 should be expected for a stoichiometric film. Nevertheless, the samples grown at 500 °C and below have an excess of Se before annealing which vanishes afterward. This could be related to extra Se in Se clusters or amorphous TaSe_{2+x}, by analogy to what observed in MoS₂ grown at low temperature by plasma enhanced-ALD.²⁰⁶ However, this would be mostly expected to occur at 250 °C, whereas the Se/Ta ratio is even larger at 400 and 500 °C. Because these samples exhibited a 3D RHEED pattern, already suspected to correspond to Ga₂Se₃, these extra Se atoms could be related to Ga_xSe_y compounds visible in the high binding energy tail in Fig. 3.28 (b). Its shrinking after annealing is in perfect accordance with the suppression of this excess of Se which makes these samples have a Se/Ta ratio very close to the ideal composition. By contrast, the samples grown at 550 °C and above are slightly Se-deficient before annealing. In these cases, it remains similar or slightly worse after annealing. This is in agreement with other studies.²²¹ and attributed to the decrease of the Se sticking coefficient with temperature. However, it is surprising that the Se/Ta ratio is the lowest in the sample grown at 600 °C and is comparatively better for a growth at 650 °C. A possible explanation could be a better cracking of the Se_x molecules on the surface, which could make them more reactive and facilitate their incorporation despite of the lower sticking coefficient.

The absence of any apparent component at the low binding energy side of the Ta 4*f* CL rules out the possibility of a large amount of metallic Ta. However, self-intercalated Ta_{1+x}Se₂ is known to be easily formed.¹⁰⁰ Another possible explanation for the Se deficiency is the replacement of Se by P atoms. It would be hardly observed in the Ta 4*f* since the P and Se atoms have relatively similar electronegativities, but this can be evidenced by the evolution of the P 2*p* CL presented in Fig. 3.30 (a). At low growth temperature, a unique doublet is clearly observed despite of the low signal. Then, a very slight shoulder progressively appears at the low binding energy side of the annealed samples grown at 500 and 550 °C. Finally, it becomes obvious on the sample grown at 650 °C. The 550 and 600 °C samples have been grown on p-type GaP substrates for which the band bending is inverted with respect to n-type GaP ones. This reduces the energy separation between the P-Ga and P-Ta components, explaining why the P 2*p* shoulder is less visible in those cases. Nevertheless, the fit in Fig. 3.30 (b) effectively reveals the presence of two components in significant amount in the 600 °C sample after annealing.

The proportion of the two components in the different samples are summarized in Fig. 3.30 (c). In this chart, the P 2*p* CL intensity is normalized with respect to the total Ga 3*d*, P 2*p*, Se 3*d* and Ta 4*f* CLs signal corrected with their relative sensitivity as described in Section 2.2.4. The variation of the P-Ga content among the samples can be explained by the different thicknesses, the signal coming from the substrate being screened by the TaSe₂ layer, as evidenced by the comparison with the 1 ML sample presented as a reference. Concerning the P-Ta component, it better correlates with the growth temperature, with a progressive increase from 250 to 550 °C and then a sudden enhancement between 600 and 650 °C for the as-grown samples. The P-Ta signal further increases after annealing but the same trend is observed afterward. Remark-

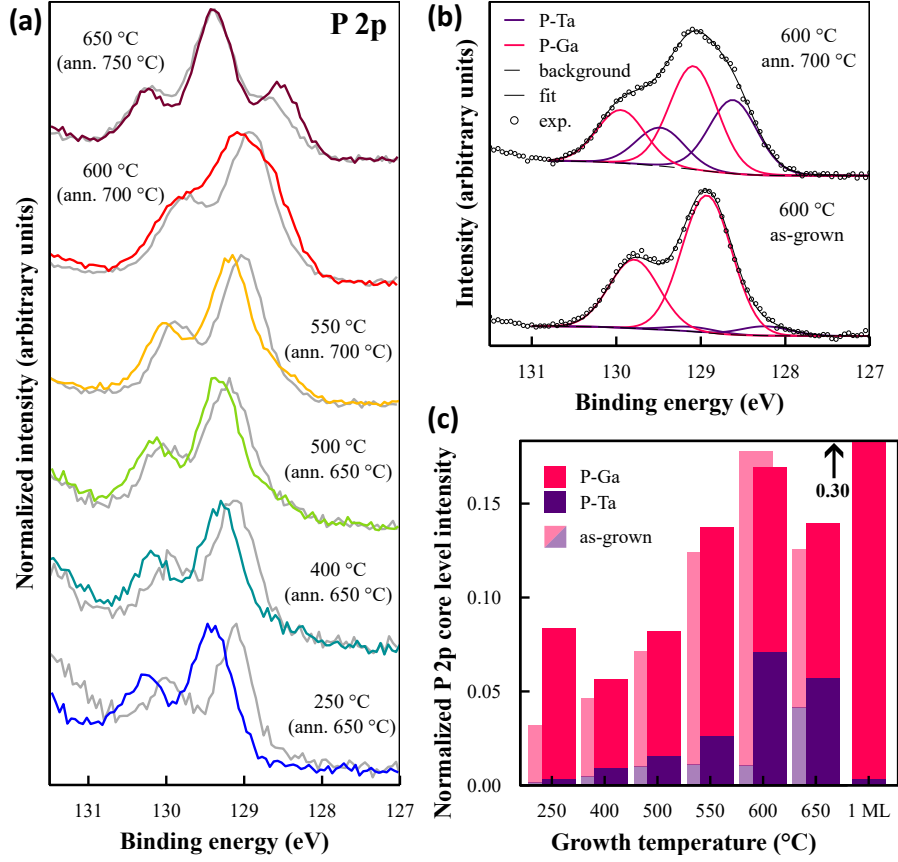


Figure 3.30: (a) P 2p CLs of 6 ML-thick TaSe₂ layers grown at various temperature before and after annealing, measured in XPS at 45°. The samples grown at 550 °C and 600 °C are grown on p-doped GaP substrate, reducing the energy separation between the P-Ta and P-Ga component because of the band bending. (b) P 2p CL fit of the sample grown at 600 °C before and after annealing. (c) Comparison of the P-Ta and P-Ga components intensity in the P 2p CL for the different samples presented in (b) before and after annealing, and for a reference monolayer grown at 600 °C and annealed at 700 °C. The signal intensity is normalized with respect to all elements, so that $I_{P2p} + I_{Ga3d} + I_{Se3d} + I_{Ta4f} = 1$ where the intensities I are corrected by the appropriate sensitivity factors.

ably, the enhancement of the P-Ta content is particularly large during the annealing at 700 °C of the sample grown at 600 °C, whereas a same annealing on the sample grown at 550 °C has a more limited effect. The fact the sample grown at 600 °C was severely Se-deficient as-grown may be an explanation. It is hence proposed that the Ta atoms that are not bounded to enough Se atoms are more likely to catch a P atom during the annealing. This means that the P diffusion remains relatively low at the growth temperature of 600 °C. By contrast, the sample grown at 650 °C which was less Se-deficient already has an important P-Ta component as-grown, indicating a non-negligible interdiffusion at this temperature. However, the annealing at 750 °C of this sample does not result in a much stronger degradation, probably because most of the Ta atoms were already saturated by either P or Se atoms.

Interestingly, the monolayers do not suffer such a degradation as proved by the reference 600 °C annealed 700 °C monolayer, which exhibits a negligible Ta-P content, not only in proportion of P 2p signal, but also in normalized intensity. Therefore, this degradation seems to be specific to the thick layers, even if it might be related to the poor vdW interface revealed by the STEM observation of the 1.4 ML sample in Section 3.2.1.b.

3.3.1.c Structure

The structure of the annealed samples is now investigated using in-plane grazing-incidence XRD. Typical diffraction patterns recorded along two different directions of the substrates on the sample grown at 550 °C and annealed at 700 °C are presented in Fig. 3.31 (a). The peak indexation confirms the epitaxial relationships previously determined.

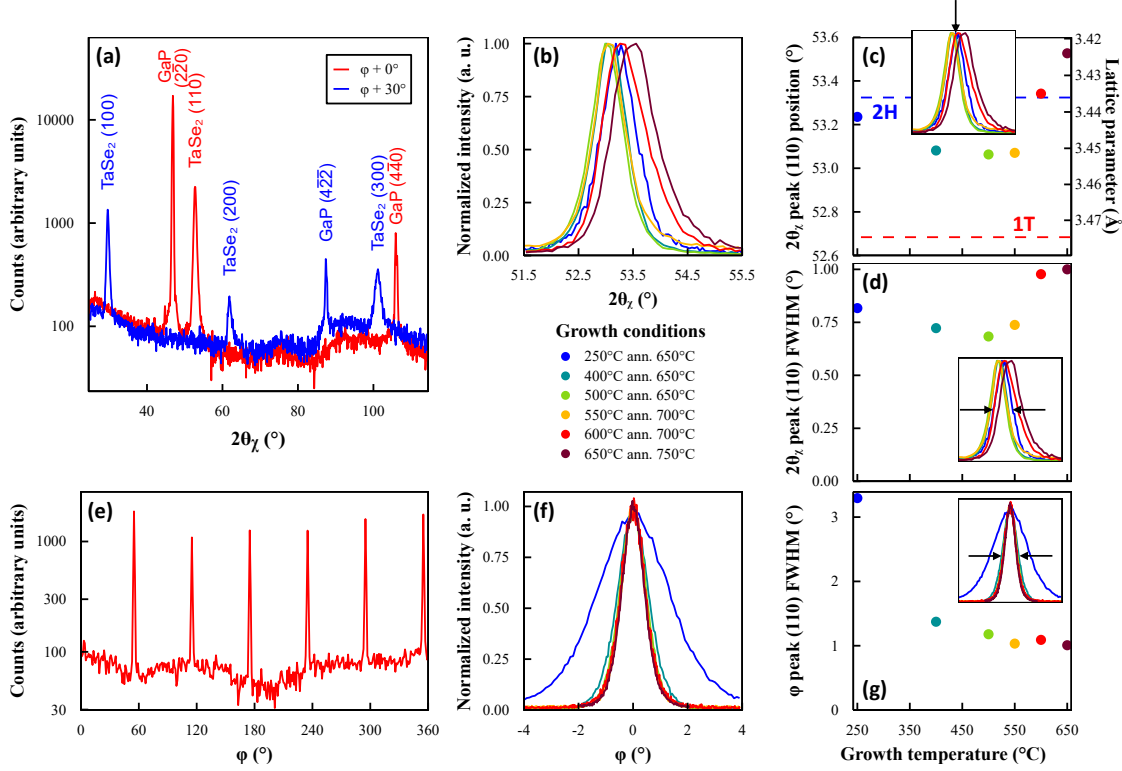


Figure 3.31: (a) In-plane grazing-incidence XRD diffraction patterns of the 6 ML-thick TaSe₂ film grown at 550 °C and annealed at 700 °C (sample T24) recorded along the GaP $\{2\bar{1}\bar{1}\}$ and $\{1\bar{1}0\}$ directions. (b) Comparison of the TaSe₂ {110} diffraction peak recorded on the layers grown at different temperatures (samples T20, T21', T22', T24, T26, T27'). (c) Position of the TaSe₂ {110} peaks in plot (b) and the corresponding lattice parameters TaSe₂. (d) FWHM of the TaSe₂ {110} peak in plot (b). (e) Full azimuthal scan on the TaSe₂ {110} peak of sample T24. (f) Comparison of the peaks obtained by the azimuthal scans on the six samples. (g) FWHM of the peaks in plot (f).

The TaSe₂ {110} peaks are compared for the layer grown under different conditions in Fig. 3.31 (b) after normalization of their intensity. The $2\theta_\chi$ angles have been corrected to ensure that the GaP $\{2\bar{2}0\}$ and $\{4\bar{4}0\}$ peaks are positioned at 47.17 and 106.31° respectively in every diffraction pattern to offset instrumental errors. The TaSe₂ {110} peaks are observed to shift toward smaller angles first and then to larger angles. The peak positions are plotted in Fig. 3.31 (c) in which the corresponding lattice parameters have been calculated. The sample grown at 250 °C matches rather well the bulk lattice parameter for the 2H phase, as well as any other phases made of the trigonal prismatic coordination (H) layers.⁴³¹ The larger lattice parameters for the samples grown between 400 and 550 °C could be related to the presence of some 1T phase but since the FWHM of the peak is close to the expected angle separation between those phases, a distinct peak should be discernible if the two phases were present in significant amount. Instead, this could be induced by the variation of stoichiometry. Indeed, Bjerkelund *et al.* reported an increase of the Ta_{1+x}Se₂ lattice parameter for a small Ta excess followed by a decrease,¹⁰² in perfect accordance with the observations of a shift toward smaller angles first and large angles then.

Nevertheless, the FWHM of the TaSe₂ {110} peaks, plotted in Fig. 3.31, are slightly reduced from 0.86 to 0.69° when the growth temperature is increased to 500 °C, which suggests an improvement of the grain size. A basic calculation of the grain size through Scherrer equation

$$L = \frac{0.89\lambda}{\Delta(2\theta_\chi) \cos \theta_\chi} \quad (3.2)$$

where λ is the X-ray wavelength and $\Delta(2\theta_\chi)$ is the FWHM of the XRD peak, gives a rather small characteristic length L of 13 nm for the crystallites in the best sample. This is however slightly better than former results on GaAs substrates²⁴⁵ and also consistent with the high nucleation density observed in Section 3.2.2.b, pointing toward an absence of seamless grain coalescence in these conditions. For growth temperature of 550 °C and above, the FWHM increases and the peaks in Fig 3.31 (b) become asymmetric. This suggests the presence of several components, which could be different Ta_{1+x}Se₂ compounds, or more likely TaP according to the preceding XPS results. Indeed, the new component appearing at large angle must have a smaller lattice parameter than TaSe₂, which could be the case for TaP, the interatomic distance being about 2.52 Å in TaP⁴³² compared to 2.54 Å in 2H-TaSe₂.¹⁰² Finally, the increase of the FWHM appears to be related to the layer inhomogeneity and rather than the grain size, which seems larger according to the triangular domains observed in AFM on Fig. 3.27 (o).

Then, the grain alignment is studied by setting the diffractometer to the TaSe₂ {110} position, at $2\theta_\chi = 53.1^\circ$, while rotating the sample around the TaSe₂ [0001] axis. The typical record is presented in Fig. 3.31 (e), in which 6 peaks are observed in accordance with the symmetry of the layer and the substrate, the mirror twins being indistinguishable in this configuration. Focusing on one of these peaks, Fig. 3.31 (f) and (g) show that the residual misalignment is different among the samples. An improvement of the in-plane alignment with temperature is observed, in accordance to previous studies on other substrates,^{264,433} but here the residual misorientation is rather small compared to other substrates at comparable temperatures. This is an encouraging result even though it may also be attributed to more covalent substrate-to-layer bonds, probably related to the formation of TaP.

To highlight the structure of the formed compounds, the layers grown at 250, 500, 550 and 600 °C are observed using STEM along the GaP $\langle 0\bar{1}1 \rangle$ zone axis in Fig. 3.32.

The TaSe₂ thickness is typically between 4 and 5 MLs, in good agreement with the estimation derived from XPS measurements presented in Table 3.11. The thickness uniformity is confirmed by the large-scale images presented at the top right for each sample. A difference is however revealed between the samples grown at 250 and 600 °C, for which the layer is rather flat, and those grown at 500 and 550 °C which exhibit some 2 and 3 ML-high islands and for which the TaSe₂-GaP interface is also rougher. These observations are in good agreement with the morphology revealed using AFM in Paragraph 3.3.1.a.

The 1T phase is only observed at the top of the stacking, in the incomplete layers. This is in agreement with the characteristics of the 1T phase being more visible at low take-off angle in XPS when the measurement is more surface sensitive. The complete layers always exhibit the trigonal prismatic coordination but are observed to be stacked in various manners, corresponding to different phases. When the trigonal prismatic layers (" >>> " shapes) are oriented in opposite directions, it corresponds to the 2H_a phase, whereas when they are shifted by one third of the lattice parameter without orientation flip, it corresponds the 3R or 2H_b stackings. The distinction between those polytypes is not really meaningful since the analysis of several images does not reveal any general rule. It is not surprising because it has been shown in other TMDCs that the energy difference between these stacking configurations is small because of the weak vdW interactions.⁴³⁴ In fact, the different layer orientations in the 3R and 2H_a phases corresponds to twins. Hence, beyond the polytype properties that may be slightly different for symmetry reasons, the absence of control over the stacking sequence also implies the formation of grain boundaries as seen in Fig. 3.32 (a). The 1T phase also exhibits such staking faults, as observed in Fig. 3.32 (c).

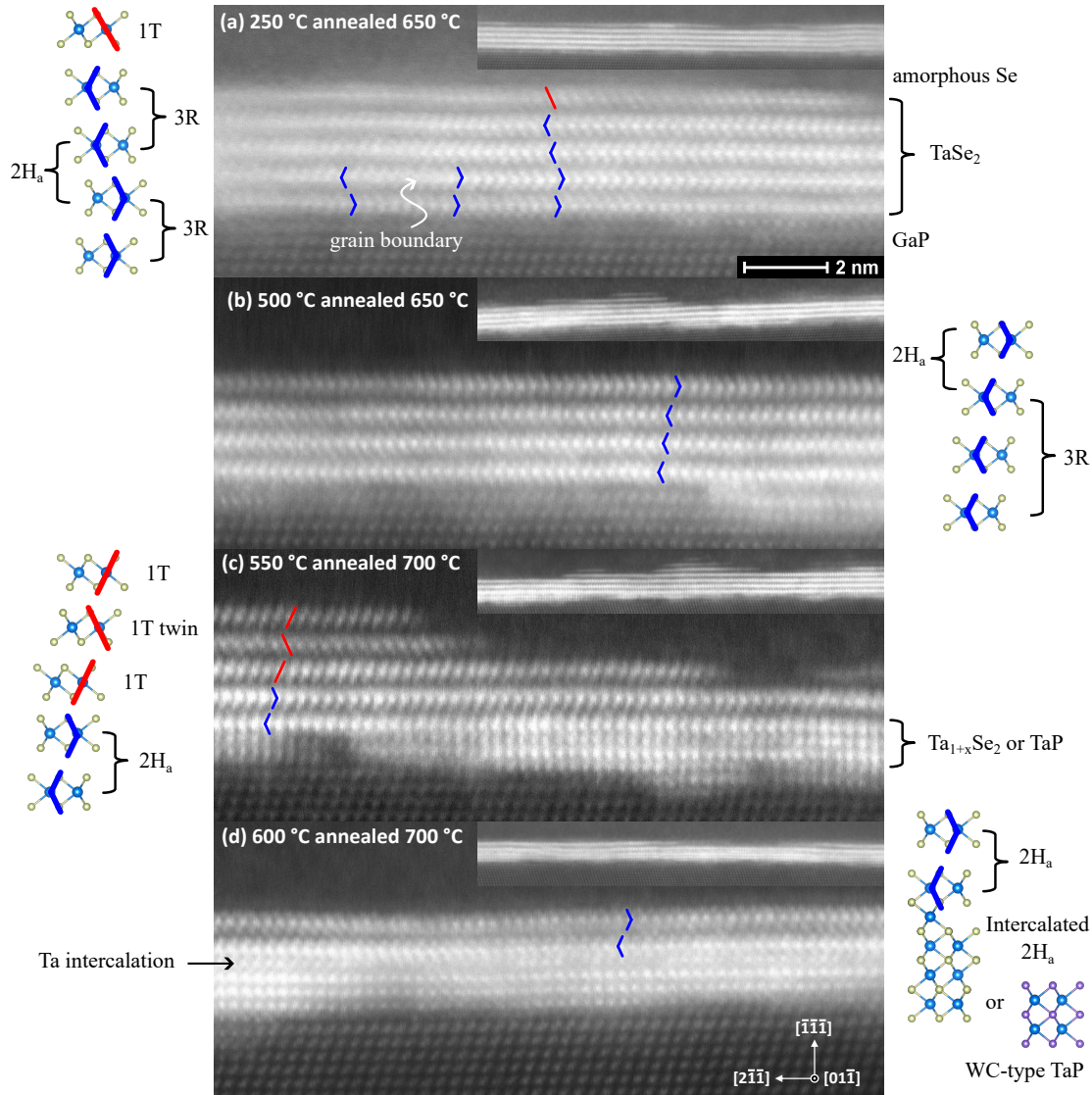


Figure 3.32: (a-d) STEM images of the 6-ML TaSe₂ layers grown at (a) 250 °C and annealed at 650 °C (sample T18), (b) 500 °C and annealed at 650 °C (sample T22'), (c) 550 °C and annealed at 700 °C (sample T24), and (d) 600 °C and annealed at 700 °C (sample T25'). The four images share the same scale. The insets show other images of the corresponding samples at a larger scale (magnification $\times 0.2$)

Finally, for the layers grown at high temperature, an interfacial compound appears between the layered TaSe₂ and the substrate. The bright Ta atoms seem regularly arranged and perfectly aligned. Interestingly, between this compound and the TaSe₂ layer, a row of Ta atoms seems to be intercalated in the vdW gap. This corresponds perfectly to a previously reported intercalation site in Ta_{1+x}Se₂,¹⁰² which is effectively aligned with the two Ta atoms in the 2H_a phase. Therefore, the dense compound could be Ta_{1+x}Se₂ with a full occupation of the intercalation sites, in good accordance with the Se-deficiency revealed on this sample using in XPS. Otherwise, it could also be TaP. Even if its stable phase is tetragonal, it has been found in a hexagonal tungsten carbide structure^{432,435} which also matches the STEM observations. Interestingly, in spite of this interfacial compound, the upper part of the film consists of pristine TaSe₂ layers. The large Se supply may prevent the degradation of the top layer while the bottom ones react with the substrate. This could explain why the monolayer grown in the same conditions does not experience this.

Finally, the STEM analysis is in agreement with the degradation of the few-layers above 500 °C suggested by the XPS and XRD measurements. It also confirms that the 1T phase is very rare, especially on the layer grown at 600 °C, in stark contrast to the monolayers. This is attributed to the presence of much larger islands on this sample, as observed in AFM, which makes the 1T phase less stable as supposed from the effect of coverage. Hence, the 1T phase is not favored at low temperature and it is also hindered by the larger grain size at high temperature, explaining why it is only found as traces at intermediate temperature. The growth of 1T multilayers would require even higher temperatures for this phase to be stable in bulk, but they are difficult to reach in MBE and incompatible with the GaP substrate.

3.3.1.d Effect of the Se flux

It has been initially hypothesized that a high Se flux would be beneficial. However, the excess Se incorporation in the substrate has been then proposed as an explanation for the surface roughening observed at intermediate growth temperature. Nevertheless, the Se content in the annealed layers has been shown to decrease with the growth temperature because of the reduction of the Se sticking coefficient. Hence, a decrease of the Se flux has been considered only for the samples grown at 250 °C. In this case, the surface is supposed to be largely populated by Se_x species and the reduction of their density could favor the diffusion of the Ta adatoms, and therefore improve the TaSe₂ crystallinity without degrading the substrate.

The samples discussed hereafter are presented in Table 3.12. The Se flux has been first reduced by one order of magnitude in sample T28 and then by a second one, so that Se/Ta atomic flux ratio is about 3 ± 1 in sample T29 according to the quartz microbalance measurement, the uncertainty being rather large at such low deposition rate.

Sample #	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Se flux (Torr)	Measured th. (ML)	Characterizations
T16	250	-	6	4×10^{-6}	5.23	RHEED, XPS
T17	250	650	6	4×10^{-6}	4.04	XPS
T20	250	650	6	4×10^{-6}	-	XRD
T28	250	-	6	2×10^{-7}	-	RHEED
T29	250	-	6	4×10^{-8}	4.12	RHEED, XPS
T29'	250	650	6	$3 \times 10^{-6(a)}$	5.55	RHEED, XRD, XPS

Table 3.12: Samples considered to study the influence of the Se flux. ^(a)Se flux during the annealing.

The RHEED patterns observed at the end of the growth are presented in Fig. 3.33 (a-c). The streaks appear clearly thinner and brighter as the Se flux is decreased, in accordance to a larger grain size or smaller in-plane misorientation. Nevertheless, transmission spots are surprisingly observed at low Se flux, in contradiction with the hypothesis of the Se being responsible for the surface roughening. After annealing, however, all samples exhibit the same streaky pattern, the transmission spots vanishing rapidly.

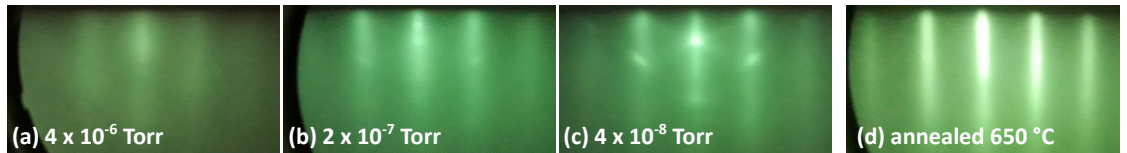


Figure 3.33: (a-c) RHEED pattern of 6 TaSe₂ layers grown at 250 °C under different Se fluxes: (a) sample T16, (b) sample T28, (c) sample T29. (d) RHEED of sample T29' grown under 4×10^{-8} Torr of Se after annealing at 650 °C.

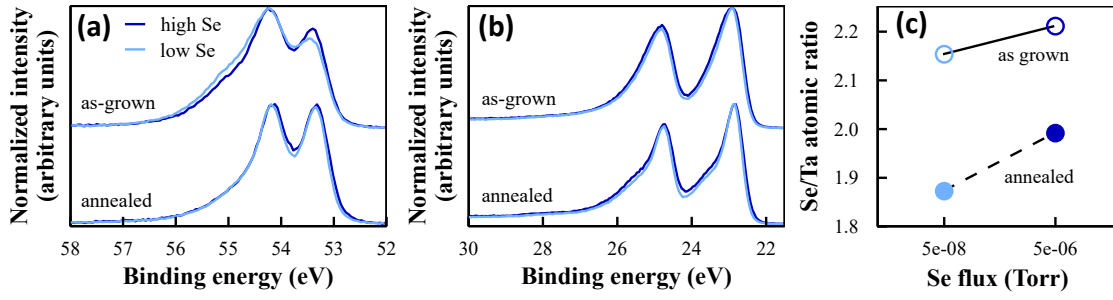


Figure 3.34: (a) Se 3d CLs and (b) Ta 4f CL of 6 TaSe₂ layers grown at 250 °C under different Se fluxes before annealing (samples T16 and T29) and after annealing (samples T17 and T29'). The CLs are recorded in XPS at a take-off angle of 45°. (c) Se/Ta ratio derived from XPS measurements at 25°.

The Se 3d and Ta 4f CLs, presented in Fig. 3.34 (a) and (b) respectively, suggest very small difference between the samples grown at the highest and lowest Se flux. Only the Se 3d CL before annealing has a different shape, with a more pronounced high binding tail for the one grown at low Se flux, which seems counterintuitive, but is consistent with the spotty RHEED pattern. Even if the formation of Ga_xSe_y in these conditions is rather unexpected, the larger roughness of the layer and the fact that this sample (T29) appears thinner than the reference one (T16) makes the Se-terminated GaP substrate more visible. In addition, the Se/Ta ratio in the layers presented in Fig. 3.34 (c) reveals that the one grown under a low Se flux is slightly Se-deficient after annealing. Since both samples have been annealed under a high Se flux, this suggests that the TaSe₂ layer already lacked of Se during the growth under the low flux, but the presence of Se-Ga component led to an estimation of the Se/Ta ratio above 2 as-grown. As previously observed for the few layers grown at 400 and 500 °C, the annealing suppresses the Ga_xSe_y compounds and reveals the Se-deficiency in the layers.

Apart from that, the very similar Ta 4f CL shapes suggest that the Se flux has no influence on the phase. The only subtle difference that can be noticed is a slightly thinner peak width for the low flux sample, which can also be observed after annealing. This is surprising because it suggests a lower defect density, in disagreement with the slight Se deficiency.

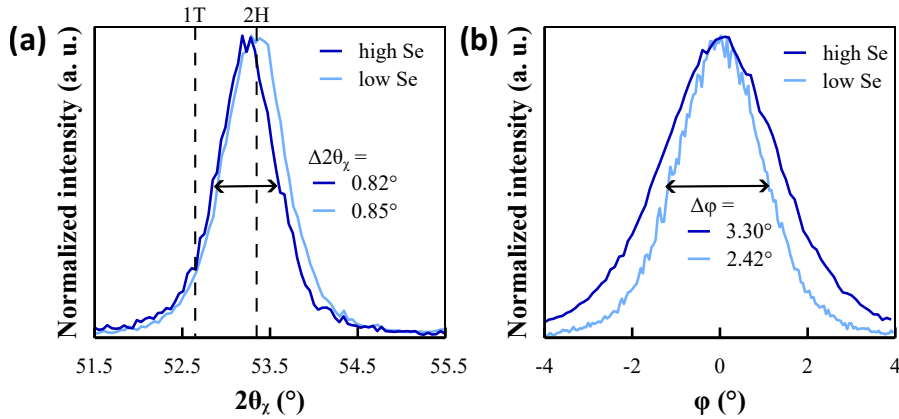


Figure 3.35: (a) Radial and (b) azimuthal XRD scan around the TaSe₂ {110} peak of the 6 ML-thick layers grown at 250 °C under different Se fluxes and annealed at 650 °C (samples T20 and T29').

A possible explanation of this apparent inconsistency would be a better crystallinity, the reduction of Se adatom density increasing the diffusion length of Ta atoms. To investigate this, in-plane grazing incidence XRD measurement have been carried out and the TaSe₂ {110} peaks are compared in Fig. 3.35 (a). The peak position remains in good accordance with the expected lattice for the H phase. A slightly broader peak is obtained for the sample grown at low Se flux but it was measured using a larger Soller slit which degrades the resolution. Based on the nearby

GaP $\{2\bar{2}0\}$ peak width, the resolution is about 0.27° and 0.44° for the samples grown at high and low Se flux respectively, indicating that the width uncertainty of 0.03° is within the measurement incertitude. However, the azimuthal scan presented in Fig. 3.35 (b) clearly reveals a narrower peak for the sample grown at low Se flux despite the lowest resolution, demonstrating less residual misorientation in this case. This is in accordance to the brighter RHEED pattern observed during the growth and may reduce the number of defects and strain at domain boundaries in the layers.

Finally, the reduction of the Se flux has both upsides and downsides, improving the in-plane orientation but leading to a slight Se deficiency. Surprisingly, it does not hinder the formation of Ga-Se bonds and even seems to degrade the morphology. Still, it must be highlighted that the variations over two orders of magnitude only results in relatively little composition change in the layer, indicating that the Se/Ta flux ratio is not a critical parameter at this temperature as long as Se remains in small excess. It confirms that the Se deficiency observed in the previous section was indeed related to a higher growth temperature.

3.3.2 Growth on GaAs

The growth of few-layers TaSe₂ on GaAs and GaP are now compared to study the influence of the substrate. In the case of monolayers, the sample grown at 550°C on GaAs exhibited a degraded morphology attributed to the lower temperature stability of this substrate and the larger Se incorporation compared to GaP. However, it has been shown that lower temperatures and Se fluxes could be preferable for TaSe₂ few-layers. Hence, two different conditions are explored for this comparative study: either 400°C under high Se flux or 250°C under low Se flux.

Sample #	Substr.	Growth T. ($^\circ\text{C}$)	Anneal. T. ($^\circ\text{C}$)	Targeted th. (ML)	Se flux (Torr)	Measured th. (ML)	Characterizations
T30	GaAs	400	-	6	5×10^{-6}	1.8	RHEED, XPS
T30'	GaAs	400	650	6	$5 \times 10^{-6(a)}$	2.53	RHEED, XPS, XRD
T31	GaAs	250	-	6	3×10^{-8}	2.89	RHEED, XPS
T31'	GaAs	250	650	6	$5 \times 10^{-6(a)}$	3.98	RHEED, XPS, XRD

Table 3.13: Samples used to discuss the influence of the substrate. ^(a)Se flux during the annealing.

The estimated thickness (Table 3.13) is largely inferior to the expectations, especially for the sample grown at 400°C and large Se flux. This could be an underestimation due to a rougher morphology, as observed in monolayers, and hypothetical Ga₂Se₃ islands, which makes the calculation through the Ta/Ga ratio irrelevant.

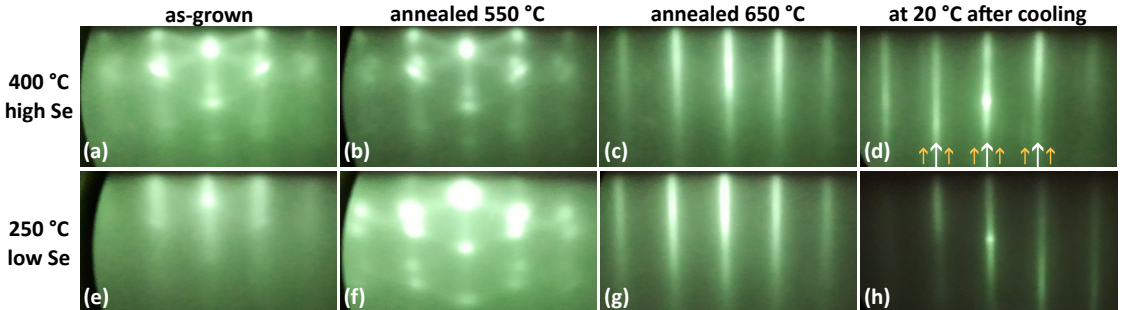


Figure 3.36: (a-d) RHEED pattern of 6 TaSe₂ layers grown on GaAs at 400°C under a Se flux of 5×10^{-6} Torr (sample T30) (a) as-grown, (b) during annealing at 550°C , (c) after annealing at 650°C , and (d) at 20°C after cooling. The white and orange arrows on image (d) indicates to positions of the main streaks and the surface reconstruction respectively. (f-g) Corresponding RHEED patterns for the sample grown on GaAs at 250°C under a Se flux of 3×10^{-8} Torr (sample T31).

The RHEED patterns of the samples grown on GaAs are presented in Fig. 3.36. Similar to GaP, the growth at 400 °C results in a spotty diagram (Fig. 3.36 (a)) whereas the one observed at 250 °C is comparatively more diffuse and less spotty (Fig. 3.36 (e)). Interestingly, when the sample grown at 250 °C is heated under Se flux for a post-growth annealing, the RHEED pattern turns first to a 3D one at 550 °C (Fig. 3.36 (f)) while it remains unchanged at the same temperature for the one grown at 400 °C (Fig. 3.36 (b)). The patterns are not identical, the former corresponding perfectly to the twinned FCC pattern observed for monolayers in Paragraph 3.2.1.d, and the latter exhibiting extra spots already observed for the few-layers grown on GaP in Paragraph 3.3.1.a. However, once the annealing temperature reaches 650 °C, both samples recover a similar streaky pattern (Fig. 3.36 (c) and (g)). Finally, after cooling to room temperature, a surface reconstruction is clearly observed on the sample grown at 400 °C (Fig. 3.36 (d)) whereas it is only barely visible on the one grown at 250 °C (Fig. 3.36 (h)). Since it matches the $\sqrt{13} \times \sqrt{13}$ CDW, this observation suggests the presence of the 1T phase in substantial amount on top of the layers, especially for the one grown at 400 °C.

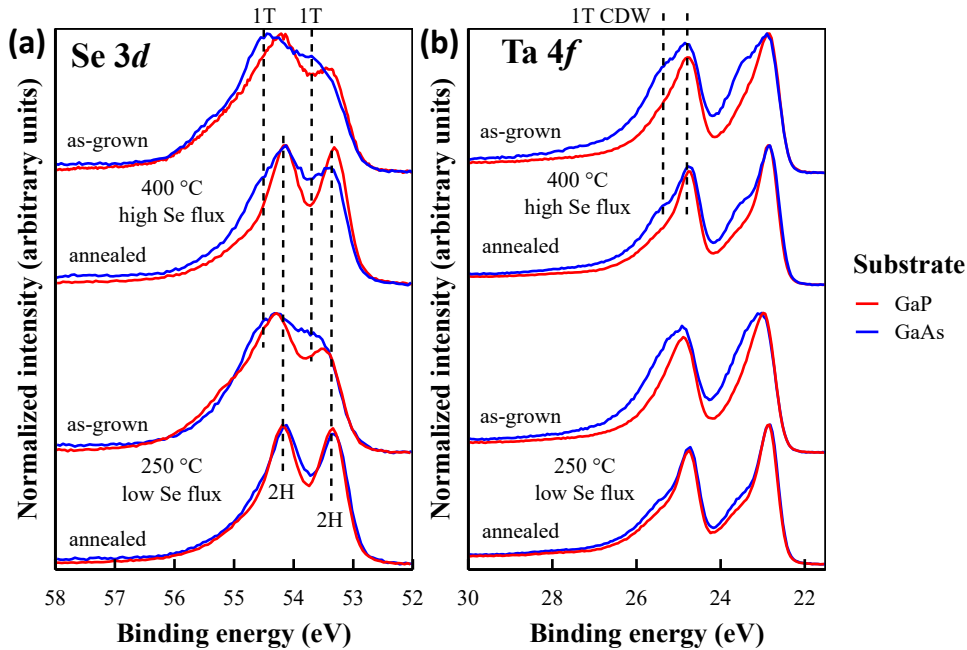


Figure 3.37: (a) Se 3d CLs and (b) Ta 4f CLs of 6 TaSe₂ layers grown on GaP or GaAs at 400 °C under high Se flux (samples T21 and T30) or at 250 °C under low Se flux (samples T29 and T31). The CLs are recorded in XPS at a take-off angle of 45°.

To confirm this, the Se 3d and (b) Ta 4f CLs measured in XPS are presented in Fig. 3.37 (a) and (b) respectively. Both before or after annealing, a substantial amount of 1T phase is effectively found in the layers grown at 400 °C on GaAs, in stark contrast to the multilayers grown on GaP. The reason for this may be the lower thickness measured on GaAs. However, as previously mentioned, the lower thickness estimation does not necessarily mean that less TaSe₂ has been deposited, but could be the result from a rougher morphology. The spots observed on the RHEED pattern during the growth and annealing process, as well as the poor coverage in the monolayer case, support this hypothesis. Finally, the 1T phase being generally observed in small islands on GaP could largely be favored on GaAs if the surface is rough. Less 1T phase is observed on the sample grown at 250 °C and low Se flux, especially after annealing, which is consistent with the preferential formation of the 1H phase at low temperature seen in monolayers, while 400 °C is close to the transition temperature determined in the first section. In addition, the sample is determined to be thicker, which could also indicate a less degraded morphology. Hence, the growth at 250 °C and low Se flux is preferable to form a purer H phase.

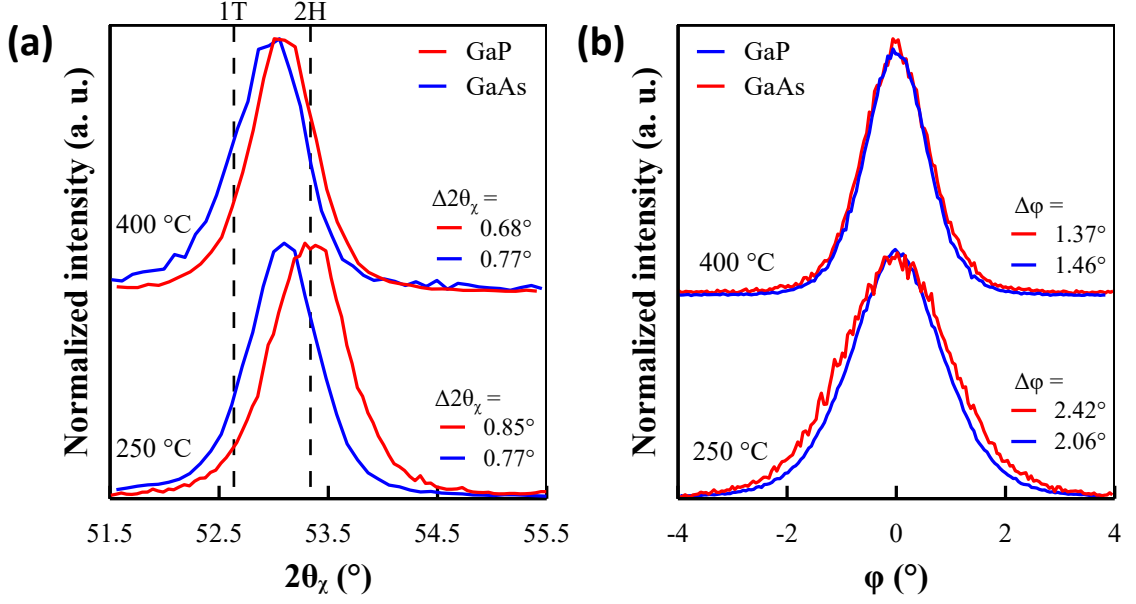


Figure 3.38: (a) Radial and (b) azimuthal XRD scan around the TaSe₂ {110} peak of the 6 ML-thick layers grown on GaP or GaAs, either at 400 °C under $4\text{--}5 \times 10^{-8}$ Torr (samples T21' and T30') or at 250 °C under $3\text{--}4 \times 10^{-6}$ Torr (samples T29' and sample T31'). Both samples grown at 250 °C are measured using 0.5° Soller slits that deteriorates the resolution compared to those measured at 400 °C.

Finally, the crystallographic properties are studied using XRD through the TaSe₂ {110} peaks. The radial ($2\theta_\chi$ - ϕ) scans presented in Fig. 3.38 (a) reveal a shift toward small angles for the two layers grown on GaAs, which could be related to the presence of 1T phase as determined from XPS. This is especially the case for the sample grown at 400 °C on GaAs, for which the {110} peak is also slightly broader than the corresponding one on GaP and asymmetric, in accordance with the presence of a phase mix. Conversely, for the sample grown at 250 °C, a slightly smaller FWHM is obtained on GaAs substrate. Similarly, the rotational alignment, investigated through the azimuthal (ϕ) scans in Fig. 3.38 (b), does not reveal sensible difference between both substrates: if the residual misorientation is slightly lower on GaAs for the growth at 250 °C, it is the reverse for a growth at 400 °C.

Finally, the layers grown on GaAs experience more important surface roughening, either during the growth or the annealing under Se. This is believed to favor a mixture of both phases when the growth occurs at 400 °C, whereas the growth at 250 °C and low Se flux seems suitable to form the H phases. The crystallinity and in-plane orientation are however comparable for the two substrates, confirming the similarity of their Se-terminated surfaces.

3.3.3 Electrical characterization of TaSe₂ few-layers

In this section, electrical characterizations are finally performed on the TaSe₂ few layers to confirm the properties of the trigonal prismatic phases and their pertinence as potential metallic contact.

3.3.3.a Work-function and band alignment

Sample #	Growth T. (°C)	Annealing T. (°C)	Targeted thick. (ML)	Flux Se (Torr)	Measured thick. (ML)	Characterizations
T16, T17, T18, T22, T22', T23, T23', T25, T25', T27:	See Table 3.11					UPS, XPS (T17)
T32	450	-	6	4×10^{-6}	4.36	UPS

Table 3.14: 6 ML-thick TaSe₂ samples considered to study the work function and band alignments. All layers are grown on GaP under Se fluxes in the $2\text{--}4 \times 10^{-6}$ Torr range.

One of the expected characteristics of the metallic TMDCs is a high work function, similar to Pt which is the highest among the metal elements.⁴³⁶ The work function can be deduced from UPS measurements by measuring the low kinetic energy photoemission cut-off. This is shown for the sample grown at 500 °C and annealed at 650 °C in Fig. 3.39 (a). In this case the cut-off at 5.5 eV is in perfect agreement with the TaSe₂ work function published in the literature.¹⁸

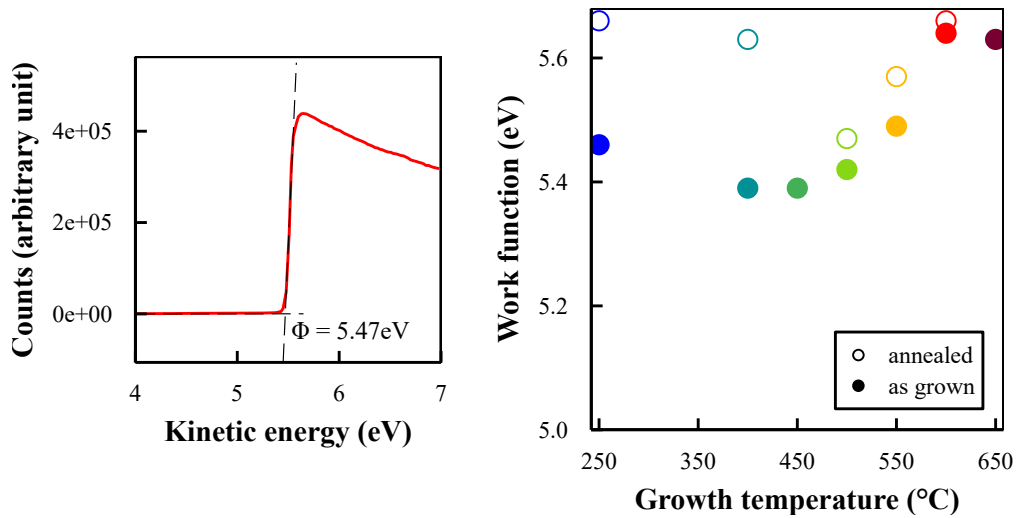


Figure 3.39: (a) Photoemission cut-off measured in UPS ($h\nu = 21.2$ eV) on sample T22' grown at 500 °C and annealed at 650 °C. (b) Work functions deduced from UPS measurements on the 6 ML-thick TaSe₂ layers grown at various temperatures (samples T16, T18, T21, T21', T22, T22', T23, T23', T25, T25', T27, T32).

Still, small work function variations are obtained among the different samples, which might be correlated to the growth and annealing temperatures as evidenced in Fig. 3.39 (b). Indeed, the samples grown at intermediate temperature have the lowest work function, and the sample grown at 600 and 650 °C have the highest one. The work function always increases after annealing but it remains below the average for the sample grown at 500 °C. For the group V TMDCs, the work function is predicted to be lower for the 1T phase.¹¹ Therefore, the residual 1T-TaSe₂ in the as-grown samples could be an explanation for the lower work-function. Similarly, it is consistent that the layer grown at 500 °C, which is believed to contain the largest fraction of 1T phase, also exhibits the lower work function after annealing.

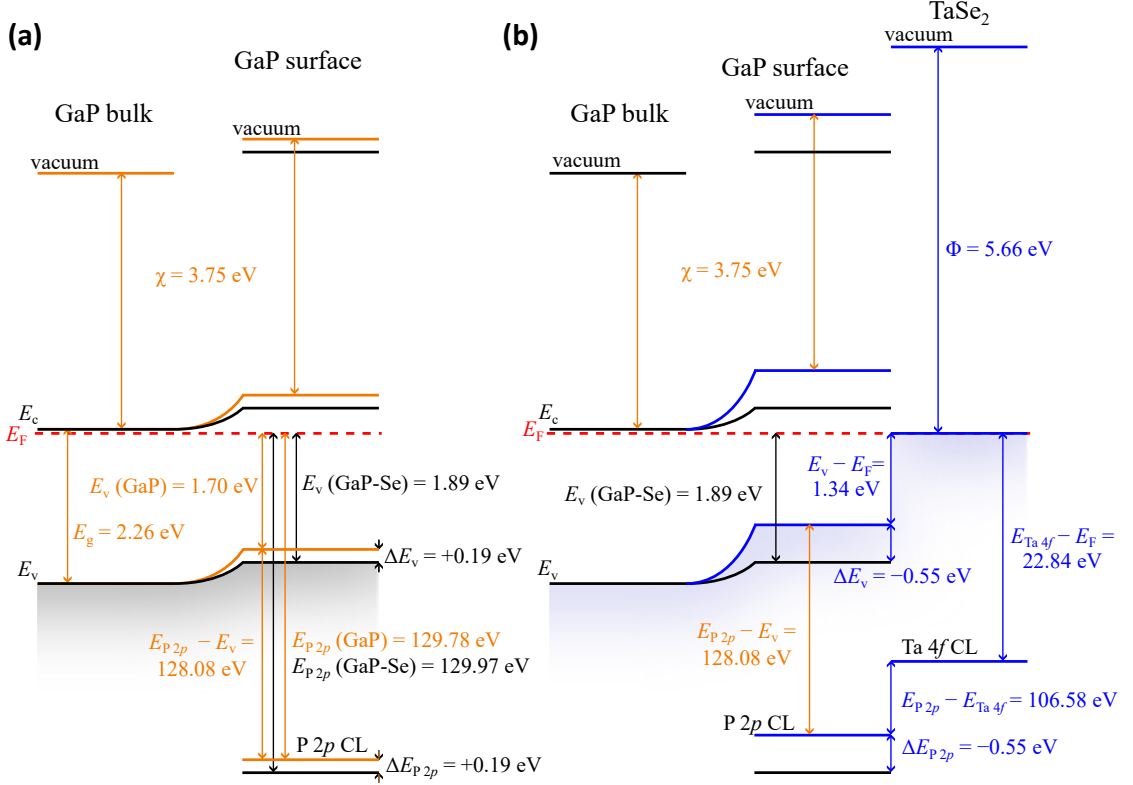


Figure 3.40: (a) Band bending on a bare (orange) and Se-terminated n-type GaP substrate (sample P2) (black). (b) Band alignment of the n-type GaP substrate after the growth of few-layers TaSe₂ at 250 °C and annealing at 650 °C (sample T17) (blue). The band bending on the Se-terminated substrate (black) have been reproduced in diagram (b) as a reference.

Since the work function at the top of the stacking does not necessarily reflect the band bending in the semi-conductor, the GaP-TaSe₂ band alignment is studied through the evolution of the P 2p CL following the method of Kraut and Waldrop.⁴³⁷ First, the band bending on a bare n-type GaP substrate and a Se-passivated one is presented in Fig. 3.40 (a). In this case, the energy separation between the P 2p_{3/2} level and the valence band edge is $E_{P\ 2p}^{GaP} - E_v^{GaP} = 128.08$ eV in XPS. Since this value must be constant for a given compound, the shift of the P 2p CL by 0.19 ± 0.05 eV toward higher binding energies in GaP-Se suggests a reduction of the band bending by the same amount, consistent with a partial passivation of the surface states.⁴³⁸ Inversely, in Fig. 3.40 (b), the growth of TaSe₂ at 250 °C and subsequent annealing result in a P 2p binding energy decrease of 0.55 ± 0.05 eV compared to the passivated substrate. Taking advantage of the fact TaSe₂ is metallic, the Fermi level edge is measured using XPS and gives $E_F = 0.03$ eV, indicating that this sample experiences a negligible photovoltage. The measured energy $E_{Ta\ 4f} - E_F = 22.84$ eV will therefore serve as a future reference. The position of the GaP valence band with respect to the Fermi level is then calculated from

$$\begin{aligned} E_v^{GaP} - E_F &= (E_{P\ 2p} - E_{Ta\ 4f}) - (E_{P\ 2p}^{GaP,ref} - E_v^{GaP,ref}) + (E_{Ta\ 4f} - E_F) \\ &= 106.58 - 128.08 + 22.84 = 1.34 \text{ eV} \end{aligned} \quad (3.3)$$

using the bare GaP sample discussed earlier as a reference for the $E_{P\ 2p}^{GaP} - E_v^{GaP}$ energy. This corresponds to a more pronounced band bending, indicating that TaSe₂ forms a Schottky contact on the n-type GaP substrate as expected from its high work function.

3.3.3.b Electrical measurements

Then, the electrical transport properties of the few-layers grow at 500 °C and below are examined to confirm the metallic behavior expected for the H phases. Table 3.15 presents some previously characterized layers that have also been grown on semi-insulating substrates and could be measured using the 4PP cryogenic set-up already employed for the 1T monolayers.

Sample #	Growth T. (°C)	Anneal. T. (°C)	Targeted th. (ML)	Se flux (Torr)	Measured th. (ML)	Characterizations
T19	250	650	6	4×10^{-6}	3.86	4PP, XPS
T21'	400	650	6	4×10^{-6}	5.43	4PP
T22'	500	650	6	4×10^{-6}	4.83	4PP

Table 3.15: Samples used for electrical characterizations. All these layers are grown on a semi-insulating GaP substrate.

Two configurations are envisaged for the 4PP measurements. The square configuration, shown in Fig. 3.41 (a) is used for samples having triangular shapes, because it enables the effects of the sample anisotropy and probe positioning to be mitigated by contact permutations. Still, the proximity of the sample borders is expected to induce an overestimation of the resistance. The correction factor is not known for triangular samples, but ranges between 0.5 and 1 for circular ones,³⁹⁰ which can be expressed as $F = 0.75 \pm 0.25$. For a sample having an elongated shape, the probes are disposed in line (Fig. 3.41 (b)) and the resistivity is calculated assuming a uniform distribution of the current over the sample width, estimated to 3.5 ± 0.1 mm, and over the distance between the inner probes, estimated at 1.4 ± 0.2 mm. The estimation of the thickness derived from the XPS measurements is used since it has been proved to be correct within the uncertainty of 1 ML using STEM. The results obtained for the different samples at 300 K, presented in Table 3.16, do not suggest a dependence of the electrical resistivity on the growth conditions. It is much lower than the value estimated on the 1T monolayer, and only slightly above the ones available in the literature for 2H crystals.^{105,439,440} Hence, these results are in accordance with the presence of the metallic H phases in the samples.

Sample #	Growth conditions	Intensity (mA)	Voltage (V)	Thickness (nm)	Geometry	Resistivity ($\mu\Omega.m$)
T19	250 °C ann. 650 °C	0.1	0.037	2.4 ± 0.6	Line	2.3 ± 1.0
T19	250 °C ann. 650 °C	1	0.179	2.4 ± 0.6	Square	3.0 ± 2.0
T21'	400 °C ann. 650 °C	1	0.091	3.4 ± 0.6	Square	2.1 ± 1.2
T22'	500 °C ann. 650 °C	1	0.149	3.1 ± 0.6	Square	3.1 ± 1.9

Table 3.16: Electrical resistivities at 300 K measured on TaSe₂ multilayers grown at different temperatures. In the square configuration, the voltage is the mean of four measurements corresponding to different contact permutations.

To confirm this, temperature dependence measurements are carried out on the three samples and presented in Fig. 3.41 (c). A linear behavior is obtained in all cases, with an increase of the resistance with temperature characteristic of a metallic material. However, the onset of the 2H phase CDW around 122 K^{105,439} would be expected to result in a resistivity drop. Its absence in every sample is therefore more consistent with the presence of the 3R phase, which exhibits a weaker CDW transition.^{100,110}

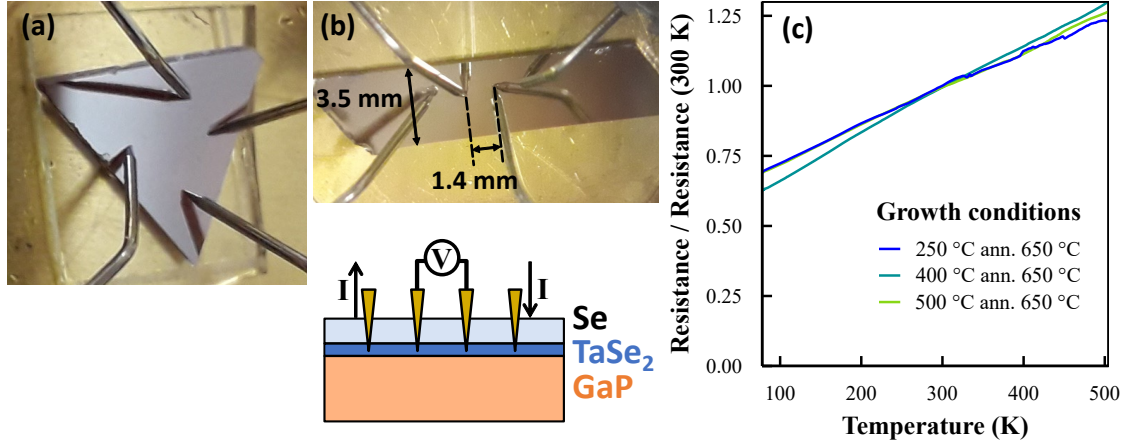


Figure 3.41: (a-b) Images of TaSe₂ on GaP samples contacted with probes arranged (a) in square and (b) in line. (c) Temperature dependence of the four-point probe resistance measured on 6 ML-thick TaSe₂ layers grown on GaP at 250 °C (sample T19), 400 °C (sample T21') and 500 °C (sample T22') and annealed at 650 °C.

Finally, the oxidation and its influence on the electrical resistance is studied. For this, the sample grown at 250 °C and annealed at 650 °C, is exposed to air after its measurement in vacuum. The sample was capped with Se during the transfer to the cryogenic setup, but this Se capping layer has been evaporated at 500 K under vacuum with the probes already connected. This enables the electrical resistance of the layer to be measured during the first minutes of oxidation in air. Its relative variation with time is presented in Fig. 3.42 (a). Before, the opening of the valve at time equal 0, the sample is measured under vacuum at regular intervals to ensure that the sample does not experience any degradation upon the injection of 0.1 mA. After air introduction, the electrical resistance increases by circa 0.1 %/hour. After 16 hours of measurements, one contact has been lost and has been rapidly fixed. The resistance does not significantly change during this intervention, suggesting a minor impact on the results, but degrades faster after that possibly due to a film of water being formed on the sample. Overall, the resistance increases by a factor of 2 in 3 days, which is not discouraging considering that the layer is only 4 ± 1 ML thick.

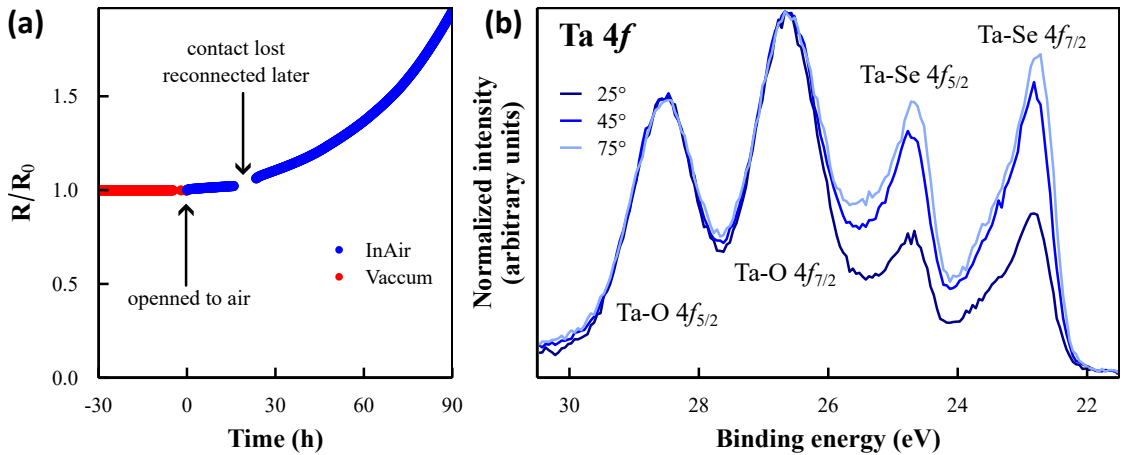


Figure 3.42: (a) Variation of the electrical resistance over the time in the TaSe₂ few-layers grown at 250 °C and annealed at 650 °C (sample T19). (b) Ta 4f CL measured on the same sample after 3 days of electrical characterization in air.

Right after the electrical measurement, the sample is transferred under vacuum for XPS characterization. The detection of the Ta 4*f* CL, presented in Fig. 3.42 (b), confirms the successful evaporation of the Se capping layer. The large doublets at high binding energy are consistent with the presence of Ta-O bonds, as expected from a substantial oxidation in air. The angle dependence shows that the oxide mostly lies near the surface, as would be expected in a layer-by-layer oxidation process. Therefore, the growth of thick TaSe₂ layers may be useful to make electrical contacts that are more stable in ambient conditions, as previously shown for exfoliated TaSe₂ flakes.⁴⁴¹

Summary

As hypothesized in monolayers, the 1T phase appears unstable in thick samples, and only a mixture of the 2H_a and 3R phases could be found in the complete layers. Similar to the monolayers, the TaSe₂ few-layers grown at low temperature on GaP exhibit a homogeneous coverage but a small grain size and poor rotational alignment. The crystallographic properties improve at intermediate temperatures, but a more degraded morphology attributed to the formation of Ga₂Se₃ is obtained, whereas the layers grown above 500 °C suffer from a lack of Se and lead to the formation of an interfacial TaP compound. Likewise, an improvement of the in-plane orientation is also achieved under a low Se flux at the cost of a slight Se-deficiency and degraded morphology. The use of a GaAs substrate does not influence the crystal quality, but favors the formation of the 1T phase probably because of a degraded morphology. Finally, the TaSe₂ layers grown on GaP between 250 and 500 °C and high Se flux exhibit a similar metallic behavior and a resistivity close to the bulk.

Conclusion

In the first section, the GaP and GaAs substrate preparation has been presented. The GaP surface can be passivated under Se, with most of the Se atoms on the top surface. However, the terraces exhibit serrated edges and every attempt to grow GaP buffer layers to avoid this has resulted in the formation of triangular pyramids. By contrast, smooth buffer layers have been successfully grown on GaAs but in this case, a well-controlled selenium flux is required to achieve the selenium passivation without incorporating a large amount of Se below the surface. Then, the growth of TaSe₂ single and few-layers on both substrates has been discussed in the second and third sections, respectively.

On GaP, the substrate temperature can be tuned to promote the growth of either the 1T, typically around 550–600 °C, or 1H-TaSe₂ monolayer for temperatures below 400 °C. However, the 1T phase being metastable, a small fraction tends to transform into the 1H one upon annealing or when the layer thickness approaches or exceeds the monolayer threshold. Though, a relatively uniform monolayer coverage of both 1H and 1T phase is achieved. The 1T-TaSe₂ monolayer is found to have a small residual misalignment with respect to the substrate, whereas it is slightly larger for the 1H one. A mirror twin could be identified in the 1T monolayer, but a photodiffraction study reveals that they must be very rare when the growth occurs at 600 °C while they can be formed at 250 °C. The growth of few-layers TaSe₂ confirms a thickness dependence in the phase stability, the 1T phase being only found on small islands on top of the few-layers, which follow various 3R or 2H_a stackings. It has also highlighted that a higher substrate temperature improves the crystallinity and in-plane orientation at the cost of a higher roughness, particularly at intermediate temperatures. In addition, above 500 °C the few-layers suffer from a Se-deficiency and an interdiffusion with the GaP substrate. Similarly, the use of a lower Se flux at low temperature improves the in-plane orientation but slightly degrades the morphology and the stoichiometry.

The epitaxy of both single and few-layers TaSe₂ on GaAs substrates results in a much rougher morphology, attributed to the easier formation of interfacial Ga₂Se₃, either during the growth or

annealing at intermediate temperature. The formation of small 3D islands tends to favor the 1T phase, even though the H phase remains dominant in the few-layers grown at low temperature.

Finally, the electrical characterization of the 1T monolayer grown on GaP demonstrates that it is a Mott insulator at room temperature with a band gap of 0.14 eV similar to the one measured in STS at 77 K. Conversely, the few-layers TaSe₂ exhibit a high work function and a metallic behavior with a measured resistivity only slightly above those reported for 2H-TaSe₂ crystals, suggesting potential applications in 2D-material contacts.

HfSe₂ growth and heterostructures

In this chapter, the growth of HfSe₂, a semiconducting TMDC, is studied. Given the degradation of the TaSe₂ morphology observed on GaAs substrates in Chapter 3, the growth is mostly performed on GaP, but the use of Si substrates is also considered. For this, a half-monolayer of GaSe is deposited first to passivate the Si dangling bonds prior to the HfSe₂ growth. Finally, TaSe₂/HfSe₂ heterostructures are investigated and first attempts of electrical characterizations are presented.

4.1 Growth of HfSe₂ on GaP(111) substrates

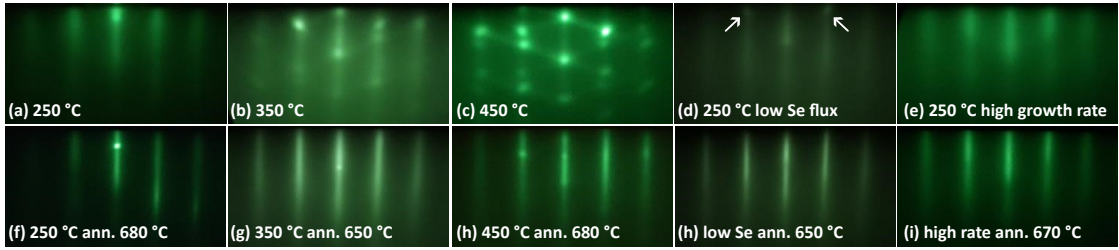
This first section focuses on HfSe₂ growth on Se-terminated GaP substrates. This material is only expected to form into the 1T phase, but the growth conditions are optimized to determine if the crystallinity, morphology and composition can be improved. The presented results complete the study initiated by Niels Chapuis,³⁹¹ pinpointing the importance of two parameters that had not been considered yet, namely the annealing temperature and the film thickness.

4.1.1 Influence of the growth conditions and annealing temperature

4.1.1.a Growth and morphology

Given the structural degradation observed in TaSe₂ elaborated at high temperatures, HfSe₂ layers are first grown at 250, 350 and 450 °C (samples H1-H3) using a high Se flux and a similar growth rate as in the previous chapter. The influence of the growth conditions at 250 °C are further studied through sample H4, in which the Se flux is decreased, and sample H5 for which a larger growth rate is used. A thickness of 4 ML is targeted for every sample, even though XPS characterization indicates a lower thickness based on the Hf/Ga ratio as reported in Table 4.1. As for TaSe₂ layers, the apparent thickness is larger on the sample grown at low temperature and increases after annealing, suggesting a better morphology or less Ga_xSe_y.

Sample #	Growth T. (°C)	Annealing T. (°C)	Se flux (Torr)	Growth rate (Å/s)	Measured th. (ML)	Characterizations
H1	250	-	5×10^{-6}	0.004	2.37	RHEED, XPS, UPS
H1'	250	680	5×10^{-6}	0.004	2.56	RHEED, XPS, UPS, XRD
H2	350	-	4×10^{-6}	0.006	1.72	RHEED, XPS, UPS
H2'	350	650	4×10^{-6}	0.006	2.27	RHEED, XPS, UPS XRD
H3	450	-	5×10^{-6}	0.004	1.7	RHEED, XPS, UPS
H3'	450	680	5×10^{-6}	0.004	2.06	RHEED, XPS, UPS XRD, STEM
H4	250	-	5×10^{-8}	0.005	2.42	RHEED, XPS, UPS
H4'	250	650	5×10^{-8}	0.005	2.76	RHEED, XPS, UPS, XRD
H5	250	-	5×10^{-6}	0.043	-	RHEED
H5'	250	670	5×10^{-6}	0.043	2.51	RHEED, XRD
H6	250	550	6×10^{-6}	0.006	2.36	XPS, UPS, XRD

Table 4.1: HfSe₂ layers grown on GaP substrates.Figure 4.1: (a-e) RHEED patterns of the HfSe₂ layers grown on GaP in various conditions (samples H1-H5). (f-i) Corresponding RHEED patterns after annealing at 650-680 °C.

The RHEED patterns in Fig. 4.1 (a-c) reveals a large influence of the growth temperature. At 250 °C, streaks are obtained but they appear slightly diffuse, although at a much lower extent than during TaSe₂ growth. At higher temperature, the transmission spots previously attributed to Ga₂Se₃ are observed. On the sample grown under a low Se flux, some tiny spots (pointed by arrows in Fig. 4.1 (d)) are also discernible, even though the RHEED pattern remains rather dim. Finally, no perceptible influence of the growth rate is noticed in Fig. 4.1 (e). As for TaSe₂, all RHEED patterns improve after annealing and finally exhibit thin streaks as shown in Fig. 4.1 (f-i) even if some dots remain visible on the one from the growth at 450 °C.

4.1.1.b Chemical and electronic properties

Fig. 4.2 (a) compares the Hf 4*f* and Ga 3*d* CLs of four of the layers grown in different conditions. The two Hf 4*f* peaks are distinguished at the low binding side and the Ga 3*d* CL, at the high binding energy side. The variation of the Ga 3*d* CL intensity is related to the different thickness of the samples, the spectra being normalized with respect to the Hf 4*f* one. If the Hf 4*f* CL position remains unchanged, a small difference in the peak width is noticed among the as-grown samples, especially at their base as pointed by the arrows. This is particularly visible in the low Se sample, for which the CL decomposition (Fig. 4.2 (c)) reveals a low binding energy compound, that could for instance be ascribed to metallic Hf-Hf bonds. Even though it suggests that a low Se flux is detrimental, a similar effect is observed at a lower extent on the sample grown at the same temperature under high Se flux. Since a Se-deficiency is unexpected in the latter, this shoulder is rather ascribed to a high defect density arising from the growth at low temperature than a lack of Se in the film. The Se 3*d* CL, presented in Fig. 4.2 (b) does not exhibit any meaningful difference between the samples. As for the TaSe₂ samples, the high binding energy tail is attributed to the Ga-Se component revealed by the CL decomposition in

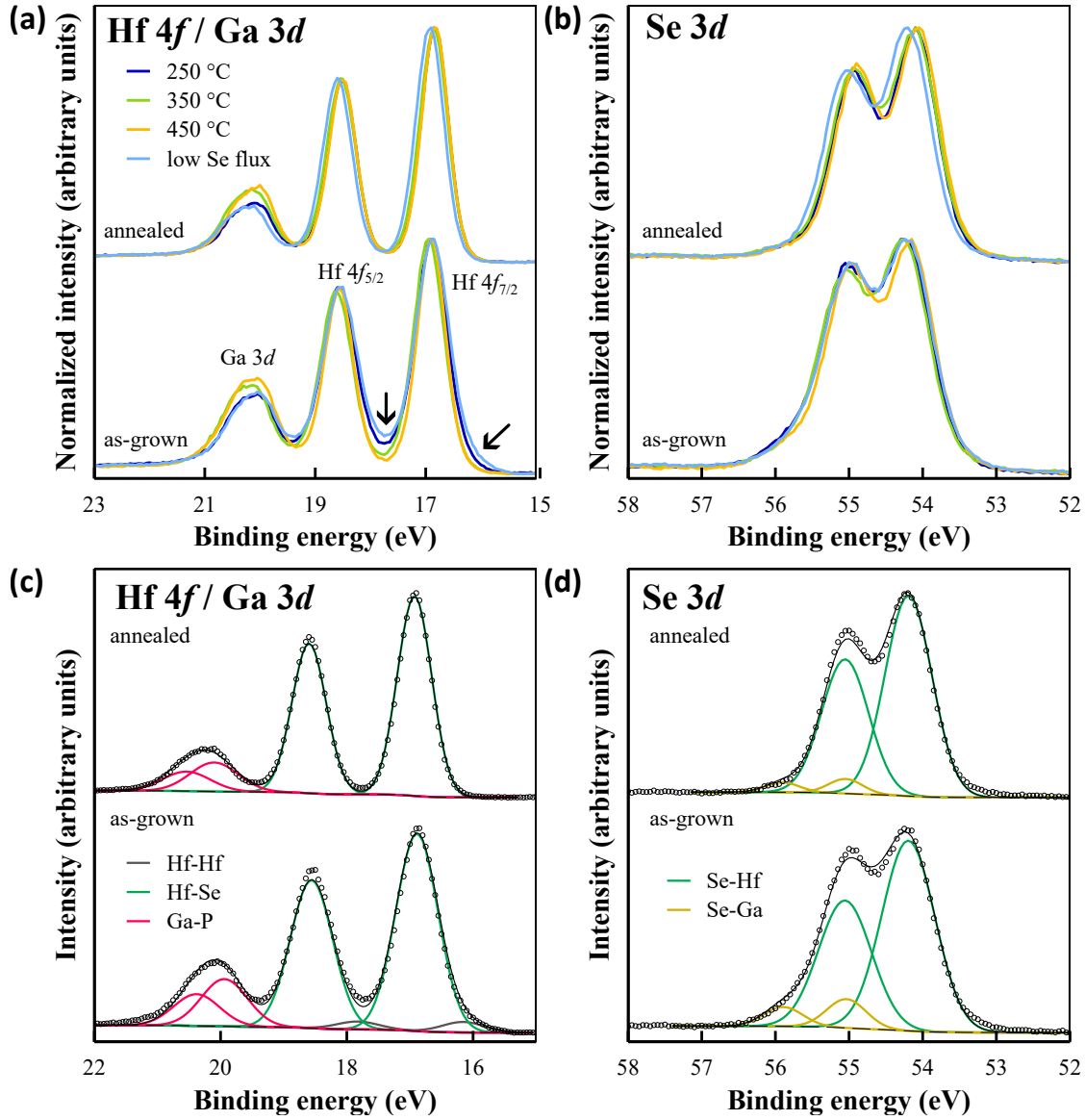


Figure 4.2: (a) Hf 4f and Ga 3d and (b) Se 3d CLs measured in XPS at 45° on HfSe₂ layers grown in different conditions (samples H1-H4), before and after annealing. (c) Hf 4f and Ga 3d and (d) Se 3d CLs decomposition of the spectra acquired on the sample grown at 250°C under low Se flux (sample H4), before and after annealing.

Fig. 4.2 (d). Therefore, only one component is attributed to HfSe₂ in accordance with a single phase expected in this material.

After annealing, all Hf 4f CLs become narrower and virtually identical, suggesting that the aforementioned defects are cured upon annealing under Se flux. In this case, they are rather well fitted by a single component as shown in Fig. 4.2 (c), while the component attributed to Se-Ga in the Se 3d CL decreases (Fig. 4.2 (d)) as previously observed in the TaSe₂ samples. A very similar result is obtained for sample H5' prepared with a higher growth rate (not shown).

The semiconducting property is confirmed using UPS measurements presented in Fig. 4.3 (a) around Γ , where the valence band is expected to reach its maximum.³⁰ As for TaSe₂, the spectra before annealing do not reveal sharp features at low growth temperatures, whereas a characteristic peak is observed at 2.8 eV for the one grown at 450 °C. It also appears on the other samples after annealing along with minor details, suggesting a better crystalline ordering. Overall, the valence band shapes are very similar among the samples, as expected for a unique phase.

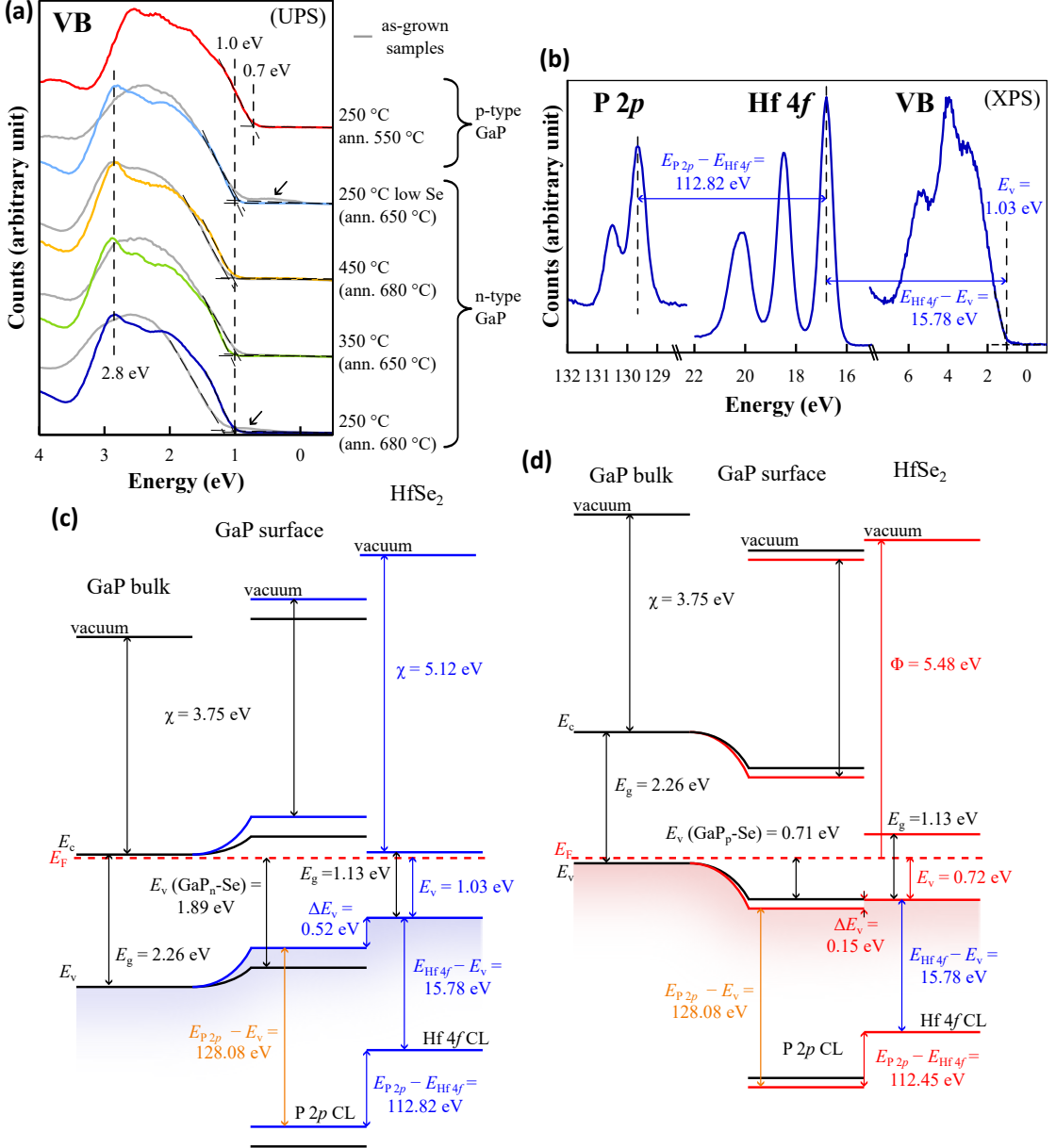


Figure 4.3: (a) Valence band measured around Γ using UPS on the HfSe₂ few-layers grown on n-type GaP in various conditions (sample H1-H4) or on p-type GaP at 250 °C and high Se flux (sample H6). (b) Energy separation between the P 2p CL, Hf 4f CL and valence band maximum in the HfSe₂ grown at 250 °C and high Se flux on n-type GaP (sample H1') measured in XPS at 75°. (c-d) Band alignment of the HfSe₂ grown at 250 °C and high Se flux on (c) a n-type (sample H1') and (d) a p-type GaP (sample H6). The valence and conduction bands at the surface of a Se-terminated GaP substrate of the corresponding doping type is represented in black as a reference.

The valence band edge is measured around 1.0 eV for the four samples grown on n-type substrates (samples H1-H4), except for the two samples grown at 250 °C which exhibit a small shoulder extending up to the Fermi level before annealing. This metallic component is attributed to the defects already suggested by Hf 4f CL measured on the same two samples. Since the shoulder vanishes after annealing, there is still no evidence that it could be detrimental to the annealed samples.

The sample H6, prepared in similar conditions as sample H1' except for a lower annealing temperature, has been grown on a p-type substrate instead. In this case, the valence band edge is found at 0.73 eV. Since the valence band edge position does not significantly vary upon annealing in samples H1 to H4, the 0.29 eV shift of the valence band compared to sample H1' is attributed to a different charge transfer depending on the substrate type. Overall, as a band gap of 1.13 eV is expected for this material,^{442,443} it shows that these layers are naturally n-type in accordance with earlier reports.^{84,88}

To investigate further the charge transfer, the band alignments with the GaP substrate are discussed through XPS measurements at 75° presented in Fig. 4.3 (b) for sample H1'. In agreement with UPS, the valence band maximum is measured at 1.03 eV in this case, which can be unambiguously attributed to HfSe₂ in spite of the larger probed depth since the valence band of the n-type GaP would be expected at higher binding energy. The measurement of the energy differences $E_{\text{Hf } 4f} - E_{\text{v}}^{\text{HfSe}_2} = 15.78$ eV and $E_{\text{P } 2p} - E_{\text{Hf } 4f} = 112.82$ eV enables the construction of the band diagram Fig. 4.3 (c) using the method of Kraut and Waldrop to determine the band offset as

$$E_{\text{v}}^{\text{GaP}} - E_{\text{v}}^{\text{HfSe}_2} = (E_{\text{P } 2p} - E_{\text{Hf } 4f}) - (E_{\text{P } 2p}^{\text{GaP,ref}} - E_{\text{v}}^{\text{GaP,ref}}) + (E_{\text{Hf } 4f} - E_{\text{v}}^{\text{HfSe}_2}) \quad (4.1)$$

where the value $E_{\text{P } 2p}^{\text{GaP,ref}} - E_{\text{v}}^{\text{GaP,ref}} = 128.08$ eV has been determined in Section 3.3.3.a. The band alignment for the p-type substrate can be deduced from the measurement of $E_{\text{P } 2p} - E_{\text{Hf } 4f}$ in Fig. 4.3 (d). The knowledge of the valence band maximum is no longer required as the energy $E_{\text{Hf } 4f} - E_{\text{v}}^{\text{HfSe}_2} = 15.78$ eV previously determined can be employed as a reference, which leads to a much smaller valence band offset on this sample. Although surprising, the influence of the substrate doping type on the band offset has already been reported in both WSe₂/GaP³³⁵ and WSe₂/GaAs⁴²⁰ heterojunctions, and attributed to a permanent electric dipole between the layer and the substrate. The vacuum level, deduced from the GaP electron affinity⁴⁴⁴ and UPS measurement of the HfSe₂ work function (shown later) gives an indication of the charge transfer depending on the substrate doping type: on p-type GaP (Fig. 4.3 (d)), the near work function match should not induce significant charge transfer whereas on n-type GaP (Fig. 4.3 (c)), a large electron transfer toward the HfSe₂ is expected, in accordance with the depletion of the GaP surface and the larger n-type doping in the HfSe₂ layer.

4.1.1.c Structure and crystallinity

The crystallinity is then studied using XRD through radial ($2\theta_{\chi-\varphi}$) scans. The HfSe₂(110) peak, shown in Fig. 4.4 (b), is very close to the GaP($2\bar{2}0$) peak, which may affect the fitting results. Therefore, the (100) peak, presented in Fig. 4.4 (a) is also considered in spite of a much weaker signal. In some spectra, an additional peak is revealed around 26.7°. It has already been observed in WSe₂ samples grown on both GaAs(111)B⁴²⁰ and GaP(111)B,³⁹¹ and attributed to a strained GaSe layer at the top of the substrate. Conversely, it has rarely been observed in the TaSe₂ ones (not shown) for which the vdW interface was not well preserved compared to the aforementioned studies. Hence, its absence in the samples grown at 450 °C or under a low Se flux may be related to a more degraded interface.

Focusing first on the five samples that have been annealed between 650 and 680 °C (samples H1-H5), the FWHM, plotted in Fig. 4.4 (d-e) ranges from 0.44 to 0.55° for the (100) peak and 0.63 to 0.70° for the (110) one, corresponding to a grain size of 15 ± 3 nm. This is comparable to the best TaSe₂ sample grown at 500 °C, but in the case of HfSe₂, no obvious dependence

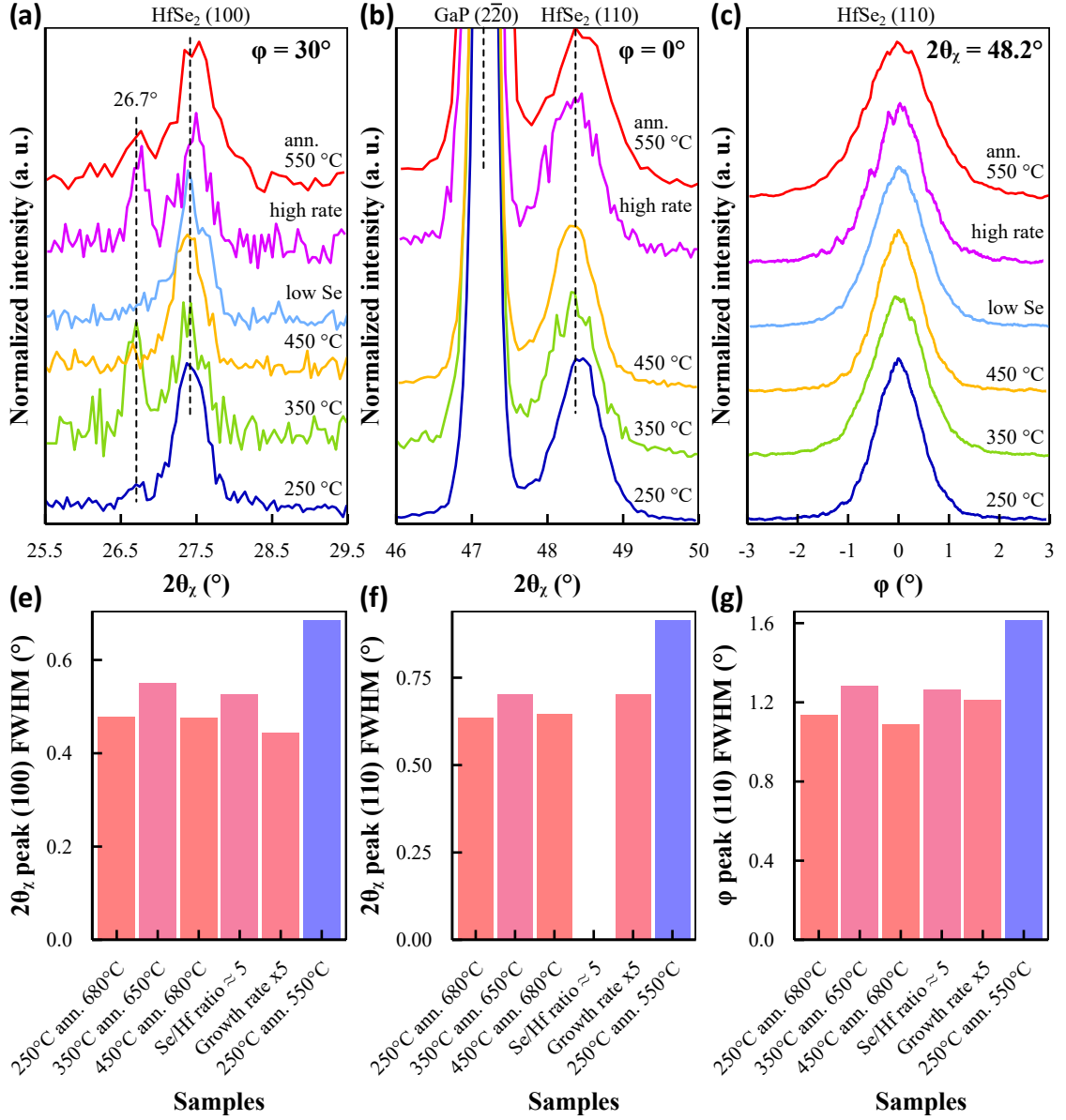


Figure 4.4: (a-c) Comparison of the in-plane grazing incidence XRD spectra recorded on the different HfSe₂ samples after annealing (H1'-H6'): (a) radial scan around the HfSe₂ (100) peak at $\varphi = 30^\circ$, (b) radial scan around the HfSe₂ (110) at $\varphi = 0^\circ$ and (c) azimuthal scan around the HfSe₂ (110) at $\theta_\chi = 48.5^\circ$. $\varphi = 0^\circ$ is defined as a GaP $\langle 1\bar{1}0 \rangle$ direction. (e-g) FWHM of the HfSe₂ peaks in the plots above.

on the growth temperature is evidenced, as well as on the Se flux and growth rate. The in-plane alignment, studied through the measurement of the HfSe₂ (110) peaks in azimuthal (φ) scans in Fig. 4.4 (c), also shows little evolution with respect to the growth parameters. In this case, the FWHM varies between 1.08 to 1.28° for the five samples, which is also comparable to the TaSe₂ film grown at 500 °C, but way better than the one grown at 250 °C (Fig. 3.31). Interestingly, the sample grown at intermediate temperature exhibits the worst properties, with both the largest misorientation and the lowest grain size, followed by the one grown using the low Se flux. However, it also corresponds to the samples annealed at 650 °C while the best ones

were annealed at 680 °C. This dependence on the annealing temperature is confirmed by the last sample grown at 250 °C and annealed at 550 °C (sample H6), for which both the grain size and in-plane orientation are largely degraded. Finally, the small influence of any growth parameter on the crystallographic properties of HfSe₂ layers is explained by the crystallization during the post-growth annealing, highlighting the importance of the latter.

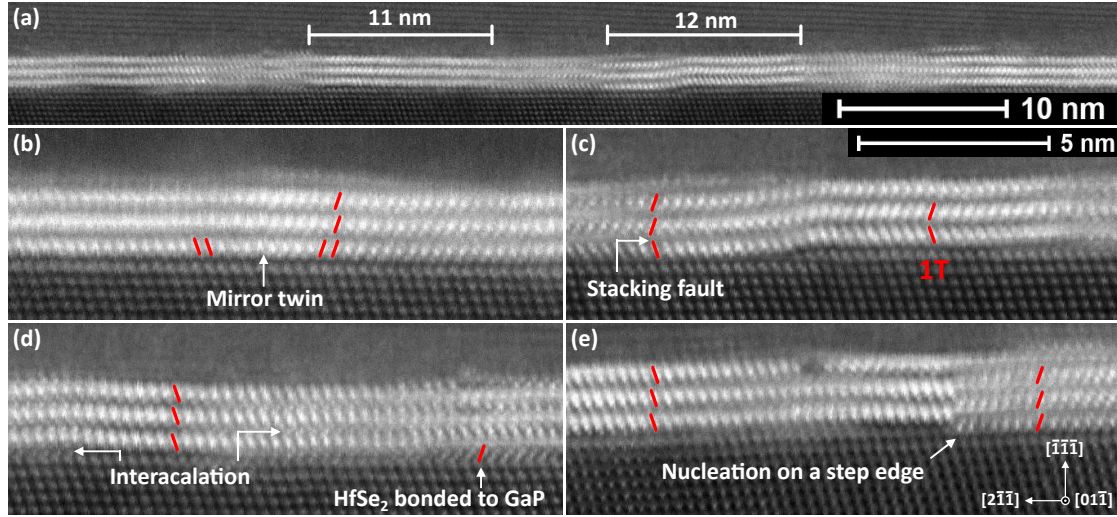


Figure 4.5: HAADF-STEM image of the HfSe₂ grown at 450 °C and annealed at 680 °C (sample H3'). (a) Large-scale image. (b-e) Focus on typical defects.

Nevertheless, the idea that the growth conditions do not matter may be qualified by the STEM characterization of the sample grown at 450 °C presented hereafter. The large-scale image in Fig. 4.5 (a) reveals that the film is 3 ML-thick, in accordance with the XPS estimation, with a good thickness homogeneity and a low roughness in spite of the 3D RHEED pattern during the growth. Some 12 ± 5 nm-large coherent domains are observed, in accordance to the preceding grain size estimation using XRD, separated by blurry areas attributed to grain boundaries. Still, looking closely to the layers, various defects are observed that are not always spotted at lower magnification. For instance, a grain boundary is shown in Fig. 4.5 (b) and a stacking fault is unveiled in Fig. 4.5 (c), the 1T layers being expected to stack on each other without 180° rotations. In Fig. 4.5 (d), intercalated atoms are observed in the vdW gap, while on the left side, the 1T-HfSe₂ even seems to share a Se atom with the Se-termination of the GaP substrate.

The latter defects may be related to atomic steps of the substrate, as in Fig. 4.5 (e), in which the nucleation of a monolayer sheet on a step edge causes a discontinuity over the whole stack. However, they also resemble those previously observed on the 1.4 ML-thick TaSe₂ sample grown at 600 °C (Fig. 3.15). It is known from TaSe₂ that layers grown at high temperatures generally exhibits higher roughness, even after annealing, which might therefore favor these kinds of defects. Even though the GaP/HfSe₂ interface appears overall less degraded than the GaP/TaSe₂ one formed at similar temperature, which is consistent with the absence of meaningful HfP compound (not shown), the absence of the GaSe peak in the HfSe₂ sample grown at 450 °C suggests that it could be further improved. Finally, although most of the properties of the HfSe₂ layers seem largely independent of the growth conditions, a low temperature and high Se flux will be preferred for the following investigations.

4.1.2 Effect of thickness

4.1.2.a Growth of thicker HfSe₂ films

The preceding analysis of the growth conditions established that a higher growth rate does not necessarily degrade the properties of the HfSe₂ layers, contrary to the general assumption in 2D material growth. Taking advantage of this, much thicker layers have been grown in approximately 1 hour using similar growth conditions to sample H5. Such thickness cannot be estimated using XPS, hence the number of layers observed in STEM images is reported instead in Table 4.2. The obtained thickness is about 60 % of the targeted one, confirming the discrepancy observed for thinner layers, but remains about 5 times larger than the latter.

Sample #	Growth T. (°C)	Annealing T. (°C)	Se flux (Torr)	Growth rate (Å/s)	Targeted th. (ML)	Measured th. (ML)	Characterizations
H7	250	650	5×10^{-6}	0.045	28	16	RHEED, XRD, STEM, UPS, XPS
H8	250	650	5×10^{-6}	0.050	30	-	Raman

Table 4.2: Thick HfSe₂ layers grown on GaP substrates.

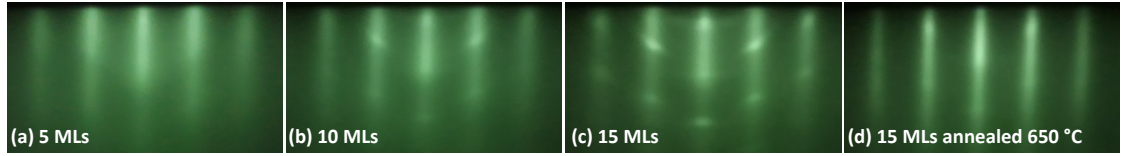


Figure 4.6: (a-d) Evolution of the RHEED pattern as function of the deposited thickness and after annealing (sample H7).

The RHEED patterns observed at different stages of the growth are presented in Fig. 4.6 (a-d). The RHEED pattern (a) is rather diffuse, in agreement with the previous sample grown in similar conditions. Then, diffraction spots appear between 5 and 10 MLs as shown in RHEED (b) and rings characteristic of polycrystalline materials become visible after the growth of 15 MLs in (c). The latter is different to the previous FCC diffraction pattern in Fig. 4.1 (c) and resemble rather the one observed for a 20-ML thick HfSe₂ layer grown on HOPG.²⁴⁶ The post-growth annealing at 650 °C removes the rings and most of the spots although some of the latter remain discernible in picture (d). Hence, the RHEED analysis suggests a progressive degradation of the layer morphology with thickness.

4.1.2.b Composition profile

The thickness of this layer enables a more precise analysis of its composition using both XPS and EDX. The atomic composition is plotted as function of the depth of analysis in Fig. 4.7 (a). The XPS is overall a more surface sensitive technique. Although the probed depth is augmented by increasing the electron take-off angle, it still mostly probes the upper layers. By contrast, the EDX enables the composition profile to be drawn by integrating the signal over the different areas presented in Fig. 4.7 (b). In addition, the two techniques are not affected the same way by the morphology: the XPS probes all the surface, including inside eventual holes or protruding islands, whereas the EDX reveals only the atoms at a given position. However, the lamella preparation using focused ion beam (FIB) can modify the composition through the implantation of Ga ions, preferential sputtering of certain atoms and redeposition of the etched species.

Different amounts of Hf and Se are obtained with the two techniques. If the XPS indicates that the layer is Se-rich, with a Se/Hf ratio around 2.30 ± 0.45 considering 10 % of uncertainty on each sensitivity factor, the EDX suggests rather the opposite with a ratio of 1.85 ± 0.30 .

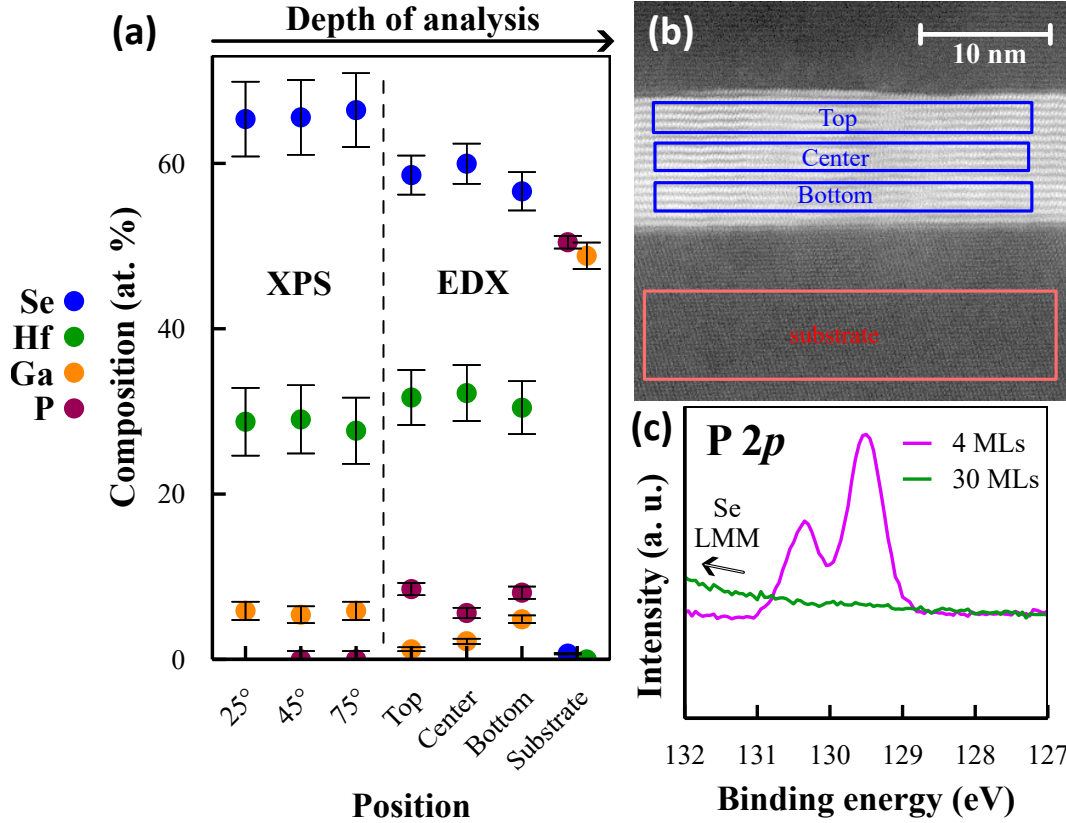


Figure 4.7: (a) Composition of the thick HfSe₂ samples measured using XPS at different take-off angles or EDX over different regions of the thick HfSe₂ layers (sample H7). (b) HAADF-STEM image showing the positions in which the EDX analysis have been performed. (c) P 2p CL measured using XPS at 75° on the thin and thick HfSe₂ layers prepared in similar conditions (samples H5' and H7). The spectra have been normalized with respect to the background.

In addition, Ga and P atoms are detected as main impurities. The EDX analysis indicates about 8 % of phosphorus while no trace is found in XPS as shown in Fig. 4.7 (c). The detection limit, estimated around 1 % for this element in a Hf and Se matrix,⁴⁴⁵ is not sufficient to explain this discrepancy. The presence of P atoms in the HfSe₂ layers is not expected from the lack of Hf-P evidence in the corresponding 3 ML sample (Fig. 4.7 (c)) and may be an artifact from the STEM lamella preparation using FIB, but it could also arise with the greater thickness as seen in TaSe₂. However, in this latter case, it would probably be scarcer at the surface for the same reason the TaP was found mostly near the substrate in TaSe₂, explaining its absence in XPS.

Gallium is detected using both techniques, suggesting that it is indeed present in the layer. The high concentration observed in XPS is however not consistent with the progressive decrease of this concentration in EDX from the substrate to the surface. A possible explanation would be that most Ga atoms are in Ga_xSe_y clusters rather than diluted into the HfSe₂ layers. Therefore, the local composition determined by EDX may significantly differs from the average one revealed using XPS thanks to its much larger analyzed area. Finally, the Se/Hf ratio is consistent with the detected impurities as the P atoms are expected to replace Se atoms, in accordance with the Se/Hf ratio lower than 2 in EDX, whereas the Ga bonded to Se ones can explain the Se/Hf ratio above 2 in XPS.

4.1.2.c Improvement of crystallinity and reduction of strain

To get further insights on the influence of the thickness, this sample is characterized using XRD and compared to the thin layer prepared in similar conditions (sample H5'). The diffraction pattern reveals the same peaks on both samples, and focusing on the HfSe₂ (100) and (110) ones presented in Fig. 4.8 (a) and (b), a smaller peak width is noticed for the thicker sample. Indeed, the FWHM of 0.41 and 0.52°, measured for the HfSe₂ (100) and (110) peaks respectively, leads to a grain size estimation of 18 ± 2 nm, which is the best result obtained in this work. The additional peak around 26.7° also appears in the thick HfSe₂ sample, but its relative intensity is much smaller, suggesting that it does not scale up with thickness. It is hence consistent with its attribution to a GaSe layer on top of the GaP substrate.

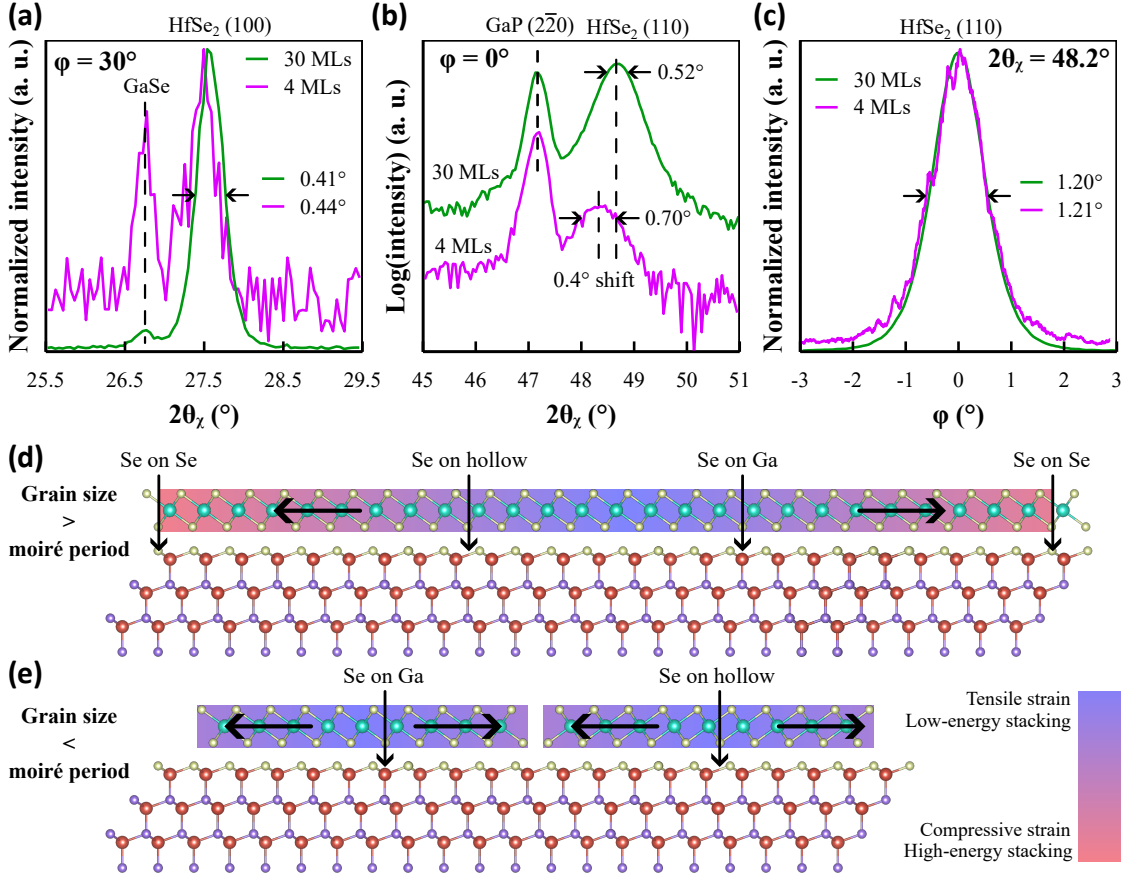


Figure 4.8: (a-c) Comparison of the in-plane grazing incidence XRD spectra recorded on the 3 and 15 ML HfSe₂ samples prepared under similar conditions (samples H5' and H7): (a) radial scan around the HfSe₂ (100) peak at $\varphi = 30^\circ$, (b) radial scan around the HfSe₂ (110) at $\varphi = 0^\circ$ and (c) azimuthal scan around the HfSe₂ (110) at $\theta_\chi = 48.5^\circ$. $\varphi = 0^\circ$ is defined as a GaP $\langle 1\bar{1}0 \rangle$ direction. (d,e) Proposed model to explain the partial strain relaxation in thin HfSe₂ layers. The "Se on Se" configuration is thought to be highest energy one because of the steric repulsion of Se atoms whereas the "Se on hollow" could be more favorable since it follows the same stacking sequence than in the bulk 1T phase (ABC stacking). Tensile strain is expected around the low-energy configurations because it maintains the favorable stacking over a larger area, and conversely, compressive strain is expected to shrink the high energies areas.

The evolution of the in-plane alignment is then shown through the measurement of the (110) peaks over the azimuths in Figure 4.8 (c). The thicker film exhibits a FWHM of 1.20° perfectly matching the thinner one, demonstrating that the misorientation is not degraded with thickness. This suggests that once the first HfSe₂ monolayer is grown on GaP, the following HfSe₂ layers

align very well on its own lattice. It seems compatible with the improvement of grain size, even though it does not explain it.

Surprisingly, a shift is observed between the thin and the thick layers in Fig. 4.8 (a) and (b), which corresponds to a decrease of the lattice parameter from 3.78 to 3.75 Å. The latter, obtained on the thick layer, corresponds much better to the reported values for HfSe₂,^{442,446} whereas every thinner layer (including those presented in Fig. 4.4) is subject to approximately 1 % of tensile strain. This effect is attributed to the influence of the GaP substrate and contrasts with the general assumption that 2D layers grow with their own lattice in vdW epitaxy. Even weak, the interlayer interactions can still induce strain in 2D systems, as for instance in moiré patterns in which both tensile and compressive strain are observed.⁴⁴⁷ Uniform strain has been reported in both vdW⁴⁴⁸ and in quasi-vdW epitaxy³⁰² when a nearly commensurate lattice matching condition exists. The small lattice mismatch between GaP and HfSe₂ and the relatively good in-plane alignment could favor an exact unit-cell coincidence, but here the strained HfSe₂ lattice remains smaller than the in-plane GaP lattice constant of 3.85 Å. Hence, low-energy stacking configurations would alternate with higher energy ones as the atom positions progressively shift in moiré-like situation sketched in Fig. 4.8 (d), in which no energy gain would be expected over an infinite layer under uniform strain. However, since the grain size (≈ 15 nm for thin layers) is of the same order of magnitude that this hypothetical moiré (13 nm for unstrained HfSe₂), favorable configurations can be extended over most of the grain by increasing the moiré size with a limited tensile strain (moiré size ≈ 21 nm for the partially strained thin layers) as illustrated in Fig. 4.8 (e). In other words, the observed mean tensile strain comes from an interplay between the local atomic arrangements and the grain size. In the thicker layer, the HfSe₂ recovers its bulk lattice parameter in accordance to the influence of the substrate being largely overcome by the elastic energy cost of strain. However, contrary to the 3D-material case, this does not seem to be released through more dislocations, as the grain size increases with thickness.

To explain this, the structure of the thick HfSe₂ film is revealed by the STEM image presented in Fig. 4.9 (a). In this case, the interface is sharper than in the previous 3-ML sample grown at 450 °C, with a clear vdW gap. This is more likely related to the lower growth temperature, rather than an effect of thickness, confirming the assumption that a low growth temperature is preferable.

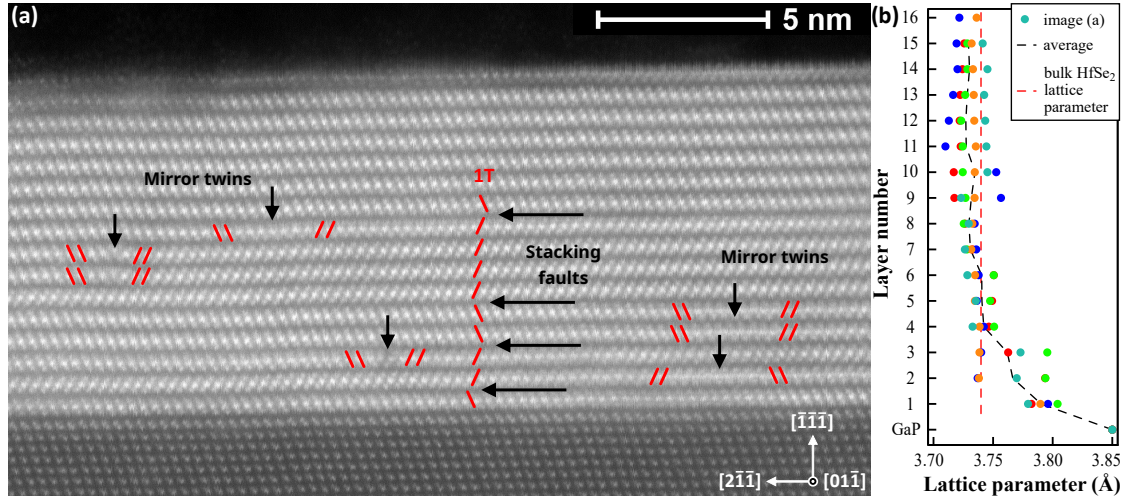


Figure 4.9: (a) HAADF-STEM image of the thick HfSe₂ sample (sample H7). (b) Lattice parameter measured in each layer of the stacking starting from the one closer to the GaP substrate (1) toward the surface (16) on 5 different STEM images. Each image was scaled considering in-plane lattice parameter of 3.85 Å in bulk GaP.

As for the thinner HfSe₂ film, the thick one only contains the 1T phase, in which the same kind of defects are observed, including stacking faults and mirror twins. Interestingly, both are more frequent near the substrate while the upper part of the film seems better ordered, with 6 consecutive unfaulted monolayers. This improvement with thickness might occur during the growth, the lateral size of the islands increasing progressively thanks to a larger adatom mobility on the already grown HfSe₂ layers. However, according to the RHEED observations, the crystallinity greatly improves during the annealing, hence it is instead proposed that the proximity of the substrate itself favors the formation of such defects in the bottom layers. This may be because the latter still have to accommodate the mismatch and eventual defects on the GaP surface, whereas the layers above are mostly strain-free as confirmed by the evolution of the lattice parameter as function of the position in the stack in Fig. 4.9 (b). In five analyzed images, the layer closer to the GaP substrate exhibits an expanded lattice parameter of 3.79 ± 0.02 Å which rapidly decreases toward the bulk lattice parameter in the following layers in accordance to the XRD analysis. This is possible because of the ability of the individual layers to slightly slide with respect to each other to release the strain, together with the fact that mirror twins do not necessarily propagate along the vertical direction and rather cancel each other with stacking faults. Thereby, the crystalline quality can improve with thickness, while also relaxing the strain. These are the well-known benefits of the vdW epitaxy, but it seems that in the HfSe₂/GaP system, the small lattice mismatch makes this happen progressively over few layers rather than abruptly at the interface. This is consistent with an earlier study in which the 2D-layers with lower lattice mismatch were found to relax slower.⁴⁴⁸

Finally, the good structural properties of the HfSe₂ layers are further confirmed using Raman spectroscopy. The spectra recorded on sample H7 for different acquisition times are compared to the signal from the bare GaP substrate in Fig. 4.10. All spectra are normalized with respect to the highest intensity peaks at 366 and 402 cm⁻¹ attributed to GaP.⁴⁴⁹

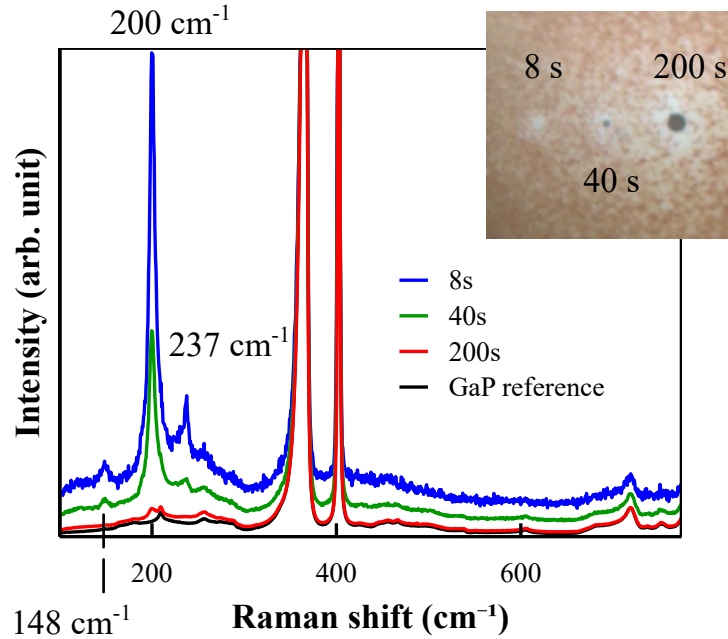


Figure 4.10: Raman spectra acquired using different integration time (sample H8) and compared to a bare GaP substrate of the same doping type. The spectra are normalized with respect to the substrate signal.

The intense peak at 200 cm⁻¹ and the small one at 148 cm⁻¹, clearly observed for the shorter acquisition time, are in good agreement with the literature on HfSe₂.²⁴⁶ The peak at 237 cm⁻¹ more likely corresponds to crystalline Se⁴⁵⁰ even if a small HfSe₂ peak has also been

reported at 228 or 235 cm⁻¹.^{246,451} The relative intensity of these peaks decreases rapidly when the acquisition time is increased, suggesting a degradation of the layers. This also corresponds to a more visible impact observed after the experiment using an optical microscope as shown in the inset. It is believed that the Se capping layer crystallizes very quickly because of the local heating induced by the laser beam, and progressively evaporates afterward, as suggested by the peak at 237 cm⁻¹. The degradation of the HfSe₂ layer can then be explained by its rapid oxidation in air.

No Raman signal has been obtained in thinner HfSe₂ layers, as for any TaSe₂ layer (not shown). It is not clear if it is related to the lattice relaxation or the better crystalline quality of the thicker HfSe₂ sample. In this regard, the absence of signal in the thin samples would mean that the strain and defects suggested by the XRD and STEM studies disturb the vibrational modes in the layers closer to the substrate. However, it could also be due to the fact that the topmost layers degrade very quickly, and the presence of many layers enables the bottom ones to be preserved. In addition, the signal from the GaP substrate is more attenuated by the thicker HfSe₂ film, improving greatly the relative peak intensities in favor of the HfSe₂ ones.

4.1.2.d Impact on the valence band

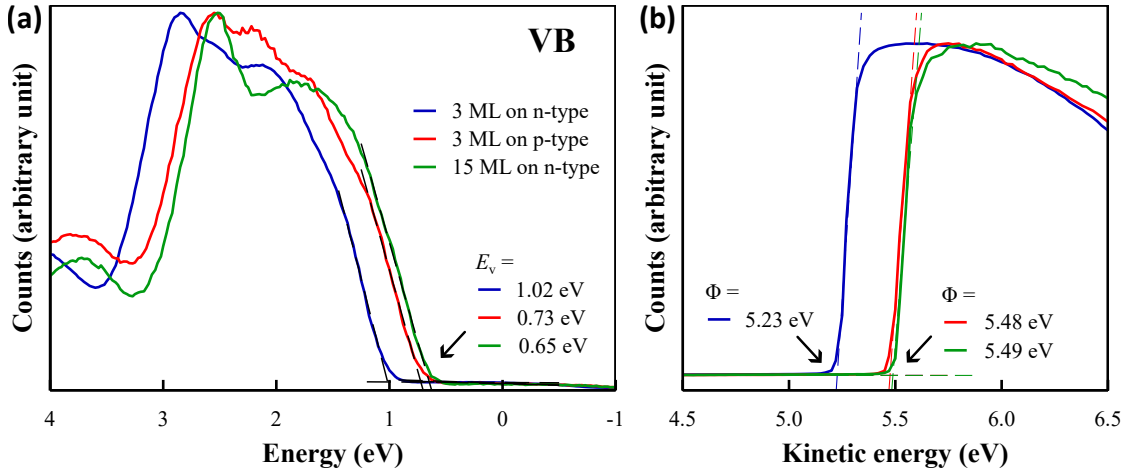


Figure 4.11: (a) Comparison of the valence band measured using UPS on the ≈ 3 ML-thick HfSe₂ layers grown at 250 °C and annealed at 680 °C on n-type GaP (sample H1') or at 550 °C on a p-type one (sample H6) and a ≈ 15 ML-thick HfSe₂ sample grown at 250 °C and annealed at 650 °C on n-type GaP (sample H7). (b) Corresponding photoemission cut-off measured in UPS ($h\nu = 21.2$ eV).

Finally, the influence of the thickness and the related film quality on the electronic properties is studied using UPS. The comparison of the valence bands in Fig. 4.11 (a) reveals a more pronounced peak at 2.5 eV on the thick layer. Overall, the whole band seems shifted toward lower binding energies and its maximum is found at 0.65 eV. This shift is not due to a reduction of the photovoltage or charge transfer from the n-type substrate in thicker layers, since it is even smaller than the valence band edge measured on the thin layer grown on the p-type substrate (sample H6) and for which these effects would be inverted. Hence, this reveals an intrinsic change of the HfSe₂ properties with the number of layers, such as a lower n-type doping or a band gap narrowing. This material is not expected to experience a significant band gap normalization with thickness compared to most of the TMDCs⁶² even though a decrease of 0.1 eV has been predicted.³⁰ However, the band gap has also been calculated to increase under tensile strain,^{452,453} signifying that the thin layers may have a larger bandgap which is reduced in the thick layers as the strain is released. Finally, the shift of the valence band edge probably arises from a combination of the aforementioned factors.

The low-energy electron cutoff presented in Fig. 4.11 (b) reveals the work function of the corresponding samples and enables the electron affinity χ to be deduced as

$$\chi = \Phi - E_g + E_v. \quad (4.2)$$

Considering the bulk band gap $E_g = 1.13$ eV,^{442,443} this gives a slightly larger electron affinity for the thin layers (5.12 and 5.08 eV for sample H1 and H6, respectively) compared to the thick layer (5.01 eV), which may be attributed to the hypothesized variation of the band gap, although an increase of the work function under tensile strain has also been predicted.⁴⁵⁴ Overall, these values are consistent with those reported by Aretouli *et al.*²⁴⁷ ($\Phi = 5.5$ eV and $\chi = 5.2$ eV) and in strong disagreement with the findings of Yue *et al.*²⁴⁶ ($\Phi = 4.4$ eV and $\chi = 4.0$ eV).

Summary

Even if the RHEED indicates a degraded morphology during the growth at high temperature, and the XPS and UPS characterizations suggest the presence of metallic defects in the layers grown at low temperature before annealing, no meaningful influence of the growth conditions is noticed afterward. Still, the high growth temperature and low flux Se are suspected to degrade the GaP-Se/HfSe₂ interface and therefore a low growth temperature and a high Se flux are preferred instead. The XRD analysis indeed demonstrates that the crystalline quality depends mostly on the annealing temperature, but also improves with thickness. In addition, some strain evidenced in the thin layers and attributed to the interaction with the GaP substrate is also relaxed with thickness. Besides, despite some Ga and P impurities are evidenced, the thick layer exhibits a Se/Hf ratio close to the ideal stoichiometry. Finally, in spite of a charge transfer depending on the substrate doping type, the position of the valence band maximum indicates that the layers are n-type overall. The shift of the valence band with thickness may, however, be rather attributed to a small variation of the band gap.

4.2 Use of GaSe-terminated Si(111) substrates

The crystallographic properties of HfSe₂ have been shown to be relatively independent of growth conditions, including the fact that it crystallizes only into one polytype. This makes it a good candidate to explore new substrates, among which Si is particularly appealing to favor the development of TMDCs at large-scale. Two strategies have been employed to prevent the formation of silicides, either chalcogen pre-wetting^{316,317} or the growth of a GaSe half-layer.³²⁹ This section focuses on the latter, which consists in the deposition of one atomic plane of Ga atoms bounded to Si and one atomic plane of Se atoms terminating the surface thanks to their lone pair of electrons. First, the GaSe growth is optimized to ensure a complete coverage and sufficient passivation, and then the growth of HfSe₂ is presented.

4.2.1 Growth of GaSe half-monolayer on Si(111)

The GaSe surface termination is prepared in the MBE chamber dedicated to selenide compounds, using the Ga effusion cell, the Se valve-cracker cell and in some cases atomic hydrogen. Here, the Si wafers preparation and GaSe growth conditions are investigated first, and then, the surface passivation and the rotational alignment of the GaSe layer are discussed.

4.2.1.a Optimization of the GaSe preparation

Si substrate preparation

The Si wafers are cleaned under an O₂ plasma, deoxidized in a 1 % HF solution, rinsed in deionized water and blown dry with nitrogen before introduction in the MBE system. The remaining oxide is desorbed upon heating to 750 °C under UHV in the MBE chamber with or without atomic hydrogen supply from 100 °C to 500 °C. In both cases, a 7×7 surface reconstruction appears around 700 °C, in accordance with earlier studies.³⁷⁸ It is well defined at 750 °C, as shown in Fig. 4.12 (a), indicating that the wafers are successfully cleaned and deoxidized.

Sample #	Substrate	Deoxidation T. (°C)	Atomic hydrogen	Characterizations
S1	Si	750	no	RHEED, AFM
S2	Si	750	up to 500 °C	AFM

Table 4.3: Deoxidized Si substrates discussed in this paragraph.

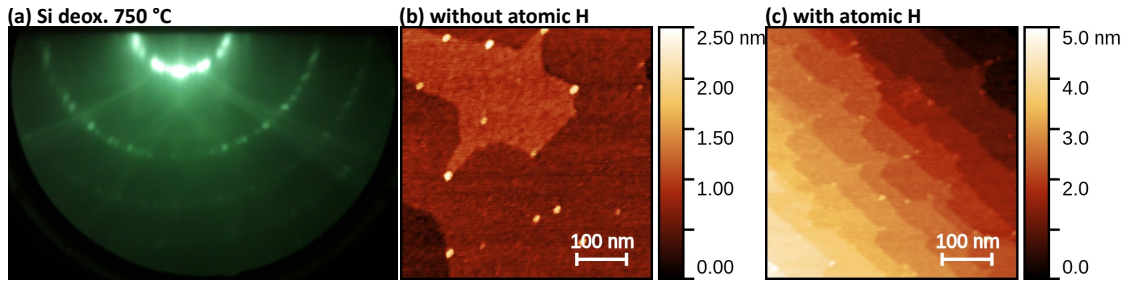


Figure 4.12: (a) 7×7 RHEED pattern of a Si substrate deoxidized at 750 °C without atomic H (sample S1). (b-c) $500 \times 500 \text{ nm}^2$ AFM images of Si substrates deoxidized under UHV at 750 °C (b) without and (c) with atomic H.

The AFM images of two samples prepared without or with atomic hydrogen supply are compared in Fig. 4.12 (b) and (c) respectively. Some dots, corresponding to 1-2 nm-high and 5-15 nm wide islands, are clearly observed on image (b) but can also be discerned on image (c). Since XPS (not shown) does not reveal any remaining trace of oxygen or carbon contamination, their origin is not clear but they do not seem to be efficiently removed using atomic hydrogen. Regarding the difference of morphology, the larger density of steps observed on sample S2 is attributed to a larger wafer miscut, the substrates being provided by a different supplier.

Self-limiting GaSe growth methods

GaSe half-layers have previously been prepared by selenization of a predeposited Ga ML.⁴⁵⁵ Later, Ohtake *et al.* argued that it was preferable to supply simultaneously Ga and Se.³²⁹ However, a careful control of the Ga flux was required to achieve the exact coverage at 520 °C. A self-limiting preparation method would be preferred. Two options are considered to achieve this taking advantage of the evaporation of the Ga_xSe_y components observed on III-V substrates in the previous chapter. In the first case (sample S3), a thick GaSe film is grown during 5 minutes at 500 °C, leading to the spotty RHEED pattern in Fig. 4.13 (a) attributed to the presence of FCC Ga_2Se_3 , and afterward the excess layers are evaporated under Se flux at 700 °C until the bright 1×1 pattern shown in Fig. 4.13 (b) is obtained. For the other samples, the growth is held for 10 minutes at 650 °C, so that only GaSe nuclei covalently bounded to Si are stable, in which cases a similar 1×1 pattern is maintained throughout the growth (not shown). The sample S4 is rapidly cooled down under vacuum after this process whereas for the following ones, an additional 3 min annealing at 650 °C under Se is made to ensure that no excess gallium remains on the surface.

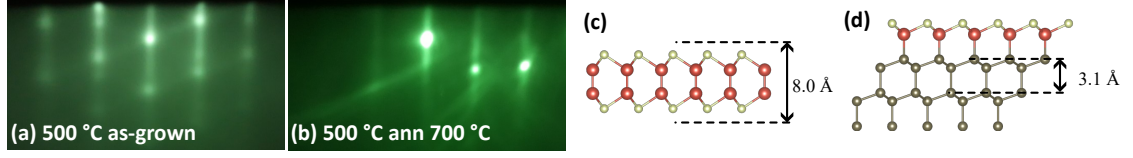


Figure 4.13: (a,b) RHEED pattern of sample S3 (a) after growth at 500 °C and (b) after annealing at 700 °C. (c,d) Expected atomic structures of (c) the GaSe monolayer and (d) the GaSe-terminated Si surface.

The thickness estimation from XPS, presented in Table 4.4, is expressed as a fraction of GaSe ML, which contains 2 rows of Ga atoms between 2 rows of Se atoms, for a total height of 7.97 Å including the vdW gap,⁴⁵⁶ as schematized in Fig. 4.13 (c). In spite of a much larger amount of deposited material, both methods lead to a GaSe thickness close to 0.5 ML, as expected for a half GaSe layer (Fig. 4.13 (d)). Still, the deposition at 500 °C followed by an annealing results in a lower thickness, as seen by the lower Se and Ga content in Fig. 4.14 (a). The reason why the Ga is in slight excess is not clear, but it may explain why a thickness slightly above 0.5 ML is obtained.

Sample #	Substrate	Deoxidation T. (°C)	Growth T. (°C)	Annealing T. (°C)	Measured th. (ML)	Characterizations
S3	Si	750	500	700	0.61	RHEED, XPS, AFM
S4	Si	700	650	-	0.7	XPS, AFM
S5	Si	750	650	650	-	AFM
S6	Si	830	650	650	-	AFM

Table 4.4: Samples compared to discuss the influence of the deoxidation temperature and GaSe growth temperature. All substrates are from supplier 1 and have been deoxidized without atomic H.

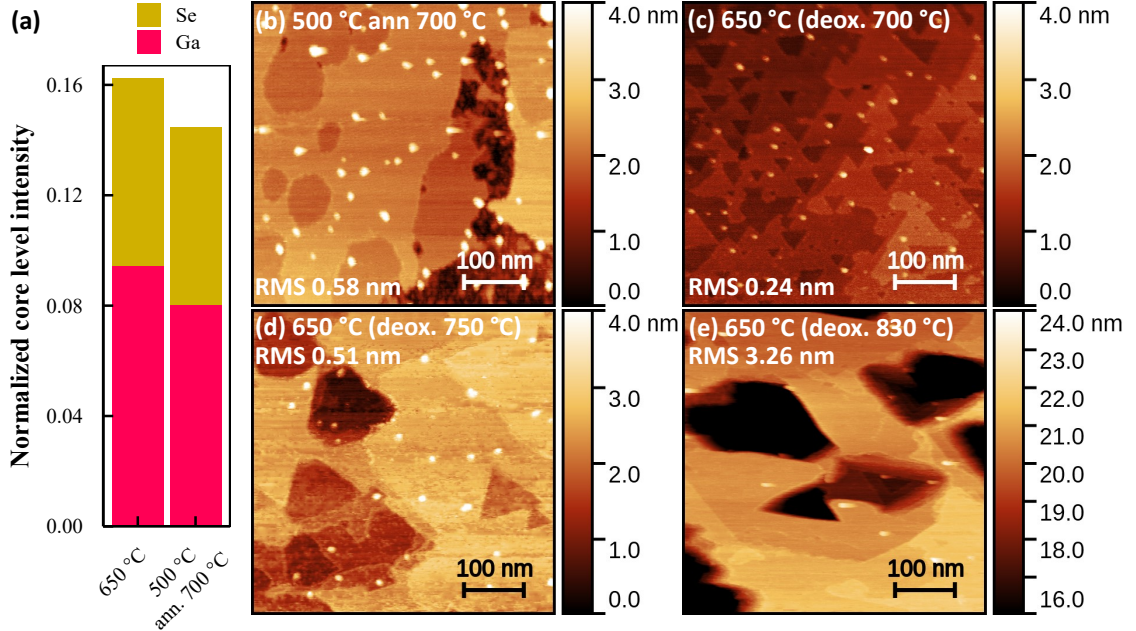


Figure 4.14: (a) Comparison of the Ga and Se content on the GaSe-terminated substrates prepared at 500 °C and annealed at 700 °C (sample S3), or at 650 °C (sample S4), according to the Se 3d and Ga 3d measured in XPS at 45°. (b-e) 500 × 500 nm² AFM images of the samples (b) grown at 500 °C and annealed at 700 °C (sample S3), or grown at 650 °C with Si surface deoxidation at either (c) 700 °C, (d) 750 °C or (e) 830 °C (samples S4, S5, and S6 respectively)

The AFM characterization of the sample prepared at 500 °C and annealed reveals large plateaus separated by cracks in which the surface is very rough, as seen at the bottom right of Fig. 4.14 (b). By contrast, the growth at 650 °C, presented in Fig. 4.14 (c), results in triangular terraces. Still, both surfaces are decorated by many small islands, similar to those observed on the deoxidized Si substrate. Apart from that, most of the atomic steps are much smaller than a full GaSe layer and better match the Si interplanar distance of 3.1 nm. Considering the estimation of a thickness near 0.5 ML, it is likely that the sample prepared at 650 °C is uniformly covered with the GaSe half-layer. Conversely the lower thickness measured on the one grown at 500 °C and annealed at 700 °C suggests that the GaSe half-layer is not complete in this case, which may be the explanation for the cracks. Therefore, the growth at 650 °C is preferred.

Besides, it is noted that the initial deoxidation temperature has an influence on the morphology of the GaSe-terminated samples, as the triangular features turn to wider and deeper pits as the annealing temperature is increased in Fig. 4.14 (d) and (e), but it has no effects on the small islands. The deoxidation temperature of 750 °C is kept for the following samples because the 7×7 RHEED pattern suggests a cleaner surface and the morphology is not significantly degraded.

Influence of the growth conditions

To further confirm that the growth is self-limiting, two samples have been grown under the same conditions for different durations (samples S7 and S8). The influence of the Se/Ga flux ratio is also investigated by decreasing the Ga flux to 0.06 Å/s and increasing the Se flux to 6×10^{-6} Torr in sample S9. The preparation details and the thickness estimated from the XPS characterization are given in Table. 4.5.

Sample #	Substrate	Growth T. (°C)	Duration (min)	Se/Ga at. ratio	Measured th. (ML)	Characterizations
S7	Si	650	10	≈ 4	0.66	XPS, AFM
S8	Si	650	1	≈ 4	0.68	XPS, AFM
S9	Si	650	10	≈ 30	0.65	XPS, AFM

Table 4.5: Samples compared to discuss the influence of the GaSe growth conditions. All Si substrates are from supplier 2. They have been deoxidized at 750 °C using atomic H up to 500 °C, and then annealed 3 minutes at 650 °C under Se flux after the growth.

The composition of the layers is shown in Fig. 4.15 (d). Not only the thickness, derived from the Ga/Si ratio, are similar among the three samples, but also the Ga/Se ratio is nearly constant even if the Ga remains in excess. Besides, the AFM images presented in Fig. 4.15 (a-c) reveal a very similar morphology for the three samples. The higher density of steps is attributed to the larger miscut of the Si substrates from supplier 2. Still, the steps appear more disordered compared to the deoxidized substrate presented in Fig. 4.12 (c), which may be related to the surface reorganization in triangular shapes. In addition, the small islands are observed on every sample, indicating that it does not depend on the growth duration or flux ratio.

The fact that the growth duration has no influence on the thickness, composition and morphology demonstrates that the growth is effectively self-limiting. Similarly, the flux ratio is not a determining parameter, and the fact Ga remains in excess in spite of a higher Se/Ga flux ratio in sample S9 suggests that it may be an artifact from incorrect sensitivity factors. Finally, the developed preparation method for half-monolayer GaSe growth proves to be robust against process variations. This may be explained by the fact the exact half-monolayer coverage is thermodynamically favored.

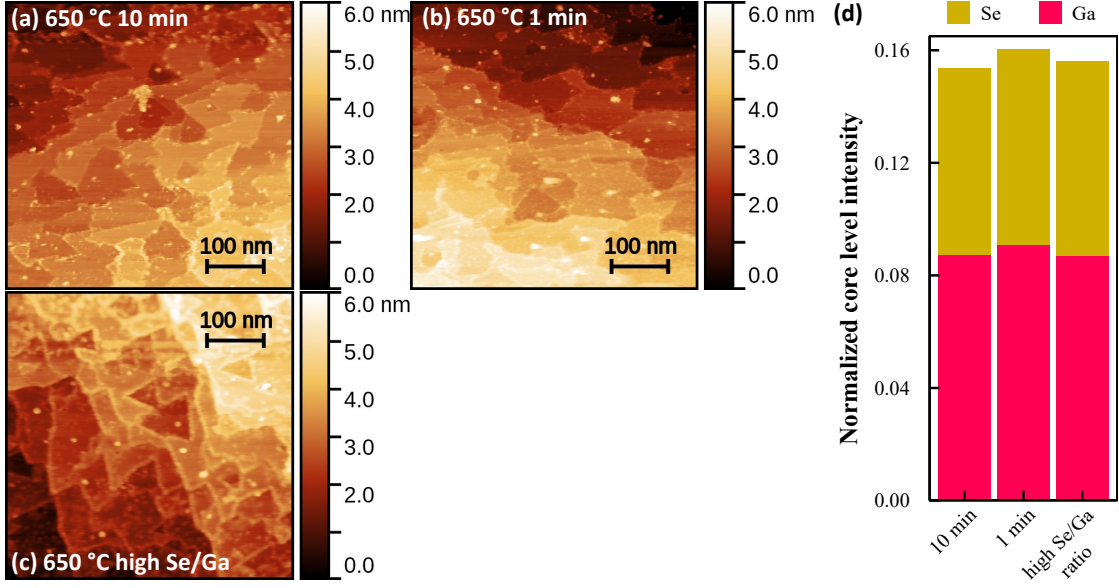


Figure 4.15: (a-c) $500 \times 500 \text{ nm}^2$ AFM images of GaSe-terminated Si substrates prepared at 650°C during (a) 10 minutes (sample S7) and (b) 1 minute (sample S8) using a Se/Ga ratio of ≈ 4 , and (c) during 10 minutes and using a Se/Ga ratio of ≈ 30 (sample S9). (d) Comparison of the Se and Ga atomic content on the three samples measured using XPS at 45° through the Ga $3d$, Se $3d$ and Si $2p$ CLs.

4.2.1.b Electronic and chemical passivation of the GaSe-terminated Si surface

To assert the ability of the GaSe half-monolayer to passivate Si substrates, some samples prepared in the previous paragraph and reported in Table 4.6 are further investigated using XPS.

Sample #	Type	Description	Supplier	Previous reference
S2	Si	Deoxidized 750°C with atomic H	Supplier 2	See Table 4.3
S3	Si-GaSe	Growth at 500°C and annealing at 700°C	Supplier 1	See Table 4.4
S4	Si-GaSe	Growth at 650°C	Supplier 1	See Table 4.4
S7	Si-GaSe	Growth at 650°C	Supplier 2	See Table 4.5
S10	Si	Deoxidized at 750°C with atomic H	Supplier 2	-

Table 4.6: Si and GaSe-terminated Si samples used to study the surface passivation.

The Si $2p$ CL measured on a Si surface exhibiting a clear 7×7 surface reconstruction after deoxidation at 750°C using atomic hydrogen (sample S2), and a GaSe-terminated one grown at 650°C (sample S7) are presented in Fig. 4.16 (a). The two substrates are n-type ones from the same supplier and were processed the same day.

Similar to the GaP and GaAs substrates, a clear energy shift of the Si $2p$ CL toward higher binding energy is observed, in accordance to a reduction of the band bending in the n-type Si substrate. Compared to previous reports, the measured Si $2p_{3/2}$ binding energy of 100.0 eV after GaSe growth is particularly high for the bulk Si component^{457,458} and indicates a Fermi level positioned near the conduction band on the surface. Hence close to flatband conditions are achieved for this n-type substrate in accordance to a good passivation of the surface states. Besides, a reasonable fit of the Si $2p$ CL acquired on the GaSe-terminated surface is achieved with a single doublet, whereas some features pointed by the arrows cannot be reproduced for the one corresponding to the bare substrate. A difference between the two CL shapes is indeed

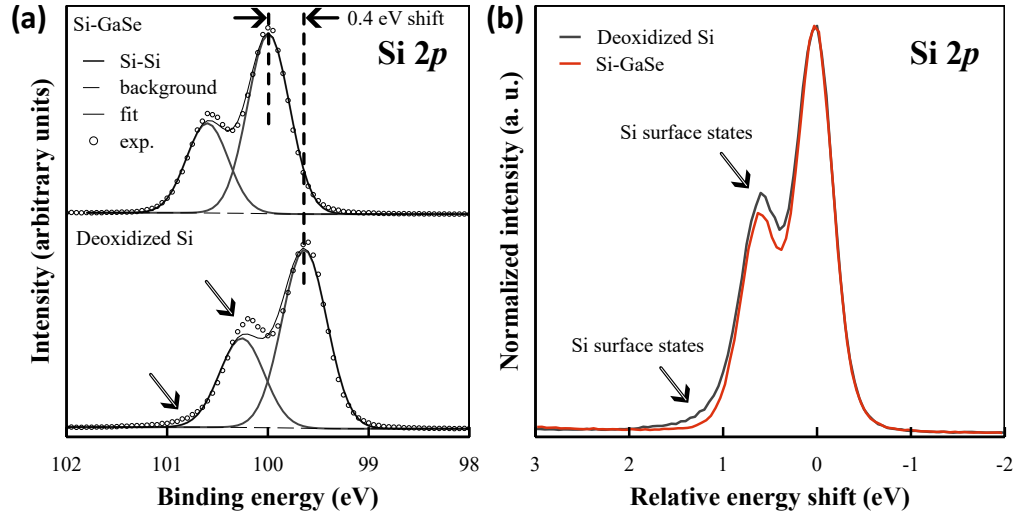


Figure 4.16: (a) Si 2p CL measured in XPS at 45° on a deoxidized Si substrate (sample S2) and a GaSe-terminated Si (sample S7), respectively, and their best fit using a single doublet. (b) Comparison of the Si 2p CLs in (a) after setting the Si 2p_{3/2} position as the energy reference.

revealed at high binding energy by their comparison in Fig. 4.17 (b), and attributed to surface states of the 7×7 -reconstructed surface for which numerous components have been reported.³⁴⁹ The absence of extra components in the GaSe-terminated surface supports the hypothesis of most of the surface states being passivated. The fact that no component arises from the Si-GaSe bonds in this case is attributed to the high electronegativity of Se atoms which compensates for the low electronegativity of the Ga ones, making the Si-GaSe bond non polar.⁴⁵⁸

To further confirm the good passivation of the GaSe-terminated Si substrates, their resistance to oxidation is studied. For this, the sample prepared at 650 °C (sample S4) is compared to a bare Si substrate that has been deoxidized using atomic H up to 700 °C and annealed up to 750 °C (sample S10). Then, the oxidation is measured thanks to the O 1s CL in the XPS survey presented in Fig. 4.17 (a).

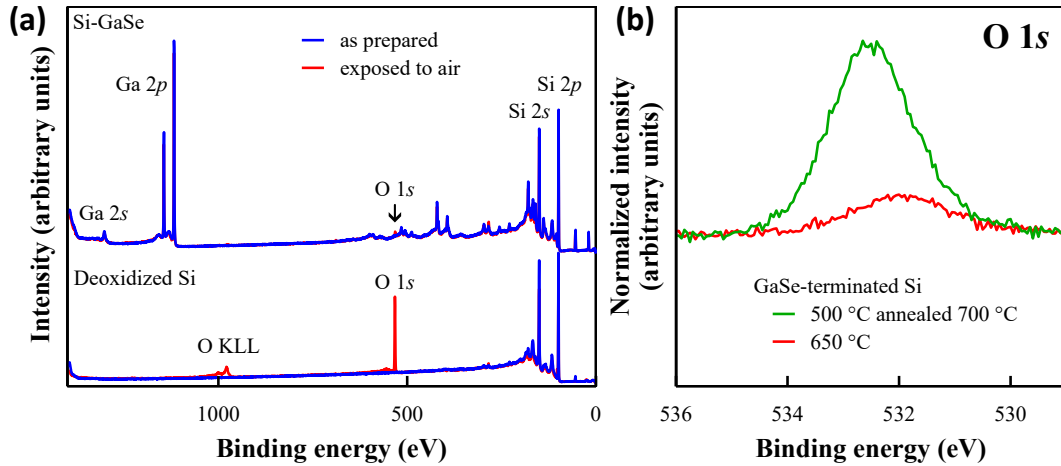


Figure 4.17: (a) XPS survey measured at 45° of a deoxidized Si substrate (sample S10) and a GaSe-terminated Si (sample S4) before and after exposure to air during 10 and 32 hours, respectively. (b) Comparison of the O 1s CL of a GaSe-terminated Si surface either grown at 500 °C and annealed at 700 °C (sample S3) or prepared at 650 °C (sample S4) after exposure to air during 32h. The spectra have been measured at 45° and normalized with respect to the background.

The difference in the initial deoxidation is not expected to play a role because neither of the two samples exhibited an O 1s CL as-prepared. The deoxidized Si substrate is measured after only 10 hours in ambient conditions but reveals a high O 1s CL peak, indicating a substantial oxidation as expected for Si. On the contrary, the sample covered by the GaSe half-layer, despite being exposed to air for 32 hours, exhibits a much lower O 1s signal. Hence, the GaSe-termination protects the Si substrate from the oxidation, in accordance to previous reports.³⁴¹ This is understood as a consequence of the lower density of surface states and surface energy.

Then, the oxidation of the GaSe-terminated surface prepared at 650 °C (sample S4) is compared to the one grown at 500 °C and annealed at 700 °C (sample S3) exposed to air for the same period. The O 1s CL, presented in Fig. 4.17 (b), is sensibly higher on sample S3, on which a thick GaSe layer was deposited and re-evaporated. This is in line with the hypothesis of an incomplete coverage of its surface by the GaSe termination suggested by the lower thickness derived from the XPS measurement and the observation of cracks using AFM in the previous paragraph. Conversely, the sample prepared at 650 °C exhibits a much lower O 1s CL, suggesting that most of the substrate is protected by the GaSe layer.

Finally, the reduced band bending, the suppression of surface states and the good resistance to oxidation not only demonstrate that an efficient electronic and chemical passivation is provided by the GaSe half-monolayer prepared at 650 °C, but it also proves that this surface termination covers most of the substrate.

4.2.1.c Absence of rotational domains

The GaSe half-layer consists of a Ga atom on top of the topmost Si atom, and a Se atom which is, in principle, oriented toward the same direction that the Si-Si bond in the zinc-blende structure. However, some authors also reported the presence of rotational twins, in which the Ga-Se bonds are oriented in the opposite direction.^{339,459} Since this would be detrimental to the growth of single oriented TMDC, the orientation of the GaSe half-layer on sample S9 is studied using the XPD method already employed in Section 3.2.2.b. In this case, the orientation of the Ga-Se bond is revealed through the variation of the Ga 3d intensity over the sample azimuth at a constant polar angle of 28.7°. This angle is chosen based on the corresponding angle in bulk GaSe, which is estimated between 28.2 ± 0.2 and $32 \pm 1.5^\circ$ depending on the polytypes and the studies.⁴⁶⁰ However, a smaller photodiffraction angle of 26° has been experimentally determined for GaSe on Si(111)³⁴³ and attributed to the proximity of the Si substrate, in which the corresponding angle is 19.5° .

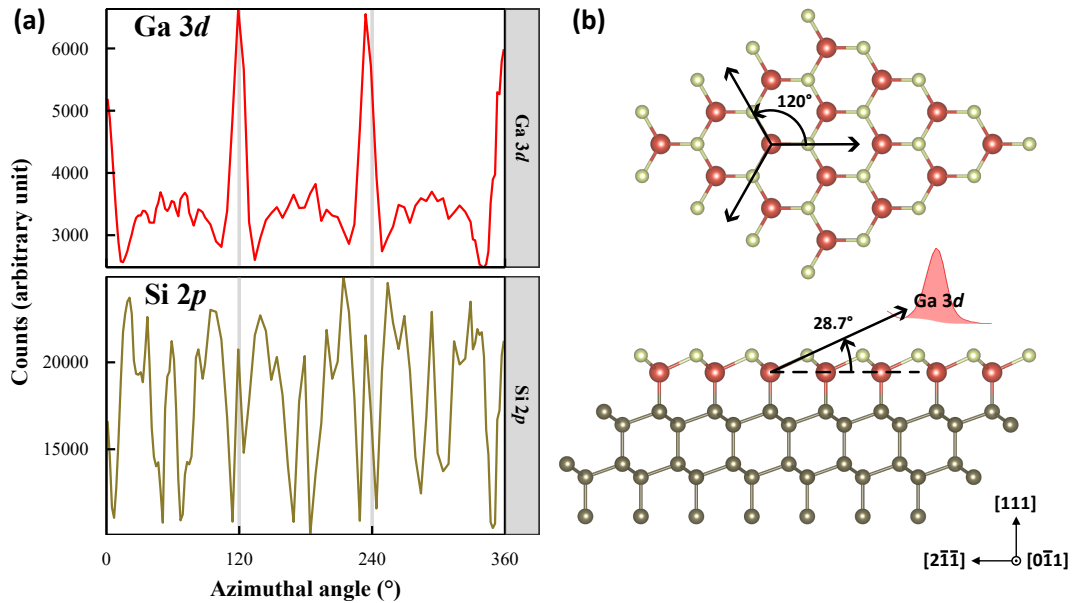


Figure 4.18: (a) XPD record measured at a constant polar angle of 28.7° on the GaSe-terminated Si sample prepared at 650 °C under high Se/Ga flux ratio (sample S9). (b) Schematics of the photodiffraction angles in the GaSe half-monolayer in top and side views.

The variation of the Si 2*p* recorded as a reference is presented at the bottom of Fig. 4.18 (b). The large number of scatterers makes its interpretation not straightforward, but the expected 3-fold symmetry is observed. Regarding the Ga 3*d* curve, only 3 prominent peaks are obtained along three equivalent high symmetry directions of the substrate. This is consistent with the presence of most Ga atoms in a single atomic plane, and rules out the possibility of a significant amount of mirror twins, which would result in peaks 60° apart.

These results contrast with the mirror twins observed in GaSe layers prepared at 450 °C,^{339,459} and are consistent with the single GaSe orientation reported for growth temperatures above 500 °C in another XPD study,³⁴³ or above 575 °C according to STM.³⁴²

Finally, the use of a substrate temperature of 650 °C not only enables a self-limiting GaSe half-layer growth, but also maintains the 3-fold symmetry of the Si (1 1 1) surface. This, together with the surface passivation, makes the GaSe-terminated Si substrate a good candidate for TMDC growth.

4.2.2 HfSe₂ growth on GaSe-terminated Si substrates

To confirm the potential usefulness of this substrate, the growth of HfSe₂ on GaSe-terminated Si is now investigated. In particular, it is necessary to ensure that the GaSe layer prevents the formation of a silicide, since HfSi_{*x*} compounds have negative enthalpies of formation.^{315,461}

4.2.2.a Thermal stability

For this first experiment, the Si-GaSe substrate is prepared using the same recipe as sample S4. Then, it is cooled under Se flux to the growth temperature of 250 °C, which is expected to better preserve the interface as seen on GaP, and 2 ML of HfSe₂ are deposited using a low growth rate and a high Se flux similar to that employed for sample H1 on GaP substrate.

Sample #	Substrate	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Measured th. (ML)	Characterizations
H9	Si-GaSe	250	-	2	1.21	RHEED, XPS
H9'	Si-GaSe	250	600	2	1.00	RHEED, XPS
H9''	Si-GaSe	250	680	2	0.48	RHEED, XPS

Table 4.7: Annealing steps for to the 2 ML sample grown on GaSe-terminated Si.

A very faint RHEED pattern is obtained after the growth at 250 °C as shown in Fig. 4.19 (a). Therefore, an annealing under Se flux is carried out since it has proven to be beneficial on GaP. The RHEED pattern progressively improves up to 550 °C, becoming slightly brighter as seen in Fig. 4.19 (b). However, a modulation of the streaks appears around 600 °C (Fig. 4.19 (c)) suggesting a surface roughening. Finally, upon further annealing at 680 °C, the RHEED pattern in Fig. 4.19 (d) reveals rings alongside spots. The former are characteristic of a randomly oriented polycrystalline material, while the latter corresponds to an untwinned FCC structure, which could be Ga₂Se₃ on Si.

To understand the cause of this degradation, the layer has been characterized using XPS at different stages of the process. Based on the Si and Hf CL intensities and considering a 0.5 ML-thick GaSe interlayer, a thickness of 1.2 ML is calculated as-grown, as reported in Table 4.7. Even if it is 40 % less than expected, this is not dissimilar to the growth on GaP. However, in this case, the thickness further decreases after annealing, in accordance with the degradation of the RHEED pattern. This is accompanied with a shrinkage of the Ga 3*d* CL compared to the Hf 4*f* one, as evidenced in Fig. 4.19 (e), which suggests an evaporation on the GaSe layer. Nevertheless, on the same plot, the Hf 4*f* CL is well fitted with a single component even once the Ga has vanished. It contrasts with the observation of a Mo-Si component in the study of Ohtake *et al.* when the Si substrate was not protected by the GaSe layer.³²⁹ Hence, it argues against the

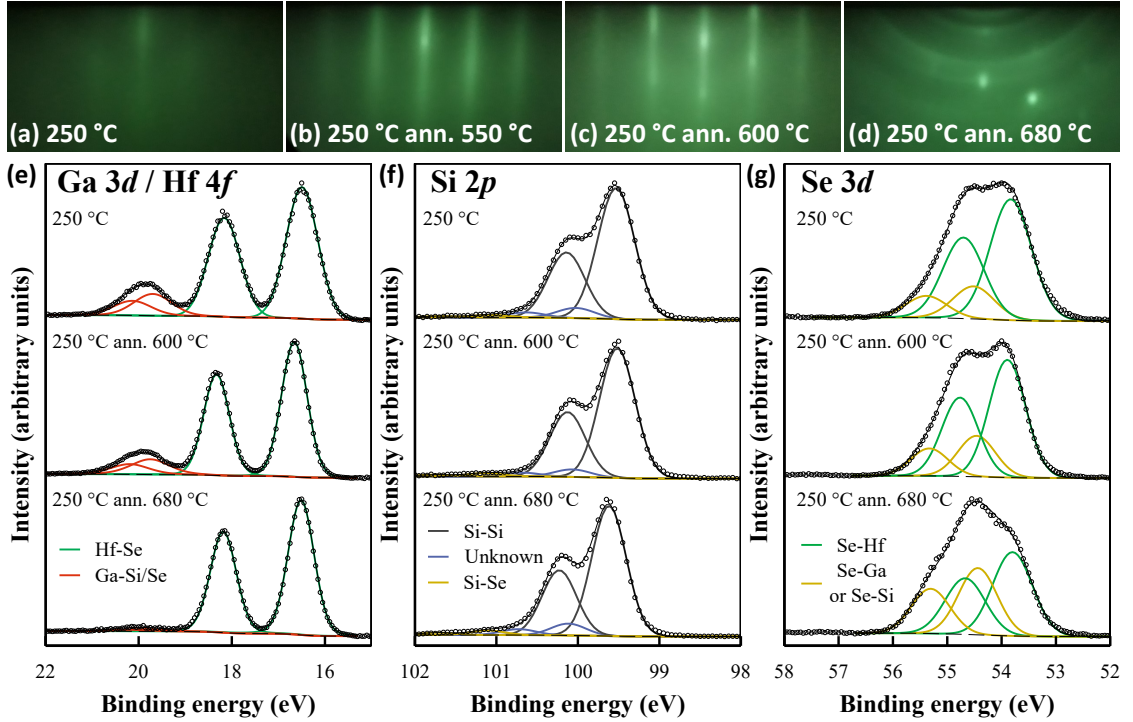


Figure 4.19: (a-d) RHEED patterns of the 2 ML HfSe₂ sample grown on GaSe-terminated Si at 250 °C (a) as grown, (b) annealed at 550 °C, (c) 600 °C, and (d) 680 °C (sample H9). (e) Hf 4f and Ga 3d, (f) Si 2p and (g) Se 3d CLs measured in XPS at 45° on the same sample at different stages.

formation of a silicide, which is further confirmed by the absence of low energy components in the Si 2p CL presented in Fig. 4.19 (f). Instead, two components are observed at high binding energies. If the small one at highest binding energy is attributed Si-Se bonds, the origin of the intermediate one is unclear. According to the previous analysis of the GaSe-terminated surface in Fig. 4.16, it is unlikely to corresponds to Si-GaSe bonds and would rather match the Si surface states but the presence of two SiSe_x compounds with different stoichiometries cannot be excluded neither. In the Se 3d CL presented in Fig. 4.19 (g), the Se-Ga and Se-Si states, that are both expected at high binding energy, are not distinguished. However, since the corresponding component increases as the Ga 3d intensity decreases, it is suggested that the Se-Ga bonds are progressively replaced by Se-Si ones during the annealing. This is consistent with the gradual enhancement of the Si 2p component attributed Si-Se bonds. Concerning the unidentified one, which remains visible at every temperature but does not follow a monotonous evolution, it is believed to be an intermediate state, probably arising from an incomplete selenization of the Si substrate.

Even if it has not been reported in the previous TMDC growths on Si{111},^{316,317,329} the formation of SiSe_x is not unexpected from the thermodynamic point of view⁴⁶² and may have been favored by the use of higher annealing temperature and Se flux. Nevertheless, its apparition is surprising since the GaSe half-layer has been determined to be stable under high Se flux up to 650 °C. This different behavior may be somehow induced by presence of the HfSe₂ layer. It is suggested that the GaSe termination is stabilized on the bare Si substrate because it has a very low surface energy compared to Si or SiSe_x surfaces. However, the interaction with HfSe₂ may change the substrate to layer energy at the expense of GaSe, which evaporates then. The diffusion of Ga through the HfSe₂ layers is indeed not surprising given the significant Ga impurities observed earlier in the 15-ML-thick film. Finally, the formation of HfSi_x seems prevented by the high Se flux which rather favors a SiSe_x compound instead.

In summary, the growth of HfSe_2 on a GaSe-terminated Si substrate is possible at low temperature, even though the substrate passivation does not seem entirely preserved. A post-growth annealing under Se flux improves the crystallinity but the temperature should be kept below 600 °C to prevent a sudden degradation of the morphology attributed to the evaporation of the GaSe layer and the formation of SiSe_x .

4.2.2.b Comparison with GaP substrates

After the stability limit has been determined, 4 MLs of HfSe_2 have been grown on GaSe-terminated Si, annealed at 550 °C and compared to the sample H6 prepared on GaP in similar conditions. Table 4.8 shows that the sample grown on Si-GaSe also appears slightly thinner than expected, even though at a lesser extent than the GaP one.

Sample #	Substrate	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Measured th. (ML)	Characterizations
H6	GaP	250	550	4	2.36	RHEED, XRD
H10	Si-GaSe	250	550	4	2.85	RHEED, XRD, STEM

Table 4.8: Samples compared to discuss the influence of the substrate on HfSe_2 growth.

The RHEED patterns recorded on the layers grown on GaP and Si-GaSe are compared in Fig. 4.20 (a-d). Both before and after annealing, they appear more diffuse on Si, suggesting a poorer crystallinity. To confirm this, in-plane grazing incidence XRD measurements have been carried out on the layer grown on Si-GaSe and compared to the already characterized sample grown on GaP in the same conditions. The HfSe_2 {110} peak is broader both along the radial (Fig. 4.20 (e)) and azimuthal axes (Fig. 4.20 (f)), indicating respectively a lower crystallinity and larger in-plane misorientation when the layers are grown on GaSe-terminated Si, in accordance with the RHEED observations.

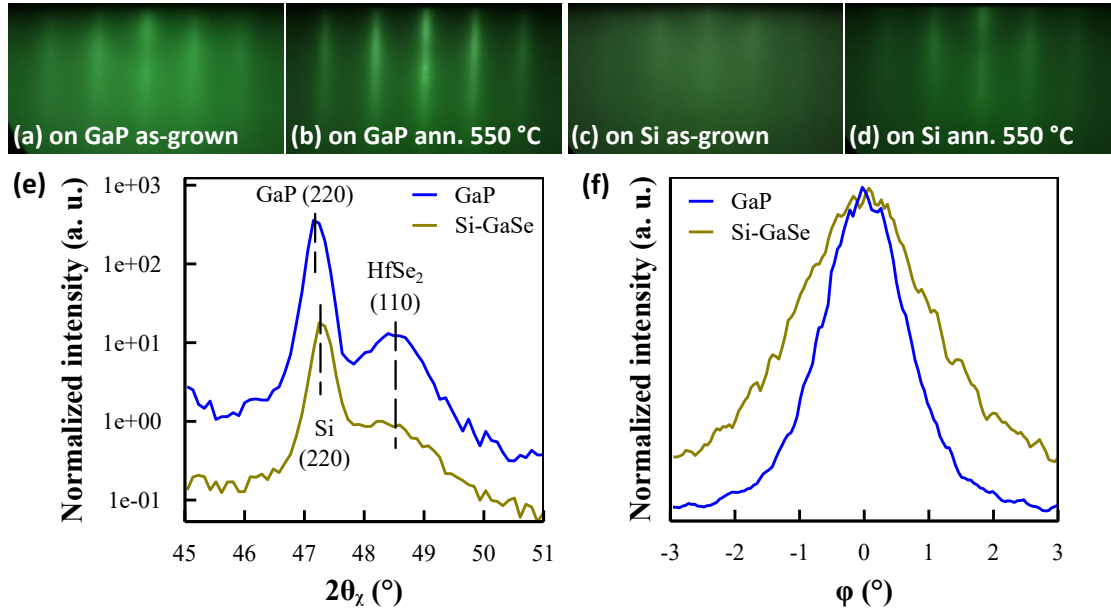


Figure 4.20: (a-d) RHEED patterns of the 4 ML-thick HfSe_2 samples grown on (a,b) GaP (sample H6) or (c,d) GaSe-Si (sample H10) before and after annealing at 550 °C (e,f) Comparison of the HfSe_2 {110} XRD peaks of the two samples in (e) radial or (f) azimuthal in-plane grazing incidence scans.

To complete these findings, the layer grown on Si-GaSe is investigated at the microscopic scale using STEM. The two typical results are observed on the same pictures in Fig. 4.21 (a). In most cases, the HfSe₂ layers are rather ordered, as on the right side, and exhibits the expected 1T phase. However, they get more disordered near the top of the stacking. Below, the topmost layer of the Si substrate appear slightly brighter in accordance to the presence of GaSe, even though some heavy atoms also seem to have diffused below the surface. Still, the interface between the substrate and the HfSe₂ layers is rather sharp in this case, whereas on the left side, a dark amorphous material is observed in between. It could be related to the small droplets observed on the substrate during the preparation, for instance SiO₂ or SiC residues from an insufficient substrate cleaning or Ga droplets from the GaSe preparation. However, it may also be an early stage of degradation, such as an agglomeration of the GaSe half-layer prior to its evaporation, or some already formed SiSe_x. On top of this, only few HfSe₂ sheets are discernible, but the bright background suggests that the dark amorphous agglomerate is mostly covered by HfSe₂ layers. However, in this case, they appear largely disordered, in accordance with the broad XRD peaks and diffuse RHEED pattern.

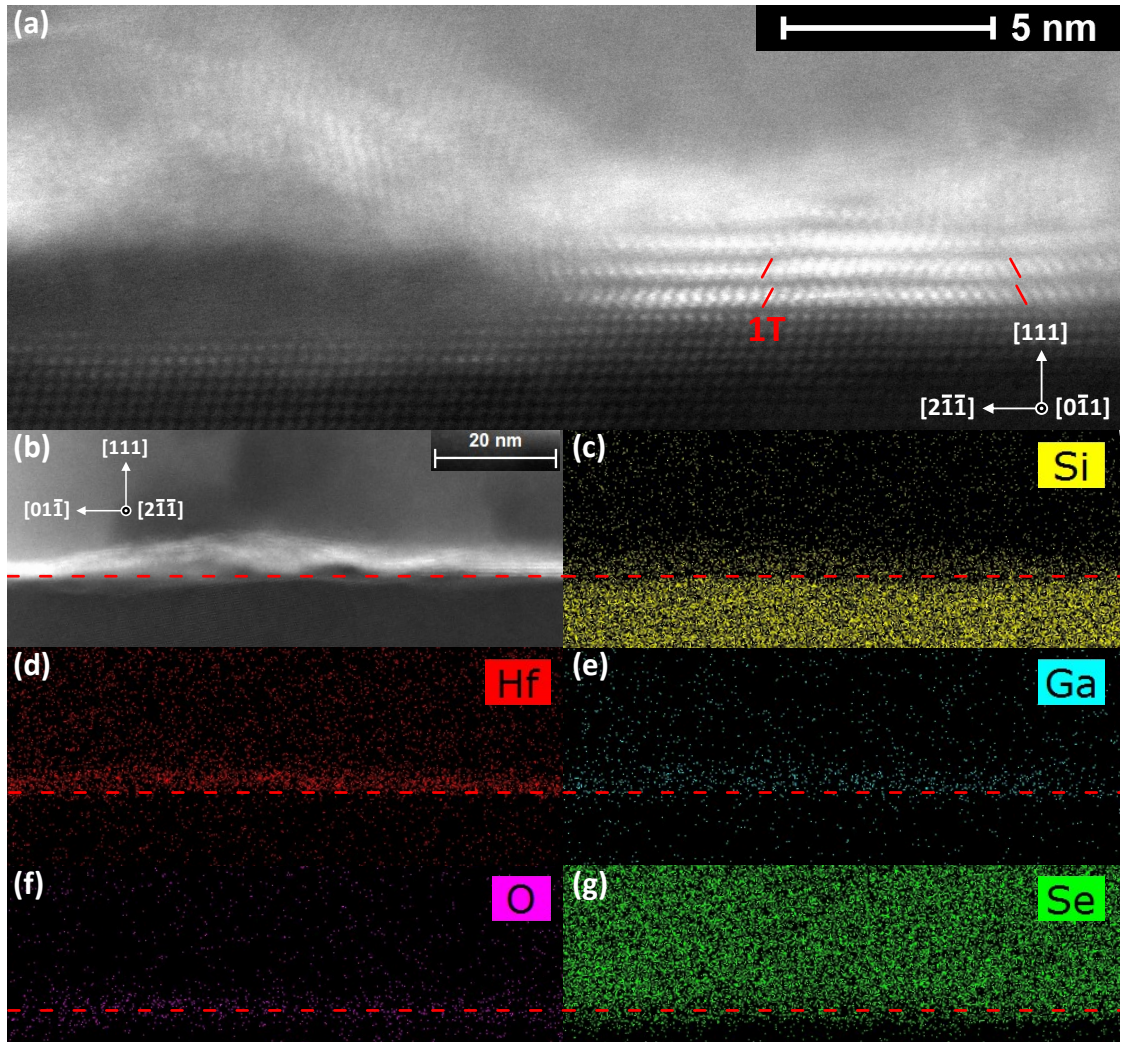


Figure 4.21: (a) HAADF-STEM image along the Si $[0\ 1\ \bar{1}]$ zone axis of the 4 ML HfSe₂ sample grown on GaSe-terminated Si at 250 °C and annealed at 550 °C (sample H10). (b) HAADF-STEM image along the Si $[2\ 1\ \bar{1}]$ zone axis of the same sample, on which the EDX analysis has been performed. (c-g) EDX mapping of the chemical elements detected on image (b).

To identify the interfacial compound, a chemical analysis using EDX has been performed on the image in Fig. 4.21 (b). The maps in Fig. 4.21 (c-g) reveal the position of Si, Hf, Ga, O and Se atoms. The position of the interface between the Si substrate and the grown material has been identified on the HAADF image and highlighted on every frame as a dashed red line. It shows that Hf and Ga atoms are mostly above the interface, which suggests a degradation of the GaSe layer but rules out the possibility of GaSe segregation. Instead, the Ga appears mixed with the HfSe₂ as previously observed in thick layers. A weak O signal is detected near the interface. It is not clear whether it originates from an insufficient deoxidation of the Si substrate or a subsequent oxidation of the sample, but it is too low to play a significant role. Finally, Se atoms are found in the capping layer, in the HfSe₂ layers and even below the Si surface, while the Si intensity decreases near the interface but remains non-negligible in the layer. Therefore, it suggests an important interdiffusion of these two elements, in accordance to the XPS observations. The SiSe₂ structures that have been reported^{463,464} consist of chains of distorted tetrahedra which strongly differ from the hexagonal symmetry of the Si {1 1 1} surface and HfSe₂. It is not surprising that it appears amorphous on the STEM images and that the HfSe₂ layer above is largely disordered.

Summary

A self-limiting preparation method for surface termination of Si(1 1 1) substrates with a half-monolayer of GaSe has been developed. It provides an efficient protection to oxidation, suggesting a good passivation, and exhibits a unique grain orientation, making it promising for TMDC growth. Indeed, the deposition of HfSe₂ on GaSe-terminated Si at 250 °C without evidence of an undesired compound paves the way toward the integration of TMDCs on Si. However, the lower stability of the GaSe surface limits the annealing temperature to 550 °C, and even in this case, the crystallinity and in-plane orientation of the layer are less good than those on GaP annealed at the same temperature. In addition, some degradation is already observed on the layer annealed at 550 °C on Si-GaSe and may be related to the formation of an interfacial SiSe_x compound. For these reasons, the final part of this work, dedicated to TMDC heterostructures and electrical measurements will be performed on GaP substrates.

4.3 Heterostructures and electrical measurements

To investigate the HfSe₂ electronic properties, suitable metallic contacts are required and TaSe₂ could play this role. Their similar atomic structures are expected to prevent the degradation of the 2D layers at the interfaces and enable the fabrication of all-epitaxial vertical devices, with for instance bottom contacts. Therefore, the growth of both HfSe₂/TaSe₂ and TaSe₂/HfSe₂ heterostructures is studied. Then, band alignment between the two materials is discussed. Finally, the first attempts to employ them are briefly presented.

4.3.1 Growth of HfSe₂ and TaSe₂ heterostructures

In this section, the two growth sequences are compared: either TaSe₂ is grown first and HfSe₂ afterward, or the reverse order. In HfSe₂, the growth temperature does not significantly impact the properties whereas in TaSe₂, a trade-off exists between morphology and crystallinity. Because sharp interfaces are desired, the lowest growth temperature is chosen here not only to get a smooth morphology, but also to limit the interdiffusion of the transition metals. For the same reason, an intermediate annealing at 650 °C is performed between the growth of the two materials. They are then characterized through XPS, XRD and STEM.

4.3.1.a X-ray photoelectron spectroscopy study

An XPS analysis is performed after the growth of the first layer which enables its thickness to be determined. Then, the thickness of the top layer is derived from the Hf/Ta ratio using the three-layer model detailed in Section 2.2.5. The results are presented in Table 4.9.

Sample #	Stacking	Growth T. (°C)	Annealing T. (°C)	Measured th. (ML)	Characterizations
T17	TaSe ₂ /GaP	250	650	4.04	XPS
HT1	HfSe ₂ /TaSe ₂ /GaP	250	650	3.72/4.04	XPS, XRD, STEM
H11	HfSe ₂ /GaP	250	650	2.77	XPS
TH1	TaSe ₂ /HfSe ₂ /GaP	250	650	4.30/2.77	XPS, XRD, STEM

Table 4.9: TaSe₂ HfSe₂ heterostructures.

The formed compounds are further analyzed using XPS through the Ta 4*f* and Hf 4*f* CLs presented in Fig. 4.22 (a) and (b) respectively. To facilitate the comparison, the energy scale has been normalized by aligning the P 2*p* CL on the position measured on sample HT1, which compensates for an evolution of the band bending upon TaSe₂ growth discussed later as well as potential photovoltage effects.

In every sample, the Ta 4*f* CL exhibits a shape very similar to those observed for the H phases in the precedent chapter, with a more pronounced shoulder for both heterostructures compared to sample T17 presented as a reference, suggesting the presence of a minor fraction of 1T phase. This is attributed to the fact that HfSe₂ crystallizes into the 1T phase and the small energy difference between these two phases in TaSe₂, which may more easily induce a phase transformation in TaSe₂ than in HfSe₂.

Nevertheless, the Hf 4*f* CL reveals a large broadening upon TaSe₂ growth in sample TH1, whereas the HfSe₂ layer grown on TaSe₂ is very similar to the bare HfSe₂ layer on GaP. The origin of the low binding energy tail is not clear, but it can reasonably be attributed to an interfacial compound or Hf atoms diffusing into the TaSe₂ layer. These effects are indeed more easily observed in the Hf 4*f* CL when HfSe₂ is grown first compared to the reverse heterostructure where the electrons from the HfSe₂ layers on top of the stacking overshadow those in the defective interface underneath. Still, if an interfacial compound was formed in the HfSe₂/TaSe₂/GaP heterostructure, it would be conversely more easily observed in the Ta 4*f* CL based on the same

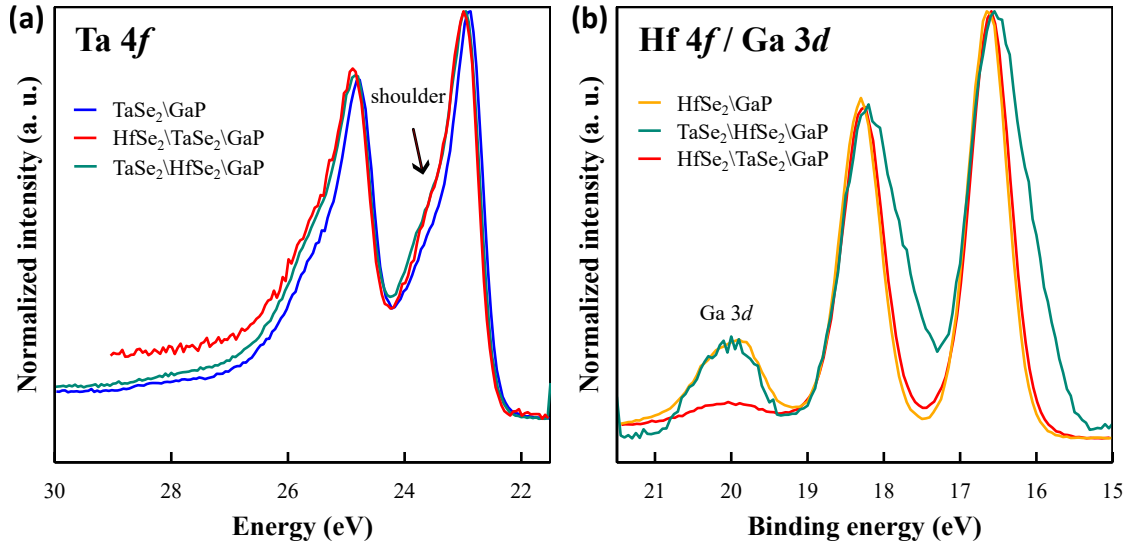


Figure 4.22: (a,b) Comparison of the (a) Ta 4f and (b) Hf 4f CLs in the bare TaSe₂ layer prior to HfSe₂ growth (sample T17), in the bare HfSe₂ layer prior to TaSe₂ growth (sample H11), in the TaSe₂/HfSe₂/GaP (sample TH1) and HfSe₂/TaSe₂/GaP heterostructures (sample HT1). All spectra are measured using XPS at 45° and the binding energy scale was corrected to have the P 2p CL at 129.47 eV.

argument. Since it is not the case, it is concluded that the growth of HfSe₂ degrades less the TaSe₂ underneath than the growth of TaSe₂ degrades the HfSe₂ layer.

4.3.1.b X-ray diffraction study

The diffraction patterns recorded on both heterostructures are shown in Fig. 4.23 (a). In sample TH1, the observation of the same HfSe₂ and TaSe₂ peaks along a given azimuth confirms that the two materials grow with the same epitaxial relationship in spite of the lattice mismatch. For the HfSe₂/TaSe₂/GaP heterostructure, though, only one azimuth is shown because the HfSe₂ (110) peak is not found while the TaSe₂ one is only barely discernible. Instead, the large peak at 55.6° is attributed to Se (003) whereas the smaller one at 45° could correspond to a (2 $\bar{1}$ 1) plane (Appendix B.6). The crystallization of the Se capping layer is due to the debonding of the sample from the carrier wafer at 170 °C. Even though crystalline Se capping layers are also protective,³⁴⁵ it is possible that the capping layer becomes porous after crystallization and therefore the oxidation of the sample may be the reason for the lack of signal from the TMDC layers. Still, this could also be explained by a poor crystalline quality.

Focusing on the TaSe₂/HfSe₂/GaP heterostructure, the crystallinity of the HfSe₂ and TaSe₂ layers is studied through the (110) peaks revealed in Fig. 4.23 (b) and the (100) peaks in Fig. 4.23 (c). Unexpectedly, a much higher signal is obtained on the TaSe₂ peaks than on the HfSe₂ ones in spite of the similar thickness, suggesting a better crystallinity for the TaSe₂ layer. This is confirmed by a slightly smaller FWHM measured on (110) TaSe₂ peak compared to the HfSe₂ counterpart, although no sensible difference is measured in the (100) peaks. In the end, the TaSe₂ peaks appear slightly thinner in this heterostructure than in the sample grown on GaP in similar conditions (0.82° for the (110) peak in Fig. 3.31), whereas the HfSe₂ layer seems slightly degraded compared to those grown on GaP (0.70° for the (110) peak of the layers annealed at 650 °C in Fig. 4.4). Hence, while the HfSe₂ layers suffer from the interdiffusion, it is believed that TaSe₂ benefits from the presence of the HfSe₂ layer underneath. This may be related to the better GaP/HfSe₂ interface suggested by the observation of the GaSe (100) peak, in good agreement with previous HfSe₂ samples grown on GaP.

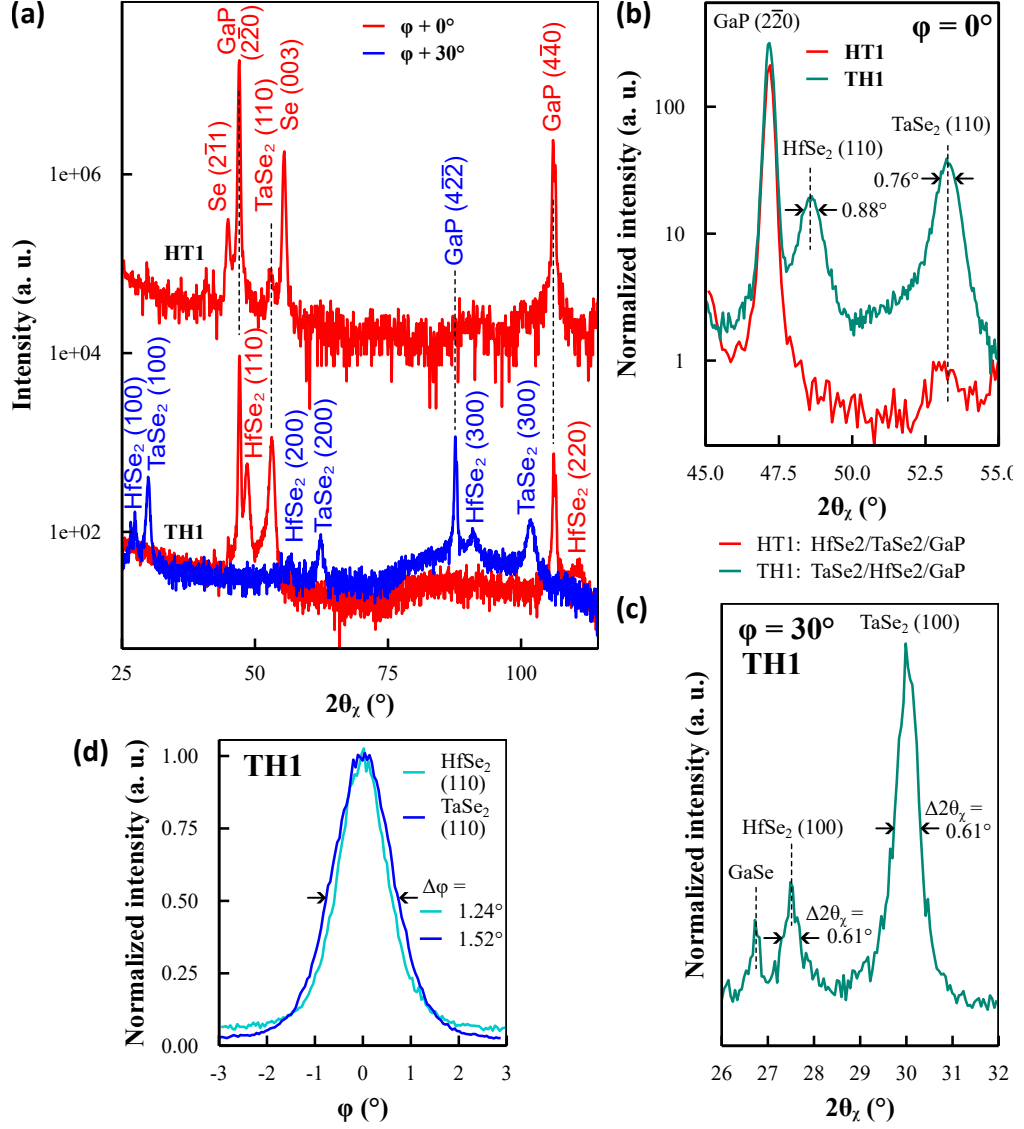


Figure 4.23: (a) In-plane grazing incidence XRD pattern of the two heterostructure recorded along the GaP $\langle 0\bar{1}1 \rangle$ (samples HT1 and TH1) and $\langle 2\bar{1}\bar{1} \rangle$ directions (sample TH1 only). (b) Magnified diffraction pattern recorded on the two heterostructures around the TaSe₂ and HfSe₂ (110) peaks. (c) Magnified diffraction pattern recorded on the TH1 heterostructure around the TaSe₂ and HfSe₂ (100) peaks. (d) Comparison of the TaSe₂ and HfSe₂ (110) peaks in the TH1 heterostructure recorded along the azimuthal direction.

To confirm this hypothesis, the in-plane alignment of the layers is studied through the HfSe₂ and TaSe₂ (110) peaks in Fig. 4.23 (d). The slightly larger rotational misalignment of the TaSe₂ compared to the underlying HfSe₂ layer is not surprising since it grows relatively to the latter. However, it is interesting to note that the FWHM of 1.52° measured on the TaSe₂ peak is much less than the misalignment of 3.29° obtained on GaP in comparable conditions. Hence, TaSe₂ aligns much better on HfSe₂ in spite of the HfSe₂ and GaP lattice parameters being close.

In the end, contrasting with the XPS results, the TaSe₂/HfSe₂/GaP heterostructure appears more appealing especially because of the good in-plane orientation obtained in this configuration compared to what can be expected when TaSe₂ is directly grown on GaP.

4.3.1.c Scanning transmission electron microscopy analysis

To complete this study, both heterostructures are investigated using STEM.

HfSe₂ on TaSe₂

Focusing first on sample HT1 revealed in Fig. 4.24 (a), 2H_a and 3R phases are observed at the bottom of the stacking as expected for the TaSe₂ layer. On the upper part, the observation of the 1T phase is consistent with the presence of HfSe₂ even though it appears quite dim. The Hf and Ta having consecutive atomic numbers, such an intensity contrast may hardly be only related to the different electron densities, and rather indicates a small rotational shift between the two layers. Besides, the layer in the center cannot clearly be identified to either phase and may be an intermediate layer containing both atoms. In addition, The TaSe₂/GaP interface is severely degraded which is consistent with our previous observations.

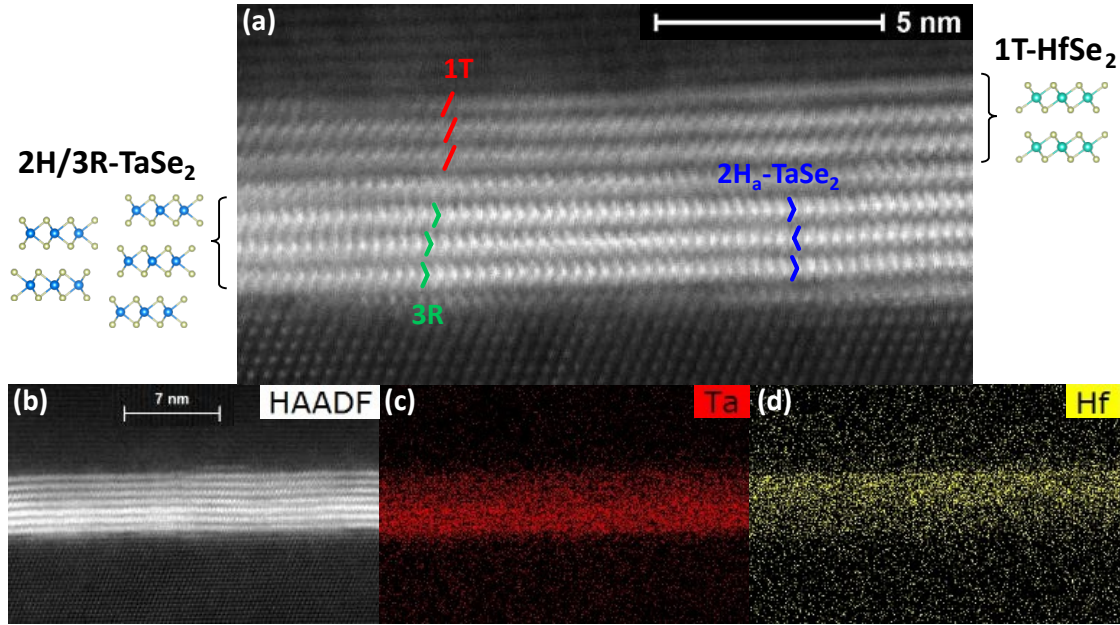


Figure 4.24: (a) HAADF-STEM image along the GaP $[01\bar{1}]$ zone axis of the HfSe₂ layers grown on TaSe₂ (sample HT1). (b) HAADF-STEM image along the GaP $[\bar{2}11]$ zone axis of the same sample, on which the EDX analysis has been performed. (c-d) EDX mapping of the chemical elements detected on image (b).

An EDX analysis presented in Fig. 4.24 (b-d) effectively reveals a significant intermixing of the two compounds, not only near the interface but in the whole stack. This may explain the virtual absence of diffraction peaks for this heterostructure in XRD, although the oxidation remains a plausible hypothesis.

TaSe₂ on HfSe₂

In the reverse heterostructure revealed in Fig. 4.25 (a), the 1T phase is mostly found at the bottom, and the 2H_a phase at the top, in accordance with the TaSe₂ being grown on HfSe₂. Still, some 1T phase is distinguished on the topmost layer on the left side, but the observation of such 1T islands was already made on the TaSe₂ few layers grown in similar conditions. Remarkably, the interface is much more preserved in this case than in the previous sample, which is also consistent with the presence of the GaSe peak and the preceding conjecture of the HfSe₂ grown at low temperature preserving much better the vdW gap between the layer and the surface than TaSe₂ does. Still, the EDX analysis presented in Fig. 4.25 (b-d) reveals an important intermixing between the two elements, although possibly to a lower extent than in the previous sample.

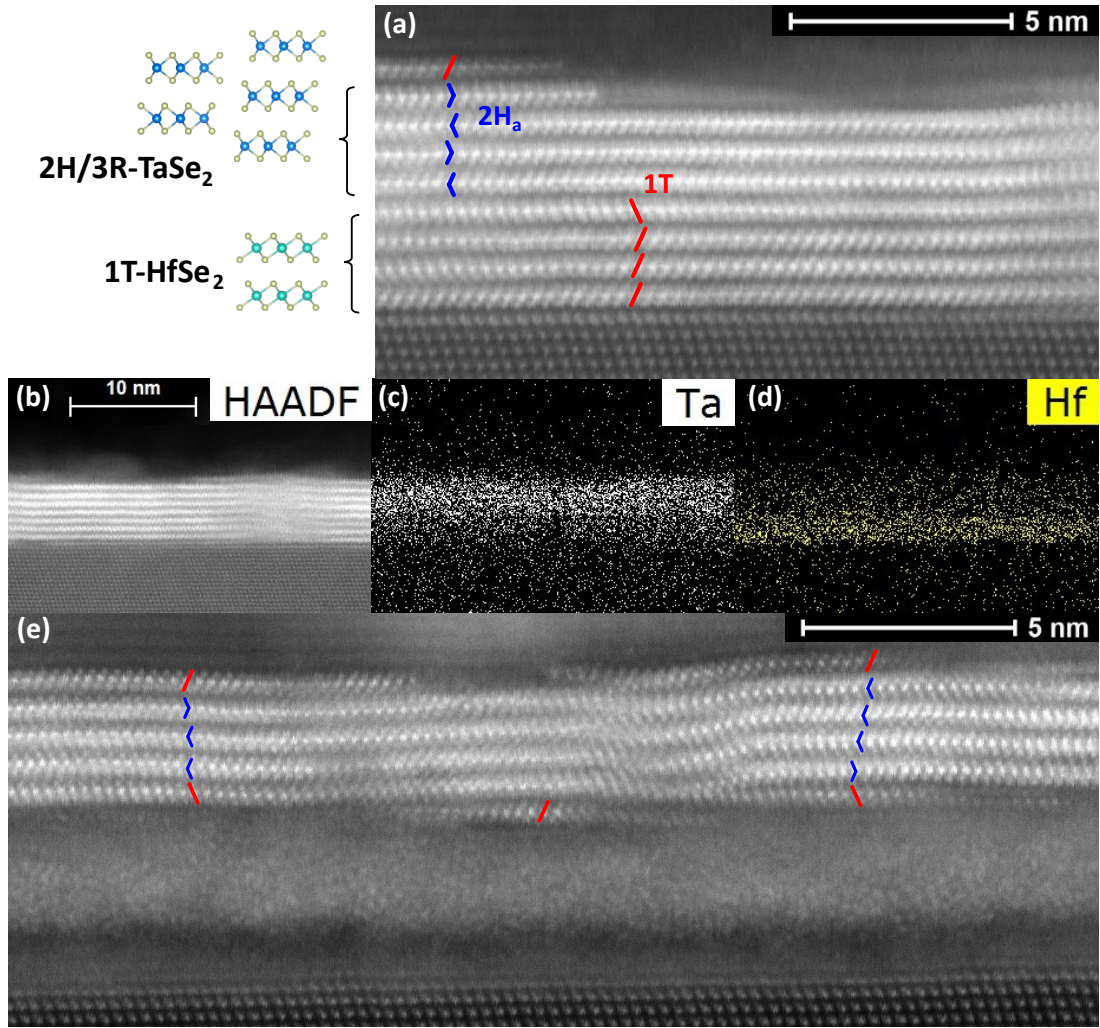


Figure 4.25: (a) HAADF-STEM image along the GaP $[01\bar{1}]$ zone axis of the TaSe₂ layers grown on HfSe₂ (sample TH1) (b) HAADF-STEM image along the GaP $[\bar{2}11]$ zone axis of the same sample, on which the EDX analysis has been performed. (c-d) EDX mapping of the chemical elements detected on image (b). (e) HAADF-STEM image of a partially oxidized region of sample TH1.

Finally, it must be mentioned that part of the sample was oxidized as shown in Fig. 4.25 (e), in apparent contradiction with the fact that this sample was not oxidized in the XRD study. This may however be explained by the order in which the characterizations have been carried out, and indicates that the HfSe₂ layers are not very stable in air even with the Se capping layer. Interestingly, the bottom layers are oxidized in this image while the H layers on top are preserved, showing that HfSe₂ is more sensitive to oxidation than TaSe₂ as could be expected from the literature.^{441,465} All the non-oxidized layers are thus presumed to be TaSe₂, and therefore it proves that the 1T island on top is indeed TaSe₂ but also reveals that some 1T-TaSe₂ is formed at the bottom. This confirms that the underlying HfSe₂ favors the growth of 1T-TaSe₂ as suggested but not clearly identified using XPS.

In summary, although the XPS rather suggested the presence of an interfacial compound in the TaSe₂/HfSe₂/GaP heterostructure, the EDX analysis revealed that both samples suffer from a large intermixing of the two transition metal atoms. Conversely, the XRD analysis shows that this sequence benefits from the better alignment of HfSe₂ on GaP together with a more preserved interface with GaP as confirmed using STEM. Hence, this sequence should be preferred in the following studies.

4.3.2 Band alignments

To evaluate the possibility of using TaSe₂ as a contact material for HfSe₂, the band alignments have been investigated in both heterostructures using XPS and UPS.

HfSe₂ on TaSe₂

Focusing first on sample HT1, the evolution of the band alignment upon HfSe₂ growth on TaSe₂ is shown in Fig. 4.26.

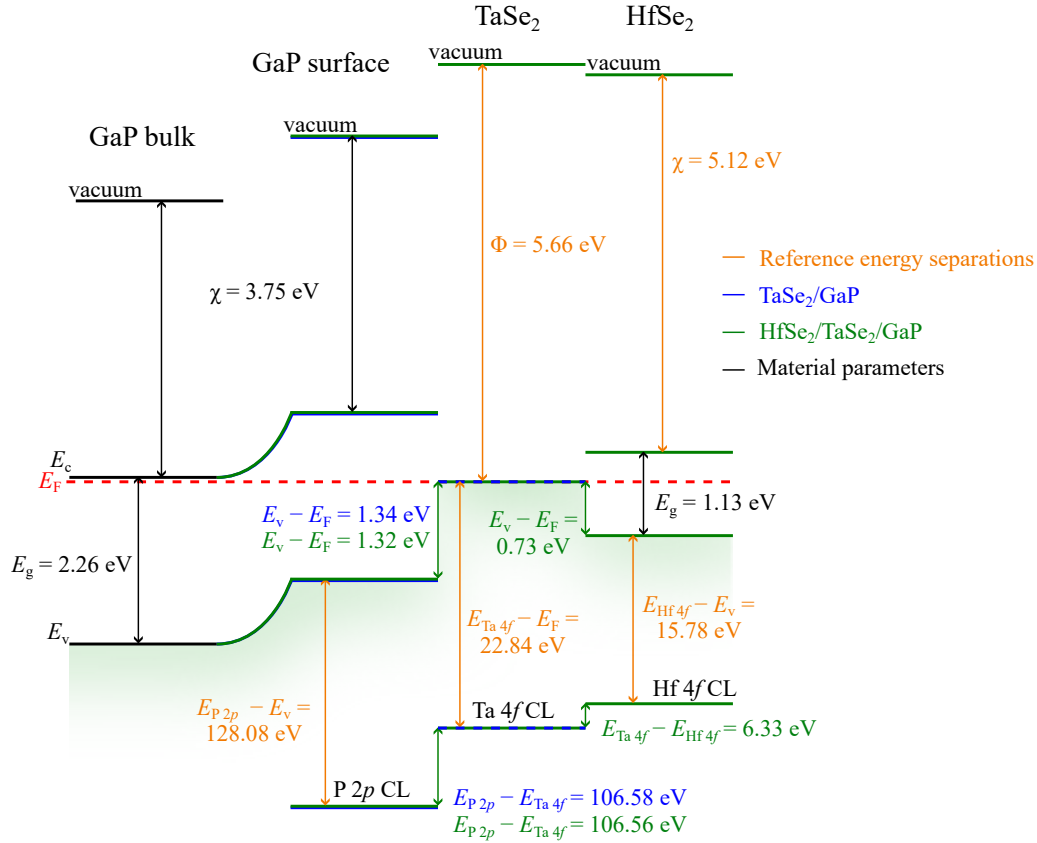


Figure 4.26: Evolution of the band alignments after growth of HfSe₂ on TaSe₂ (HT1). The band positions previously determined before HfSe₂ growth are represented in blue (sample T17). The layers are grown on a n-type GaP substrate.

The TaSe₂/GaP band alignment previously on sample T17 in Fig. 3.40 is represented in blue. After annealing, the Fermi level position is determined from the measured Ta 4f CL binding energy, which is unaltered by the HfSe₂ growth. Inversely, the HfSe₂ valence band maximum calculated at 0.73 eV from the Fermi level based on the $E_{Hf4f} - E_{Ta4f}$ energy difference significantly differs from the HfSe₂ layer grown on n-type GaP in Paragraph 4.1.1.b. This is explained by the fact TaSe₂ being a metal completely screens the charge transfer from the GaP substrate owing to its large density of state, while inducing little charge transfer as expected from the relatively good work function matching. As a result, the HfSe₂ valence band maximum is very similar to the one measured on p-type GaP.

The position of the HfSe₂ valence band is further corroborated by the UPS measurements on this sample (not shown), revealing a valence band maximum 0.79 eV and a work function of 5.39 eV, the slight difference being attributed to photovoltage in the UPS experiments.

TaSe₂ on HfSe₂

The same procedure is employed for the TaSe₂/HfSe₂/GaP heterostructure, leading to the band alignment sketched in Fig. 4.27.

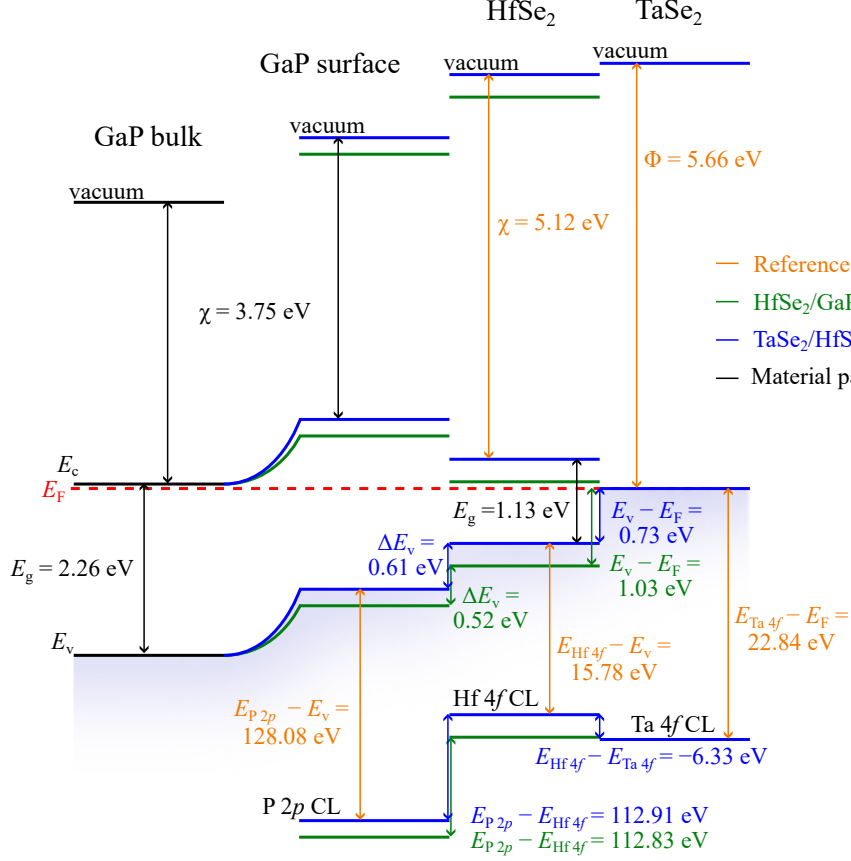


Figure 4.27: Evolution of the band alignments after growth of TaSe₂ on HfSe₂ (sample TH1). The band positions previously determined for the bare HfSe₂ layer grown at 250 °C and annealed at 650 °C are represented in green (sample H1'). Both samples are grown on a n-type GaP substrate.

The band alignment previously established on the 3 ML-thick HfSe₂ film grown on n-type GaP in Fig. 4.3 (c) has been reproduced in green. Again, the Fermi level position after TaSe₂ growth is determined from $E_{Ta\ 4f} - E_F = 22.84\text{ eV}$. The valence band maximum in the HfSe₂ and GaP deduced from the $E_{Hf\ 4f} - E_{Ta\ 4f}$ energy is found at 0.73 eV in perfect agreement with the other heterostructure. In this case, the valence band position, as well as the GaP-HfSe₂ valence band offset deduced from the $E_{P\ 2p} - E_{Hf\ 4f}$ difference, changes upon TaSe₂ growth. Interestingly, the final position of the GaP valence band maximum (1.34 eV) matches very well the TaSe₂/GaP and HfSe₂/TaSe₂/GaP heterostructures, showing that the band bending in GaP is rather governed by the TaSe₂. Similarly, the absence of enhanced n-type doping in the HfSe₂ in spite of the large depletion of the GaP surface shows that the electrons are accumulated in the TaSe₂ instead.

Overall, the analysis of the band alignment reveals no influence of the stacking order as the large density of states of the metallic TaSe₂ prevails over the semiconducting HfSe₂ and GaP. This is found to erase the high electron doping induced by the n-type substrate, leading to slight n-doping consistent with the HfSe₂ grown on p-type GaP. Finally, little charge transfer is expected between HfSe₂ and TaSe₂ owing to their similar work function, in agreement with a previous study.¹⁸

4.3.3 Electrical characterization

In this last section, the electrical transport in the HfSe_2 layers and heterostructures are finally investigated. First, we try to measure the resistivity of the thick HfSe_2 layers in lateral transport using both 3D and 2D contacts. Then, given the very high resistance of the film and recognizing that 2D contacts would rather benefit for vertical devices, a first attempt of a tunneling diode is presented. Because of the high sensitivity of HfSe_2 to oxidation, test structures are only made using the mask in the MBE chamber and protected by a Se capping layer afterward.

4.3.3.a Lateral transport

Thick HfSe_2 samples have been grown using the high growth rate recipe already used in Section 4.1.2. Thanks to the mask in the MBE-chamber, it is patterned to form various structures including a line on which metallic contacts are deposited at intervals of 2 and 4 mm as shown in Fig. 4.28 (a,b). For this, two different metallic materials are compared, either Mo evaporated under vacuum at 100 °C in the MBE chamber (sample H12), or TaSe_2 layer grown at 250 °C and annealed at 650 °C (TH2). Mo is chosen for its good resistance to oxidation and because its work function estimated at 4.6 eV⁴³⁶ should be sufficiently low to contact HfSe_2 , provided that no Fermi level pinning exists. Conversely TaSe_2 is not expected to be an ideal contact on HfSe_2 , but could benefit from a less defective interface. In both cases, the layers are grown on semi-insulating GaP substrates and protected from oxidation by 40 nm of amorphous Se, introducing a parallel resistance of approximately 3 G Ω as measured between two isolated pads (not shown).

Sample #	Stacking	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Characterizations
H12	Mo/ HfSe_2 /GaP	250	650	30 nm/30	4PP
TH2	TaSe_2 / HfSe_2 /GaP	250	650	6/30	4PP

Table 4.10: Patterned HfSe_2 samples with electrical contacts.

First, two-probe measurements on both contacts reveal linear IV curves shown in Fig. 4.28 (c), proving that both materials can be contacted by the tip, even though the TaSe_2 contact appears more resistive probably because of its much lower thickness. Similarly, two-probe measurements through the HfSe_2 film presented in Fig. 4.28 (d) also reveal linear IV curves, suggesting ohmic Mo/ HfSe_2 and TaSe_2 / HfSe_2 contacts, but in this case, it is not clear why a much larger resistance is measured with TaSe_2 .

To extract the contact resistance, short and long intervals have been measured using both the two and four-probe methods. However, a very small resistance (290 k Ω) is obtained for the shortest distance with Mo contacts, suggesting an overlap of the Mo contacts pads as sketched in Fig. 4.28 (e). The broadening of the patterns is attributed to the gap between the sample and the mask in the MBE chamber (see Paragraph 2.1.5). In addition, the resistance was only barely measurable (above 500 M Ω , not shown) in three of the five 4-mm intervals. Hence, only few two-probe measurements with Mo contacts are presented in Fig. 4.28 (f) with the distances corresponding to either interval being corrected considering 2 mm-large contacts.

By contrast, the significant resistance obtained over the small distances with TaSe_2 contacts suggests no overlap, probably because the TaSe_2 thickness rapidly decreases below 1 ML near the contact edge. This enables four-probe measurements to be made on both 2 mm and 4 mm intervals even if the measured resistances were larger overall, as seen in Fig. 4.28 (g). In this plot, a contact width of 1.65 mm is estimated in order to have the resistance as function of distance intercepting both axes at 0 for four-probe measurements. A higher resistance is measured in the two-probe configuration for the same distances, suggesting a non-negligible contact resistance as shown by the positive intercept of the regression line at distance equals to 0. However, since another set of four-probe measurements revealed an even larger resistance at each position

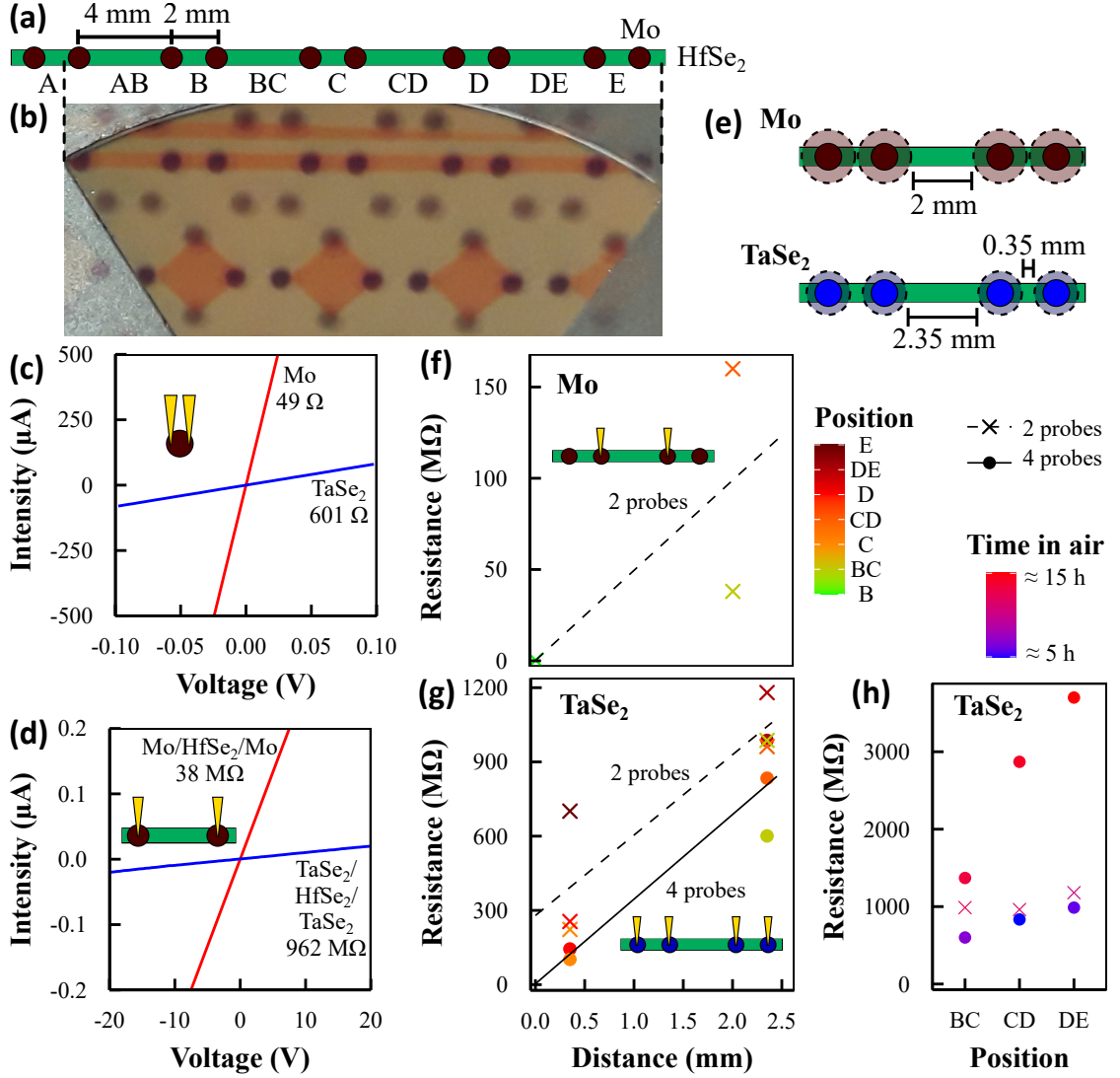


Figure 4.28: (a) Schematics and (b) picture of the HfSe₂ line structure with Mo contacts (sample H12). (c) Current-voltage (IV) curves measured using 2-probes on either the Mo or TaSe₂ contact pads. (d) IV curves measured using 2-probes over the 4-mm large intervals through the HfSe₂ layer using either Mo or TaSe₂ contacts. (e) Schematics of the contact pad broadening for either Mo or TaSe₂ contacts. (f-g) Measured resistance as function of the pad corrected separation, in either 2 or 4 probes configuration, for (f) Mo and (g) TaSe₂ contacts. (h) Evolution over the time of the resistance measured at different positions on the 4-mm large intervals with the TaSe₂ contacts.

afterward (Fig. 4.28 (h)), this is more likely related to a degradation of the sample over the time. The cause is not clear because it was not the case for the sample with Mo contacts (not shown), but the oxidation of the sample is suspected, either through the Se capping layer or after its evaporation under the microscope light.

Overall, different issues including the pad broadening, spatial inhomogeneities and progressive degradation made the extraction of the contact resistance through transfer length method impossible. Still, a resistivity down to 0.5 Ω.m with Mo contacts and 5 Ω.m with TaSe₂ ones have been demonstrated. It is much more than the 2×10^{-4} Ω.m measured by Radhakrishnan *et al.*⁸³ but comparable to the 8 Ω.m reported by Liu *et al.*⁸⁷ in bulk crystals. In one hand, the high resistivity is consistent with the expected semiconducting character of the HfSe₂ and

the reduced n-type doping in the thick layer observed in UPS. This can suggest a rather low density of defects compared to Se-deficient crystals exhibiting a much lower resistivity.⁸⁷ On the other hand, a high resistivity may also originate from a very low carrier mobility. Hall effect measurements would be valuable to disentangle these effects, but they could not be carried out on such highly resistive samples.

4.3.3.b First attempt of a tunneling diode

Given the difficulty to study the lateral transport in the HfSe₂ layer, tunneling diodes are investigated as an alternative application of the TMDC heterostructures. For instance, the confinement of carriers in atomically thin layers can be exploited to achieve negative differential resistance in resonant-tunneling diodes.⁴⁶⁶ In Esaki diodes, a similar characteristic arises from band-to-band tunneling in broken gap heterostructures with a sharp interface, as shown using a WSe₂/SnSe₂ junction.⁴⁶⁷ A previous work by Niels Chapuis demonstrated a staggered gap configuration between the p-type WSe₂ and n-type HfSe₂ which could be employed in a backward diode. This still needs to be confirmed with electrical characterizations, but given the high resistivity of the semiconducting TMDC, metallic contacts are also required.

Sample #	Stacking	Growth T. (°C)	Annealing T. (°C)	Targeted th. (ML)	Characterizations
THWT	TaSe ₂ /HfSe ₂ /WSe ₂ /TaSe ₂ /GaP	250	650	4/8/8/4	Two probes

Table 4.11: Heterostructure proposed as a tunneling diode.

Therefore, a TaSe₂/WSe₂/HfSe₂/TaSe₂ heterostructure is considered to achieve this, the WSe₂ on HfSe₂ stacking order being preferred due to a lower interdiffusion.³⁹¹ The four layers are grown at 250 °C through the MBE mask using similar growth conditions to those previously employed for the HT1 and TH1 heterostructure. After the growth of each material, the stack is annealed at 650 °C and the mask is shifted by 1 mm to form staggered structures as schematized in Fig. 4.29 (a). The two different structures shown in Fig. 4.29 (b) come respectively from the square and diamond apertures in the mask. Notably, the top and bottom TaSe₂ contacts do almost not overlap with the diamonds, whereas an $\approx 0.5 \text{ mm}^2$ overlap is visible with the squares. A too small overlap may introduce a significant series resistance because of the lateral transport in semiconducting layer. Conversely, a larger overlap increases the probability of a short-circuit through a conductive defect.

Based on the band offsets determined by Niels Chapuis and the preceding analysis of the HfSe₂/TaSe₂ heterostructure, the expected band alignments have been sketched in Fig. 4.29 (c). Although the TaSe₂/WSe₂ alignment is purely speculative, the high work function of TaSe₂ appears well suited to contact the p-type WSe₂. The proximity between the valence band of the WSe₂ layer and the conduction band of the HfSe₂ should enable electrons and holes to recombine at low voltages under reverse polarisation, while a larger forward voltage is required to overcome the 0.56 eV valence band offset between the HfSe₂ and WSe₂ or the 0.96 eV offset at the conduction band. This should lead to an asymmetric IV curve characteristic of a backward diode in which higher current are found in reverse bias, provided that the calculated 0.40 eV barrier at the TaSe₂/HfSe₂ contact can be overcome.

The electrical characterization of the layers in the two-probe configuration reveals a linear IV curve in most of the devices, as shown in Fig. 4.30 (a). The resistance is reproducible for a given type of structure: $38 \pm 5 \text{ k}\Omega$ for the diamond structures and $13 \pm 3 \text{ k}\Omega$ for the square ones. Since it is not far the expected sheet resistance of $1.5 \text{ k}\Omega/\square$ determined in the previous chapter (Paragraph 3.3.3.b), it is suggested that the resistance corresponds to the lateral transport in the TaSe₂ layer. Hence, the diodes are in short-circuit, either due to a direct contact between the two TaSe₂ layers or a significant conduction through defects in the HfSe₂ and WSe₂ layers.

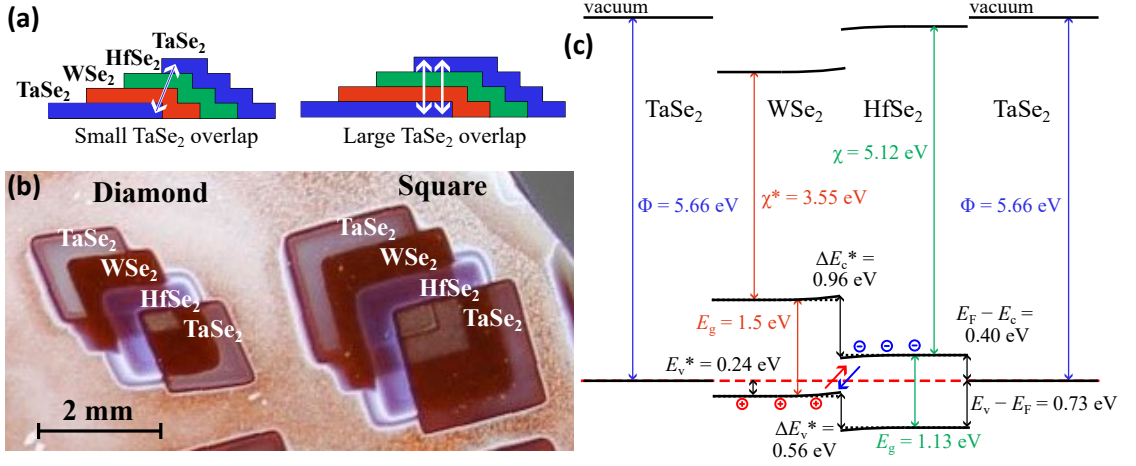


Figure 4.29: (a) Schematics and (b) picture of the diodes. (c) Expected band alignment in the heterostructure. *Values from Niels Chapuis.³⁹¹

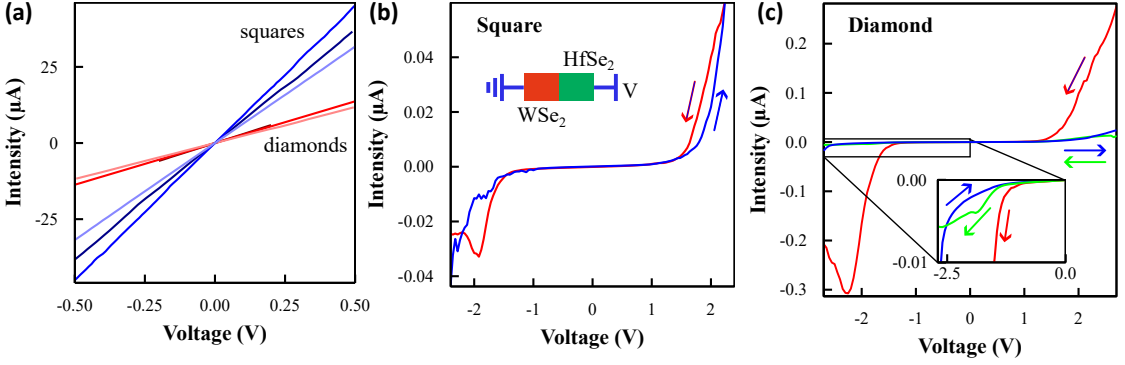


Figure 4.30: (a) Linear IV characteristics of most diodes. (b-c) Schottky IV characteristics of (b) a square and (c) a diamond diode, measured through increasing (blue) or decreasing (red and green) voltage sweeps. The WSe₂ side of the diode is grounded while the voltage is applied on the HfSe₂ side.

In few devices, however, a Schottky behavior and a resistivity in the order of 100 MΩ near 0 V is observed, as shown for a square structure in Fig. 4.30 (b). In these cases, the curves are relatively symmetric with voltages threshold around 2 ± 0.5 V, much larger than the expected from the barrier heights. Interestingly, a different behavior is observed depending on the sweep direction. When the measurement starts with a negative voltage on the HfSe₂ side, no particular feature is observed, whereas an intensity extremum is usually reached around 2 V in the negative region when the measurement starts from the positive region. This behavior could be repeated several times in both structures, but the intensity is usually not reproducible as shown by the large difference between the curves in Fig. 4.30 (c) recorded on a diamond structure.

Even if a negative differential resistance is obtained, this effect more likely arising from a resistive switching as previously been reported in transition metal oxides.⁴⁶⁸ Recent reports of resistive switching in both oxidized²⁴⁸ and defective HfSe₂⁴⁶⁹ indeed supports this hypothesis. Finally, if the lack of reproducibility of this behavior is consistent with a conduction through defects, it also suggests that the stability and controllability of such a mechanism is not guaranteed. In this regard, it is worth noting that the different behavior between the few devices was rather unexpected given that the large active areas should favor an homogeneous distribution of defects. However, it is possible that all diodes were initially short-circuited, but the oxidation of the conduction channels has reset the diodes to a blocked state. The absence of tunneling current

at small reverse bias in this case, though, may be attributed to the barrier at the TaSe₂/HfSe₂ interface, calling for a metallic material with a lower work function for this contact.

Summary

In this section, HfSe₂ and TaSe₂ heterostructures have been grown. If XPS suggests the existence of an interfacial compound when HfSe₂ is deposited first, the XRD analysis indicates that TaSe₂ benefits from the better in plane orientation of the underlying HfSe₂ layer. The TaSe₂/HfSe₂/GaP stacking sequence appears thus preferable in spite of the unavoidable Ta and Hf interdiffusion. The study of the band alignments confirm that HfSe₂ layers maintain their n-type doping while in contact with TaSe₂ in spite of small charge transfer between these materials. A very high resistivity has been measured in the thick HfSe₂ layers, suggesting a good stoichiometry but low electron mobility. This leads us to consider other applications for HfSe₂ layers, even though the first attempt of a tunneling diode was not conclusive.

Conclusion

HfSe₂ is a semiconducting TMDC which has only been found in the 1T phase. The HfSe₂ layers grown on GaP exhibit either a poor morphology, attributed to the formation of FCC Ga₂Se₃ at high growth temperature or metallic defects at 250 °C. After annealing though, the properties of HfSe₂ layers show little dependence on the growth parameters, and rather depends on the annealing temperature and the thickness. Thick layers not only revealed a better crystallinity, but also a complete lattice relaxation by contrast to thin layers that are partially strained due to the small lattice mismatch with GaP. Despite all layers exhibits a n-type character, a shift of the valence band maximum from 0.7–1.0 to 0.65 eV is also observed when increasing the thickness from 3 to 15 MLs.

Si(111) substrates have also been considered for the growth of HfSe₂. For this, a substrate termination consisting of a GaSe half-monolayer has been prepared using a self-limiting method. The good chemical and electronic passivation and unique rotational alignment of the Si-GaSe surface makes it promising for vdW epitaxy. However, the GaSe layer is degraded during HfSe₂ growth at 250 °C and evaporates around 600 °C. It is replaced by an interfacial amorphous SiSe_x compound certainly favored by the high Se flux. Consequently, both the crystallinity and in-plane alignment of the HfSe₂ layer grown on Si substrates appear largely degraded compared to those grown on GaP.

In the last section, TaSe₂ is suggested as a potential contact for HfSe₂. If the study of TaSe₂ and HfSe₂ heterostructures underscores the interdiffusion of the two materials as a main issue, it also highlights the good rotational orientation of the TaSe₂ layer grown on HfSe₂ as an encouraging result. Even if the band alignments demonstrate a limited charge transfer between these materials due to their similar work functions, the electrical characterizations reveal several challenges that remain to be addressed. The high resistivity of the layers makes the measurements of the carrier mobility and the extraction of the contact resistance impossible. Conversely, a conduction through defects is identified in vertical heterostructures. Finally, the air sensitivity of the HfSe₂ appears as an important concern for processing and the stability of the devices.

Conclusion

This thesis explored the growth of TMDCs on 3D semiconducting substrates using MBE. After a survey of the large diversity of compounds and properties, this work focused on a metallic one, TaSe₂, and a semiconducting one, HfSe₂. The presentations of the existing growth techniques highlighted the needs for an improvement of the crystallinity of layers grown using MBE and the different strategies to achieve this. Even though the lattice mismatch is not an issue in vdW epitaxy, the choice of an appropriate substrate is a determining factor. However, the use of conventional semiconducting substrates is highly desirable for the developments at larger scale.

The surface passivation of GaP and GaAs with selenium is demonstrated, then the benefits of these substrates are compared through the growth of TaSe₂. Focusing first on GaP, the selective growth of 1H and 1T-TaSe₂ is achieved by varying the growth temperature, although the metastability of the 1T phase is highlighted. In particular, a significant influence of the thickness, and more probably of the cluster size, is revealed. Hence, very little 1T phase is found in the few-layer samples, which consisted mainly of a mixture of 2H_a and 3R stackings. At low temperature, the films exhibit a small grain size but a smooth morphology. Both the grain size and the in-plane orientation are improved at higher growth temperatures, but the samples experience then a substantial surface roughening attributed to the formation of Ga₂Se₃, which can be evaporated around 650 °C during a post-growth annealing, leading to a partial recovery of the morphology. The easier incorporation of Se in GaAs makes this substrate particularly prone to this effect, and therefore less suitable than GaP, which is otherwise very similar. Finally, the monolayers grown at 550-600 °C reveals 20-nm large domains, with a good in-plane orientation and a suppression of mirror twins demonstrated at the nucleation stage. However, these temperatures cannot be employed for few-layers which suffer from a Se-deficiency above 500 °C along with the formation of an undesired TaP compound at the TaSe₂/GaP interface. Regarding the electronic properties, the H phases appear as conventional metals, exhibiting a resistivity of $2 \pm 1 \text{ } \Omega \cdot \text{m}$ at 300 K in few-layers, while the 1T phase obtained in single layers not only exhibits the expected $\sqrt{13} \times \sqrt{13}$ CDW, but also reveals a much higher resistivity and a 0.13 eV band gap, confirming that it is a Mott insulator at room temperature.

This work has then investigated the growth of HfSe₂ and related heterostructures. Contrasting with the influence of the growth temperature in TaSe₂, the crystalline quality of the HfSe₂ layers grown on GaP is nearly independent of the growth conditions. Instead, the annealing temperature and the thickness are found to play a determining role. Interestingly, the small lattice mismatch between HfSe₂ and GaP induces some strain in the thin layers which is released in thicker films alongside an improvement of the crystalline quality. The use of Si (111) substrates is also considered, since the self-limiting growth of a GaSe half-monolayer is shown to efficiently passivate their surface and exhibited a single rotational orientation. However, it becomes unstable after the deposition of HfSe₂ and finally evaporates around 600 °C. If the high Se flux prevents the formation of HfSi_x, the appearance of a SiSe_x compound seems responsible for a much more degraded crystalline quality compared to the samples grown on GaP. Then, the growth of TaSe₂/HfSe₂ and HfSe₂/TaSe₂ heterostructures on GaP are compared, and in both cases, the band alignments reveal a small electron transfer from HfSe₂ to TaSe₂. Overall, the HfSe₂ layers exhibit consistently a n-type character which is however reduced in thick layers. Indeed, the electrical characterization of the HfSe₂ layers revealed a very high resistivity

in agreement with a low residual doping, but also suggesting a low carrier mobility. Finally, the investigation of a vertical heterostructure suggesting a conduction through defects further confirms the hypothesis that an improvement of the layer crystallinity is mandatory for the use of HfSe₂ in electronic applications.

Overall, either a high growth temperature, as shown in TaSe₂, or a high annealing temperature, as revealed in HfSe₂ is beneficial to improve the crystallinity of TMDC layers. However, the chemical stability of the substrates at such temperatures is a real concern as illustrated by the formation of undesired Ga₂Se₃, TaP, or SiSe_x compounds. Among the three substrates studied in this thesis, GaP appears the most suitable, leading to a better morphology than on GaAs and a better crystallinity than on Si, but it is also the most expensive. Inversely, the use of Si substrate is appealing for large scale integration, but it would require a more stable substrate termination than the GaSe half-layer. The growth of lattice matched GaP on Si could be considered but the temperature would be still limited to circa 650 °C. The wide-bandgap GaN and AlN, and insulating Al₂O₃ are currently the best alternatives for improved thermal stability, but unlike the zinc-blende substrates investigated in this thesis, the suppression of mirror twins may be less straightforward on wurtzite (0001) surfaces, while the control of the rotational alignment on Al₂O₃ appears particularly challenging.³⁰² In this regard, substrate engineering strategies exploiting step bunching³⁰³ and substrate miscut^{263,267} seem promising. However, the use of insulating CaF₂ that have been recently proposed as a gate dielectric⁴⁷⁰ is also an appealing option given its similar FCC structure and lattice parameter matched to Si.

Besides potential improvements of the material quality, the successful growth of wafer-scale continuous TMDC layers encourage us to consider the fabrication of devices. In particular, electrical contacts are required to demonstrate a potential resistive switching in the Mott insulating 1T-TaSe₂ monolayer. Regarding the lateral transport in HfSe₂, although better metallic contacts could be beneficial, the high resistivity appears currently as the bottleneck, for which a modulation of the electron density through a gate would be valuable to make a transistor. In this work, a physical mask has been employed to avoid transfer or lithography processes, but the large broadening of the patterns and the very limited number of devices that could be made highlight the limits of this approach. In the near future, it would be possible to deposit contacts through a stencil mask with smaller apertures that has been developed by Victor Vanduyngaert for NbSe₂. The use of a III-V-based semiconducting backgate can be considered, following the successful implementation of a GaInP/GaAs stack at IEMN by Clément Barbot, although more temperature stable lattice-matched combinations such as AlAs/GaAs, AlP/GaP or GaP/Si would be preferred.

In the long term, however, the integration of an oxide gate dielectric and the use of lithography processes will be unavoidable to increase the device performances and density to industrial standard. This implies numerous challenges to address, notably to develop metal deposition, oxide growth and etching procedures that do not degrade the TMDC layers underneath. TaSe₂ could be valuable as a metallic contact in this context. The lack of material-selective etching solutions for TMDCs may be circumvented by recent layer-by-layer etching techniques.^{471–473} Despite most research has focus on the air-stable WX₂ and MoX₂, the rapid oxidation of HfSe₂ could be turned into an advantage to form HfO₂, a high- κ dielectric.³⁰ To this end, a study of the oxidation kinetics is mandatory to precisely control the remaining HfSe₂ thickness, and ensure that it does not oxidize through grain boundaries, which are frequent in MBE-grown materials.

Finally, bringing valuable insights the influence of the TMDC growth parameters and a better understanding of substrate-layer interactions in 2D/2D and 2D/3D heterostructures, this work represents a step forward on a very long way toward 2D-material-based electronics.

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Appendices

A Mask for MBE with cotations

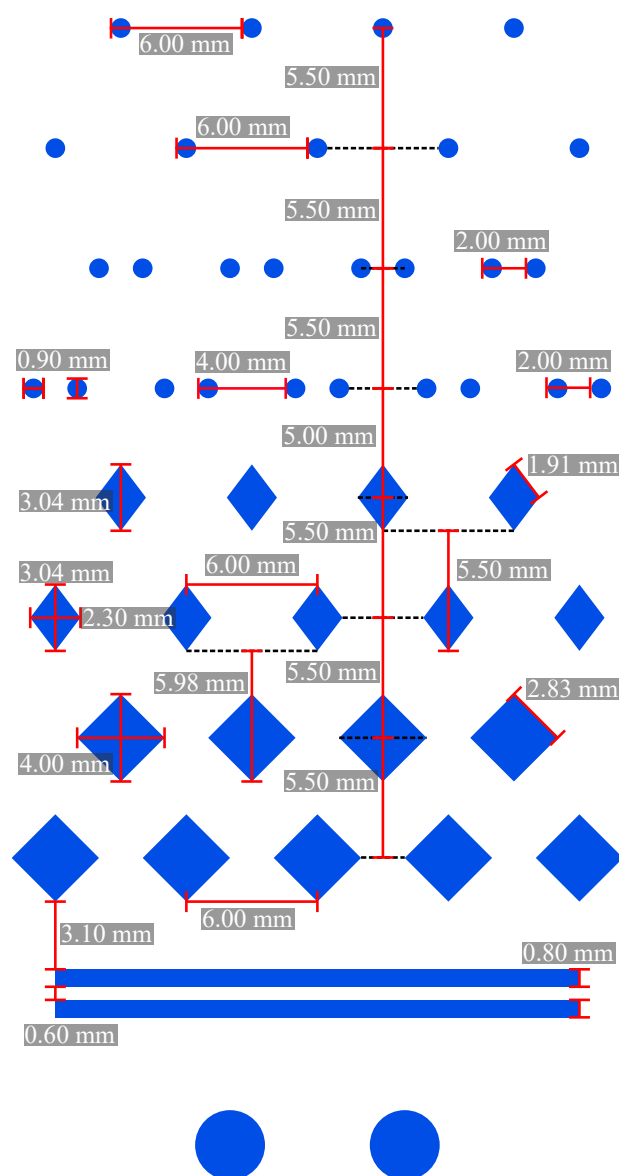


Figure 31: Mask patterns with targeted dimensions.

B Diffraction peak position calculation

This appendix presents tables for XRD peak position and the methods to calculate them.

B.1 Calculation method

The peak positions are deduced from the Bragg's law (Eq. 2.21) with the interplanar distances calculated using the following formula for a cubic lattice

$$d_{hkl} = \frac{1}{\sqrt{h^2 + k^2 + l^2}} \quad (3)$$

or for hexagonal one

$$d_{hkl} = \frac{a}{\sqrt{\frac{4}{3} \frac{h^2 + k^2 + hk}{a^2} + \left(\frac{l}{c}\right)^2}}. \quad (4)$$

The lattice parameters a and c are summarized in Table 12.

Material	Space group	a (Å)	c (Å)
Si	Fd $\bar{3}$ m	5.431 ⁴⁷⁴	-
GaP	F $\bar{4}$ 3m	5.4505 ⁴⁷⁴	-
GaAs	F $\bar{4}$ 3m	5.65325 ⁴⁷⁴	-
1T-HfSe ₂	P $\bar{3}$ m1	3.733	6.146 ⁴⁴²
1T-TaSe ₂	P $\bar{3}$ m1	3.4769	6.2722 ¹⁰²
2H-TaSe ₂	P6 ₃ /mmc ⁴⁷⁵	3.4391	12.7067
3R-TaSe ₂	R3m	3.4348	19.177 ¹⁰²
Se	P3 ₁ 21	4.366	4.953 ⁴⁷⁶

Table 12: Crystal parameter used for XRD peak calculation.

The calculation has been made for every combination of the integers h , k and l from -12 to 12, then all diffracting angles larger than 120° are removed. For the 1T phase, the calculation is done with the primitive cell, which means that all planes diffract. For 2H and 3R phase, the considered cell is larger resulting in many d_{hkl} in the range of interest. However, it is no longer a primitive cell so many of them does not result in a diffraction peak for symmetry reasons. Such extinction conditions can be found in the *International tables for crystallography*⁴⁷⁷ provided that the space group of the material and the atom positions in the lattice are known. Comparing the Tables 17, 18, and 19, it is seen that the (00 l) planes of 1T-TaSe₂ are confounded with (002 l) and (003 l) of 2H and 3R respectively, except for the small position shift due to the slightly different monolayer height. Similarly, the $\{hk0\}$ planes are almost identical. Finally, neither the in-plane nor out-of-plane diffraction patterns can be used to distinguish those phases, explaining why ($\bar{1}0l$) planes have been used in the literature to this purpose.¹⁰⁰ Note that for readability, the equivalent planes are removed after consideration of the extinction conditions.

B.2 Si peak positions

Families of planes	2θ ($^\circ$)	2θ with $K\beta$ ($^\circ$)
$\{111\}$	28.46	25.65
$\{220\}$	47.34	42.51
$\{311\}$	56.17	50.32
$\{400\}$	69.19	61.69
$\{331\}$	76.45	67.94
$\{422\}$	88.12	77.8
$\{511\}$	95.05	83.53
$\{333\}$	95.05	83.53
$\{440\}$	106.83	92.95
$\{531\}$	114.23	98.63
$\{620\}$	127.72	108.33
$\{533\}$	137.12	114.39

Table 13: XRD peak positions calculated for Si.

B.3 GaP and GaAs peak positions

Families of planes	2θ (°)	2θ with $K\beta$ (°)	Families of planes	2θ (°)	2θ with $K\beta$ (°)
{111}	28.36	25.56	{111}	27.32	24.63
{200}	32.86	29.6	{200}	31.65	28.52
{220}	47.16	42.35	{220}	45.37	40.77
{311}	55.95	50.13	{311}	53.78	48.21
{222}	58.67	52.52	{222}	56.38	50.5
{400}	68.91	61.45	{400}	66.11	59.02
{331}	76.12	67.66	{313}	72.94	64.93
{420}	78.47	69.67	{420}	75.16	66.83
{422}	87.72	77.47	{224}	83.83	74.21
{511}	94.6	83.16	{511}	90.24	79.56
{333}	94.6	83.16	{333}	90.24	79.56
{440}	106.28	92.52	{440}	100.96	88.31
{531}	113.6	98.16	{531}	107.56	93.52
{600}	116.12	100.05	{442}	109.81	95.27
{442}	116.12	100.05	{600}	109.81	95.27
{620}	126.89	107.76	{620}	119.18	102.3
{533}	136.09	113.76	{533}	126.81	107.7
{622}	139.5	115.82	{622}	129.52	109.54
			{444}	141.73	117.11

Table 14: XRD peak positions calculated for GaP.

Table 15: XRD peak positions calculated for GaAs.

B.4 HfSe₂ peak positions

Families of planes	2θ
$\{001\}$	14.41
$\{100\}$	27.59
$\{002\}$	29.06
$\{101\}$	31.26
$\{102\}$	40.5
$\{003\}$	44.21
$\{2\bar{1}0\}$	48.79
$\{111\}$	51.14
$\{103\}$	52.91
$\{200\}$	56.97
$\{112\}$	57.79
$\{201\}$	59.09
$\{004\}$	60.23
$\{202\}$	65.21
$\{104\}$	67.49
$\{2\bar{1}3\}$	67.94
$\{203\}$	74.82
$\{005\}$	77.68
$\{3\bar{1}0\}$	78.23
$\{3\bar{1}1\}$	80.07
$\{114\}$	81.06
$\{105\}$	84.28
$\{3\bar{1}2\}$	85.52
$\{204\}$	87.61
$\{300\}$	91.35
$\{301\}$	93.15
$\{3\bar{1}3\}$	94.55
$\{2\bar{1}5\}$	97.34
$\{006\}$	97.63
$\{302\}$	98.59
$\{205\}$	103.98
$\{106\}$	104.27
$\{3\bar{1}4\}$	107.43
$\{303\}$	107.86
$\{220\}$	111.39
$\{221\}$	113.34
$\{2\bar{1}6\}$	118.29
$\{310\}$	118.58
$\{222\}$	119.38

Table 16: XRD peak positions calculated for 1T-HfSe₂.

B.5 TaSe₂ peak positions

Families of planes	2θ (°)
{001}	14.12
{002}	28.46
{100}	29.67
{101}	33
{102}	41.58
{003}	43.27
{110}	52.65
{103}	53.35
{2 $\bar{1}$ 1}	54.79
{004}	58.9
{112}	60.93
{200}	61.6
{201}	63.55
{104}	67.32
{202}	69.22
{113}	70.44
{005}	75.84
{203}	78.25
{114}	82.92
{105}	83.48
{3 $\bar{1}$ 0}	85.28
{3 $\bar{1}$ 1}	87.01
{204}	90.45
{3 $\bar{1}$ 2}	92.21
{006}	95.03
{2 $\bar{1}$ 5}	98.55
{300}	100.36
{3 $\bar{1}$ 3}	100.93
{301}	102.13
{106}	102.64
{205}	106.24
{302}	107.5
{214}	113.64
{303}	116.86
{007}	118.71
{2 $\bar{1}$ 6}	118.75

Table 17: XRD peak calculated positions for 1T-TaSe₂.

Families of planes	2θ (°)
{002}	13.94
{004}	28.09
{100}	30
{102}	33.22
{104}	41.56
{006}	42.69
{106}	53.06
{110}	53.27
{112}	55.35
{008}	58.07
{114}	61.3
{200}	62.35
{202}	64.24
{108}	66.74
{204}	69.74
{2 $\bar{1}$ 6}	70.55
{0010}	74.7
{206}	78.52
{1010}	82.54
{2 $\bar{1}$ 8}	82.71
{210}	86.44
{212}	88.13
{208}	90.41
{214}	93.19
{0012}	93.44
{2 $\bar{1}$ 10}	97.94
{1012}	101.19
{216}	101.71
{300}	101.88
{302}	103.61
{2010}	105.79
{304}	108.89
{218}	114.15
{1112}	117.52
{306}	118.09

Table 18: XRD peak positions calculated for 2H-TaSe₂.

Families of planes	2θ (°)
{003}	13.85
{006}	27.91
{101}	30.41
{10 $\bar{2}$ }	31.49
{104}	35.52
{015}	38.29
{009}	42.42
{107}	44.98
{018}	48.79
{110}	53.34
{113}	55.39
{1010}	57.15
{0012}	57.68
{116}	61.27
{10 $\bar{1}$ 1}	61.67
{20 $\bar{1}$ }	62.65
{202}	63.27
{204}	65.73
{205}	67.55
{119}	70.41
{207}	72.28
{208}	75.18
{0210}	81.98
{1112}	82.44
{2011}	85.89
{3 $\bar{1}$ 1}	86.76
{3 $\bar{1}$ 2}	87.32
{3 $\bar{1}$ 4}	89.54
{125}	91.21
{3 $\bar{1}$ 7}	95.66
{218}	98.46
{300}	102.06
{303}	103.77
{2110}	105.28
{306}	108.98
{3 $\bar{1}$ 11}	109.35
{309}	118.08

Table 19: XRD peak positions calculated for 3R-TaSe₂.

B.6 Se

Families of planes	2θ (°)
$\{100\}$	23.53
$\{101\}$	29.73
$\{110\}$	41.36
$\{102\}$	43.69
$\{2\bar{1}1\}$	45.4
$\{200\}$	48.13
$\{201\}$	51.76
$\{003\}$	55.67
$\{112\}$	56.17
$\{103\}$	61.26
$\{202\}$	61.73
$\{210\}$	65.29
$\{3\bar{1}1\}$	68.31
$\{2\bar{1}3\}$	71.67
$\{300\}$	75.42
$\{203\}$	76.62
$\{3\bar{1}2\}$	77.04
$\{301\}$	78.27
$\{104\}$	81.86
$\{302\}$	86.68
$\{220\}$	89.87
$\{3\bar{1}3\}$	91.03
$\{2\bar{1}4\}$	91.41
$\{221\}$	92.64
$\{310\}$	94.63
$\{204\}$	96.19
$\{311\}$	97.43
$\{303\}$	100.62
$\{222\}$	101.04
$\{4\bar{1}2\}$	105.94
$\{105\}$	107.12
$\{400\}$	109.28
$\{214\}$	110.93
$\{401\}$	112.25
$\{223\}$	115.7
$\{2\bar{1}5\}$	117.43

Table 20: XRD peak positions calculated for trigonal Se.

C List of publications

Articles

- H. Koussir, Y. Chernukha, C. Sthioul, E. Haber, N. Peric, et al. “Large-area epitaxial Mott insulating 1T-TaSe₂ monolayer on GaP(111)B”. *Nano Letters* 23.20 (2023), pp. 9413–9419. DOI: <https://doi.org/10.1021/acs.nanolett.3c02813>
- C. Sthioul, Y. Chernukha, H. Koussir, C. Coinon, G. Patriarche, et al. “Thickness dependence in phase formation and properties of TaSe₂ layers grown on GaP(111)B”, *ACS Applied Materials & Interfaces*, 17.6 (2025), 10027-10037. DOI: <https://doi.org/10.1021/acsami.4c17204>
- N. Chapuis, C. Sthioul, A. Mahmoudi, M. Bouaziz, C. Coinon, et al. “Electronic properties of the selenium passivated GaP(111)B surface: Towards growth of large scale quasi-van der Waals 2D/3D heterostructure”. *Physical Review Materials* 9.7 (2025), p. 074002. DOI: <https://doi.org/10.1103/pv8b-89gg>

Conferences

- C. Sthioul, H. Koussir, Y. Chernukha, N. Chapuis, E. Haber, et al. “Molecular beam epitaxy of TaSe₂ on GaP(111)B”. In: *Colloque du GDR/GDR-I HOWDI*. 2023.
- C. Sthioul, Y. Chernukha, H. Koussir, C. Coinon, G. Patriarche, et al. “Growth of metallic TaSe₂ on GaP(111)B substrates”. In: *23rd International Conference on Molecular Beam Epitaxy (ICMBE 2024)*. 2024.
- C. Sthioul, Y. Chernukha, H. Koussir, C. Coinon, G. Patriarche, et al. “Epitaxial 2D HfSe₂ Semiconductor/TaSe₂ Metal van der Waals Heterostructure”. In: *23rd European Workshop on Molecular Beam Epitaxy (EuroMBE 2025)*. 2025.