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Van der Waals epitaxy of WSe_2 , HfSe_2 and their heterostructure on $\text{GaP}(111)_\text{B}$ substrate in a tunnelling device perspective

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Epitaxie van der Waals de WSe_2 , HfSe_2 et de leur hétérostructure sur substrat $\text{GaP}(111)_\text{B}$ dans la perspective de dispositifs tunnel

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Après cela je considèrai en général ce qui est requis à une proposition pour être vraie et certaine; car puisque je venais d'en trouver une que je savais être telle, je pensai que je devais aussi savoir en quoi consiste cette certitude. Et ayant remarqué qu'il n'y a rien du tout en ceci: je pense, donc je suis, qui m'assure que je dis la vérité, sinon que je vois très clairement que pour penser il faut être, je jugeai que je pouvais prendre pour règle générale que les choses que nous concevons fort clairement et fort distinctement sont toutes vraies, mais qu'il y a seulement quelque difficulté à bien remarquer quelles sont celles que nous concevons distinctement.

René Descartes

VAN DER WAALS EPITAXY OF WSe₂, HfSe₂ AND THEIR HETEROSTRUCTURE ON GaP(111)_B SUBSTRATE IN A TUNNELLING DEVICE PERSPECTIVE**Abstract**

Two-dimensional materials (2DMs) offer unique properties primarily due to their crystallographic structure, which consists of weakly coupled layers composed of one to few atomic planes where the atoms are covalently bonded. This specific structure results in the absence of dangling bonds at the surface, allowing the formation of heterostructures without the need to adapt the crystal lattice parameter. Among 2DMs, **transition metal dichalcogenides (TMDCs)** of formula MX₂ (M=metal, X=Se, Te or S) are particularly interesting because, unlike graphene, some of them have band gaps ranging from 0.5 to 2 eV and present a wide variety of band structure alignments. These properties make TMDCs promising candidates for various components, including those based on the inter-band tunnelling effect. Until now, most devices have been manufactured using exfoliated or transferred layers or flakes, which introduces significant issues regarding interface integrity, precise rotational alignment between successive layers, and process reliability.

In the last decade, **Molecular Beam Epitaxy (MBE)** growth has garnered significant interest in developing TMDC-based heterostructures, especially on 2D substrates like graphene, h-BN, or mica, due to the natural van der Waals interface between the epi-layer and the substrate surface. Additionally, a new generation of heterojunctions has emerged using 3D substrates such as insulating Al₂O₃(0001) or AlN(0001), emphasizing the critical importance of surface preparation before growth. Recently, the successful growth of a WSe₂ monolayer as well as that of large-area, highly oriented MoSe₂/WSe₂ heterostructures have been demonstrated on a selenium-passivated GaAs(111)_B surface. This raises new interest in using III-V semiconductors as substrates for TMDC-based optoelectronic and microelectronic device development. However, Monte Carlo simulations have highlighted the necessity of high growth temperatures to enhance the TMDC grain size, which makes GaP a suitable alternative to GaAs, thanks to its similar crystallography and significantly higher thermal stability.

In this work, we study the MBE growth of few-layer WSe₂ and HfSe₂, as well as that of the HfSe₂/WSe₂ heterostructure on a GaP(111)_B substrate. Each step of the process has been investigated, with particular emphasis on the substrate surface preparation, the crystalline quality of the obtained layers and the preservation of the interface integrity of the heterojunction. We show that the use of a combination of atomic hydrogen and cracked phosphine in a three-step deoxidation sequence allows to get a smooth deoxidized GaP(111)_B surface. To favour the formation of a quasi van der Waals gap between the substrate and the TMDC overlayer, selenium termination of the GaP(111)_B surface is then achieved. Thanks to a combination of experimental techniques, we then demonstrate the epitaxy of WSe₂ and HfSe₂ on GaP(111)_B-Se, emphasizing the critical role of the growth temperature and subsequent Se-annealing treatment on the polytype formation, structural and morphological properties. The resulting layers show clear epitaxial relationships with the GaP(111)_B substrate and a well-defined van der Waals interface. WSe₂ reveals a p-type doping and a staggered type-II band alignment with the GaP substrate, while HfSe₂ exhibits a type-I band alignment and a highly n-doped character. Finally, we discuss the challenges in developing a GaP/HfSe₂/WSe₂ heterostructure due to the formation of a (Hf/W)Se_x compound, whereas the GaP/WSe₂/HfSe₂ stacking presents promising results with a staggered type-II band alignment leading to a p-n junction.

Keywords: material science, transition metal dichalcogenides, molecular beam epitaxy, photoelectron spectroscopy, grazing incidence x-ray diffraction, transmission electron microscopy

ÉPITAXIE VAN DER WAALS DE WSe_2 , HfSe_2 ET DE LEUR HÉTÉROSTRUCTURE SUR SUBSTRAT $\text{GaP}(111)_\text{B}$ DANS LA PERSPECTIVE DE DISPOSITIFS TUNNEL**Résumé**

Les **matériaux bidimensionnels (2MDs)** offrent des propriétés uniques principalement dues à leur structure cristallographique, composée de couches faiblement couplées constituées d'un à quelques plans atomiques où les atomes sont liés de manière covalente. Cette structure spécifique entraîne l'absence de liaisons pendantes à la surface, permettant la formation d'hétérostructures sans nécessité d'adaptation du paramètre de maille. Parmi les 2MDs, les **dichalcogénures de métaux de transition (DMTs)**, de formule MX_2 (M =métal, X =Se, Te ou S), sont particulièrement intéressants car certains d'entre eux possèdent des bandes interdites allant de 0,5 à 2 eV et offrent une grande variété d'alignements de bandes. Ces caractéristiques en font, des candidats prometteurs pour le développement de divers composants, notamment ceux basés sur l'effet tunnel inter-bandes. Jusqu'à présent, la plupart des dispositifs ont été fabriqués en utilisant des couches ou des flocons exfoliés ou transférés, introduisant des problèmes significatifs concernant la qualité des interfaces ainsi que la fiabilité du processus.

Au cours de la dernière décennie, la croissance **épitaxiale par jets moléculaires (EJM)** a suscité un grand intérêt pour le développement d'hétérostructures basées sur les DMTs, notamment sur des substrats 2D comme le graphène, h-BN ou le mica en raison de l'interface van der Waals naturelle entre la couche épitaxiée et le substrat. En parallèle, une nouvelle génération d'hétérojonctions a émergé, utilisant des substrats 3D tels que $\text{Al}_2\text{O}_3(0001)$ ou $\text{AlN}(0001)$, et soulignant l'importance cruciale de la préparation de la surface avant croissance. Ainsi, la croissance d'une monocouche de WSe_2 ou celle d'une hétérostructure $\text{MoSe}_2/\text{WSe}_2$ ont été réalisées sur une surface $\text{GaAs}(111)_\text{B}$ précédemment passivée sous sélénium, suscitant un nouvel intérêt pour l'utilisation de semi-conducteurs III-V comme substrats pour le développement de dispositifs basés sur les DMTs. Cependant, des simulations Monte Carlo ont souligné la nécessité de températures de croissance élevées afin d'améliorer la taille des grains des DMTs, faisant du GaP une alternative appropriée au GaAs, grâce à sa stabilité thermique nettement supérieure.

Dans ce travail de thèse, nous explorons la croissance par EJM de quelques couches de WSe_2 et de HfSe_2 , ainsi que celle de l'hétérostructure $\text{HfSe}_2/\text{WSe}_2$ sur un substrat $\text{GaP}(111)_\text{B}$. Chaque étape du processus a été étudiée, avec une attention particulière à la préparation du substrat, à la qualité cristalline des couches obtenues et à la préservation de l'intégrité de l'interface de l'hétérojonction. Nous montrons que l'utilisation d'une combinaison d'hydrogène atomique et de phosphine craquée dans une séquence en trois étapes permet d'obtenir une surface $\text{GaP}(111)_\text{B}$ lisse et complètement désoxydée. Pour favoriser la formation d'un quasi-gap de van der Waals entre le substrat et la couche DMT, la terminaison au sélénium de la surface de $\text{GaP}(111)_\text{B}$ est ensuite réalisée. Grâce à une combinaison de techniques expérimentales, nous démontrons l'épitaxie de WSe_2 et de HfSe_2 sur $\text{GaP}(111)_\text{B}\text{-Se}$, en soulignant le rôle crucial de la température de croissance et d'un recuit sous Se sur la formation des polytypes, les propriétés structurales et morphologiques. Les couches résultantes présentent des relations épitaxiales claires avec le substrat $\text{GaP}(111)_\text{B}$ et une interface van der Waals bien définie. WSe_2 présente un dopage de type p et un alignement de bandes de type II avec le substrat GaP, tandis que HfSe_2 révèle un alignement de bandes de type I et un caractère fortement dopé n. Enfin, nous discutons des défis du développement d'une hétérostructure $\text{GaP}/\text{HfSe}_2/\text{WSe}_2$ en raison de la formation d'un composé $(\text{W}/\text{Hf})\text{Se}_x$, tandis que l'empilement $\text{GaP}/\text{WSe}_2/\text{HfSe}_2$ montre des résultats prometteurs avec un alignement de type II et une jonction p-n claire.

Mots clés : science des matériaux, dichalcogénures de métaux de transition, épitaxie par jets moléculaires, spectroscopie photoélectronique, diffraction des rayons x en incidence rasante, microscopie électronique à transmission

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Introduction

With the increasing demand for devices with improved performance, strong and active efforts have been deployed to add new functionalities to standard silicon devices, addressing new and diverse challenges. If germanium or III-V semiconductors (among others) have been largely considered, the emergence of **Two-dimensional Materials (2DMs)**, and their promising characteristics ranging from semi-metal to semiconductors to insulating, have driven huge interests for the last decades¹.

In contrast with conventional three-dimensional (3D) bulk materials, 2DMs are defined by the reduction of one dimension down to one or a few atomic planes, without surface dangling bonds, the successive 2D-layers being linked together via van der Waals interactions². This specific feature is very appealing for heterostructure fabrication since it relaxes the constraint of lattice parameter matching encountered with 3D materials. Introduced since the late 1940's (hexagonal BN was used in cosmetics in 1940, P.R. Wallace³ evidenced graphene in bulk graphite in 1948), 2DMs have been studied rather scarcely until the successful mechanical exfoliation of single and few-layer graphene demonstrated by Novoselov & Geim in 2004. From this point, their interest have significantly increased, motivating the rapid development of novel 2D layered materials (Table 1), which includes h-BN, black phosphorus, numerous oxides and **Two-dimensional Transition Metal Dichalcogenide (TMDC)**, already described by Wilson & Yoffe⁴ in 1969.

graphene family	graphene	hBN 'white graphene'	BCN	fluorographene	graphene oxide
2D chalcogenides	MoS ₂ , WS ₂ , MoSe ₂ , WSe ₂		semiconducting dichalcogenides: MoTe ₂ , WTe ₂ , ZrS ₂ , ZrSe ₂ , etc.	metallic dichalcogenides: NbSe ₂ , NbS ₂ , TaS ₂ , TiS ₂ , NiSe ₂ , etc.	
				layered semiconductors: GaSe, GaTe, InSe, Bi ₂ Se ₃ , etc.	
2D oxides	micas, BSCCO	MoO ₃ , WO ₃	perovskite-type: LaNb ₂ O ₇ , (Ca,Sr) ₂ Nb ₃ O ₁₀ , Bi ₄ Ti ₃ O ₁₂ , Ca ₂ Ta ₂ TiO ₁₀ , etc.		hydroxides: Ni(OH) ₂ , Eu(OH) ₂ , etc.
	layered Cu oxides	TiO ₂ , MnO ₂ , V ₂ O ₅ , TaO ₃ , RuO ₂ , etc.			OTHERS

Table 1: Current 2D library, extracted from ⁵. In **blue**, stable monolayer under ambient conditions; in **green**, probably stable in air; in **pink**, unstable in air but maybe stable in inert atmosphere. In **grey**, 3D compounds successfully exfoliated down to monolayers. Cell OTHERS includes borides, carbides, nitrides.

This last material family has shown excellent properties, such as efficient light harvesting or sensitive photo-detection, making them strongly promising for the next generation of electronic and optoelectronic devices⁶. Besides, their unique properties can be tuned to modulate the free carrier type and density for **Field Effect Transistor (FET)** and p-n junctions^{7, 8}.

Up to now, the vast majority of the 2DM-based devices have been developed using flakes obtained by exfoliation or by **Chemical Vapor Deposition (CVD)**, yet growth by **Molecular Beam Epitaxy (MBE)** has driven huge interests in the last decade. Thus, graphene monolayers have been successfully grown on SiC^{9, 10, 11}, silicon¹², h-BN¹³ and sapphire¹⁴ substrates, evidencing an alternative method to the more traditional graphitization of SiC substrates. On the other hand, monolayer and multilayer h-BN has been recently grown on nickel foil^{15, 16, 17}, cobalt thin films¹⁸ and on graphite substrates¹⁹. Last, if the epitaxial growth of TMDCs on 2D substrates like graphene²⁰, h-BN²¹ or mica²² has been widely studied, the use of 3D substrates remains less explored. Among others, MOCVD-produced AlN on silicon substrate has shown promising results due to its wide bandgap, notably creating a semiconductor-on-insulator integration scheme with MoSe₂^{23, 24}. In parallel, beyond its insulating behaviour, single crystal sapphire substrate has been also envisioned thanks to its natural hexagonal symmetry and high thermal stability, with promising results in WSe₂, MoSe₂ or PtSe₂ monolayer growth^{25, 26, 27}. On the other hand, the need of semiconducting substrates for various opto- and microelectronic applications have promoted the use of conventional III-V semiconductors as substrates, and notably GaAs(111) which was first studied by Ueno *et al.*^{28, 29} for the growth of MoSe₂ and NbSe₂ after properly passivating the surface with sulphur. Recently, Pierucci *et al.*³⁰ have successfully grown a WSe₂ monolayer on a selenium-passivated GaAs(111)_B surface, while Ohtake *et al.*³¹ demonstrated the growth of large-area, highly oriented MoSe₂/WSe₂ heterostructures on a similar substrate. Meanwhile, it has been observed³² and calculated using Monte Carlo simulation³³ that high growth temperatures are required in order to enhance the grown grain size. Considering this goal, GaP could become a suitable alternative to GaAs, thanks to its similar crystallography and a significantly higher thermal stability³⁴.

Therefore, this work propose to investigate the growth of few layers WSe₂ and HfSe₂ on GaP(111)_B as well as the growth of the HfSe₂/WSe₂ heterostructure, whose band alignment is supposed suitable for tunnel device development³⁵. Indeed, the traditional use of 3D compounds induces major issues in the tunnelling interface integrity, mainly due to the lattice matching requirement, which can be easily avoided with TMDCs. Therefore, the predicted WSe₂/HfSe₂ p-n junction with a strong type II band alignment is of great interest for tunnelling diode development. Each step of the whole process is investigated, evidencing four challenges: the substrate preparation, the optimization of both WSe₂ and HfSe₂ growth on GaP(111)_B, and the development of the WSe₂/HfSe₂ vertical heterojunction.

The chapter 1 is dedicated to overviewing the state of the art, first introducing the 2D TMDC class of materials, before reporting the different synthesis methods employed for TMDC thin film production. A third part is devoted to WSe₂ and HfSe₂, highlighting their structural and electronic specificities, before presenting a projection of a heterostructure using both materials.

The chapter 2 details the different experimental techniques used in this work for MBE growth as well as for the layer characterization.

The preparation of the GaP(111)_B surface is divided in two main steps: its deoxidation, and the selenium termination, both presented in the chapter 3. The optimization of the first process aims at the determination of the best combination of key experimental parameters, *i.e.* the atomic Hydrogen exposure time, the oxide removal temperature and the cracked Phosphine flux, to get a smooth and deoxidized surface. We then present and discuss trials of homoepitaxial growth of GaP(111)_B, although not successful within our experimental parameter range. The Selenium passivation is focused on preventing the formation of sub-surface GaSe while obtaining an efficient surface passivation and

maintaining a smooth surface suitable for further TMDC growth with a formation of a van der Waals interface.

The chapter 4 presents a thorough study of the growth and post-growth annealing temperature impact on the nucleation, the polytype formation, the morphology and structural properties of the WSe₂ epi-layer. The effect of the growth rate on the overall layer quality is also discussed, and a possible relationship between polytypism and layer thickness is highlighted. The epitaxy of a continuous pure 2H phase WSe₂ layer is then clearly established, although the maximum average grain size remains in the 30-50 nm range. Finally, the valence band offset and the band alignment at the GaP(111)_B-Se/WSe₂ interface is determined, evidencing a p-type character of the WSe₂ overlayer and a staggered type-II band alignment.

Prior to the development of the WSe₂/HfSe₂ heterojunction, the chapter 5 describes the direct growth of HfSe₂ on GaP(111)_B-Se, focusing on the impact of the growth parameters on the quality of the interface and the epi-layer. Once more, the optimization of the TMDC layer grain size is one major concern, coupled with the band alignment with the substrate. Last, we discuss the challenges in developing a GaP/HfSe₂/WSe₂ heterostructure, as this stacking tends to favour the formation of a (Hf/W)Se_x compound. On the other hand, the GaP/WSe₂/HfSe₂ stacking shows promising results with grains exceeding 50 nm in size, while exhibiting a well-defined van der Waals interface between the two TMDCs layers. We evidence the formation of a staggered type-II band alignment with a clear p-n junction.

State of the art and PhD work objectives

In this Chapter dedicated to the state of the art, we will first introduce the **Two-dimensional Transition Metal Dichalcogenide (TMDC)** class material, highlighting their structures and electronic and optical specificities. Thorough this work, we will evidence their great interests in micro and optoelectronic device development due to their unique properties. In a second time, we will report the different synthesis methods used for TMDC thin films production, ranging from top-down exfoliation to **Molecular Beam Epitaxy (MBE)** growth. A detailed discussion on this last technique will allow us to point out the different steps of the process, highlight the key parameters and their impact, and finally list the common substrates, their applications and limitations. In addition, the third part of this chapter will focus on the interests and the growth of WSe_2 and HfSe_2 , two materials selected for this work. We will detail their structural and electronic specificities, before presenting a projection of a heterostructure using both materials. Last, we will summarize the different motivations of this PhD work along with the different experimental challenges to overcome.

1.1 Two-dimensional Transition Metal Dichalcogenides (TMDCs)

1.1.1 General physical presentation and main properties

Among the 2D materials, **TMDCs** appear to be one of the most promising class of materials for new generation of nanoelectronic devices development. In this section, we present the classification of TMDCs based on their structure and then focus on the general electronic properties of semiconducting materials.

1.1.1.1 TMDC structures

The chemical formula of TMDC is described as MX_2 , where M is a **Transition Metal (TM)** from group IV to VII (Hf, Ta, W, Mo, Re . . .) and X is a chalcogen (S, Se or Te)³⁶, forming layered structures with two chalcogen atomic planes surrounding one transition metal atomic plane with strong intralayer bonding. Contrarily to 3D materials, the interlayer bonding, due to van der Waals interactions, is weak and responsible for their peculiar properties, especially the lack of surface dangling bonds and the occurrence of various layer-stacking orders. In monolayer, TMDCs can be classified in several structural phases, the most common ones being **Trigonal prismatic (1H)** and **Octahedral (1T)** unit cells coordination, as presented in Figure 1.1.

Depending on the peculiar chemical structure of the TMD, the thermodynamically stable phase can be either 1H or 1T, but other metastable phases such as orthorhombic distorted 1T' can be obtained^{37, 38}, yielding formation of hybrid structures^{39, 40}. Experimental observations have shown that TMDCs including a group VI TM are keener to form 1H stable phase and 1T' metastable phase, excepting WTe_2 ^{38, 41}, which exhibits a stable 1T' phase.

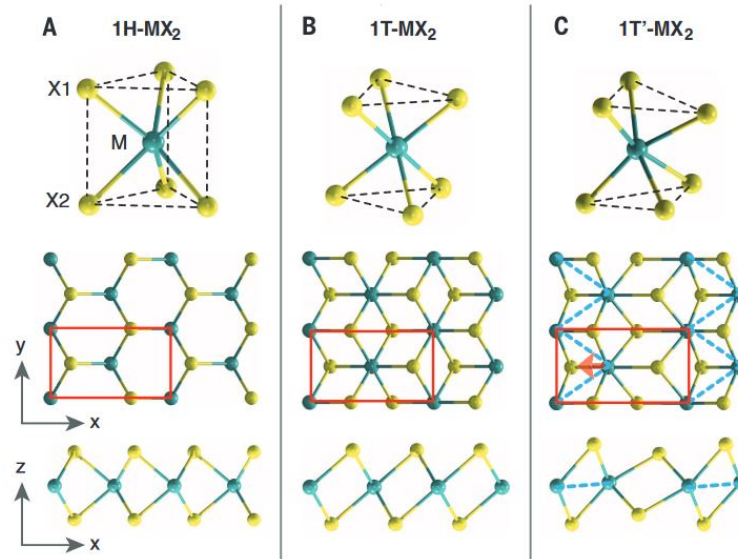


Figure 1.1: Atomistic structures of monolayer transition metal dichalcogenides MX_2 . M stands for (W, Mo) and X stands for (Te, Se, S). (A) 1H- MX_2 in ABA stacking with $P6m2$ space group. (B) 1T- MX_2 in ABC stacking with $P3m2$ space group. (C) 1T'- MX_2 , distorted 1T- MX_2 , where the distorted M atoms form 1D zigzag chains indicated by the dashed blue line. From⁴²

The stability of 1H or 1T arises from the electronic configuration of transition metal and the d-orbital splitting in each crystal field^{41, 43, 44}. For example, the d_{z^2} sub-band at lower energy in group VI-TM based TMDCs is splitting off due to the 1H coordination necessary for bonding all six valence electrons to six chalcogen atoms. As group-VI TM atoms have two electrons for filling this sub-band, the trigonal prismatic coordination 1H is stabilized^{43, 45}. On the other hand, group-IV TM atoms do not have the two electrons needed for filling the d_{z^2} sub-band, therefore 1T octahedral coordination will stabilize instead of 1H⁴⁵ in order to minimize the total energy (Figure 1.2). In the same way, the 1T lattice is reported for group-V TM based TMDCs e.g. sulphides and selenides of vanadium and tantalum, with the possibility of 1H formation in TaS_2 and TaSe_2 ^{38, 45}. Group VII TMDCs are generally in a distorted octahedral structure³⁶. In the case of unstable 1T structure, the lattice is spontaneously distorting into orthorhombic metastable 1T' phase, which can result in the formation of metal-metal bonds as observed in MoS_2 and WSe_2 single layer^{42, 46} (Figure 1.1c).

In the multilayer regime, the structural phases are classified according to different stacking orders, or polytypes. The most commonly encountered ones are referred to 2H, 3R and 1T (Figure 1.2), digits referring to the number of layers per repeat unit and the letter standing for the hexagonal, rhombohedral and tetragonal symmetry, respectively^{37, 38}.

Observation of such variety of coordination and stacking orders induces a large range of electronic properties in single or multi-layer. In 1969, Wilson & Yoffe have reported a large amount of layered TMDCs with their electronic properties⁴ (Table 1.1). Overall, 42 stable TMDCs compounds have been

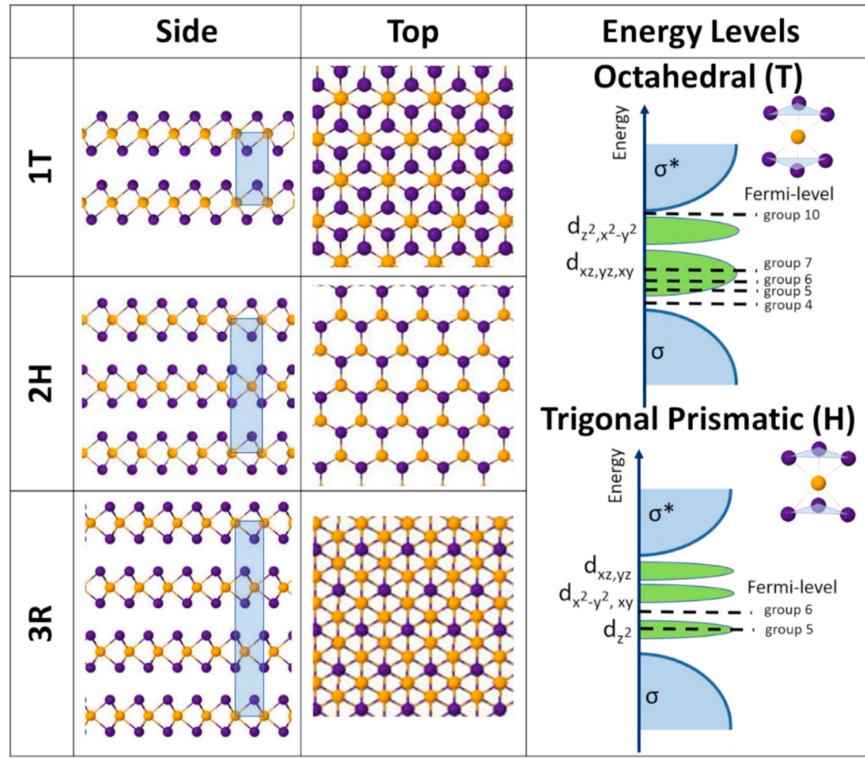


Figure 1.2: Schematic of 1T, 2H, and 3R TMDCs from ⁴⁷. The basic electron energy diagram of the octahedral and trigonal prismatic coordinated TMs is also shown. The Fermi-level position depending on the number of d-electron (group in the periodic table) are indicated.

recently identified using **Density Functional Theory (DFT)** in the **Local Density Approximation (LDA)** by Ataca et al.⁴⁸, supported by Rassmussen and Thygesen⁴⁹ using the G_0W_0 approximation, exhibiting behaviour from superconductor to semiconductor. This in turn paves the way for future innovative devices, from large area Mott insulator development with 1T-TaSe₂^{50, 51} to intercalated 1T-TiS₂ electrodes in Lithium batteries⁵² and semiconducting 2H-MoSe₂/2H-WSe₂ heterostructure in which the interlayer charge transfer can be controlled⁵³.

Group	M	Properties
IV	Ti, Hf, Zr	Semimetals, Semiconducting ($E_G=0.2-2$ eV)
V	V, Nb, Ta	Narrow band metals or semimetals. Superconducting. Charge density wave (CDW).
VI	Mo, W	Sulphides and selenides are semiconducting ($E_G \sim 1$ eV). Tellurides are semimetallic.
VII	Tc, Re	Small-gap semiconductors.
X	Pd, Pt	Sulphides and selenides are semiconducting ($E_G=0.4$ eV). Tellurides are metallic. PdTe ₂ is superconducting.

Table 1.1: Electronic properties of different layered TMDCs (from ³⁶)

1.1.1.2 Electronic and optical properties of semiconducting TMDCs

Among the semiconducting TMDCs from group IV and VI, several stable compounds ($M=Mo, W; X=S, Se$) show layer-dependent properties with an indirect to direct bandgap transition when reducing the thickness down to the monolayer due to quantum confinement. The key aspect of single layer group VI TMDCs is the location of the **Valence band maximum (VBM)** and **Conduction band minimum (CBM)** at the two high-symmetry point K and K', corresponding to the corners of the 2D hexagonal Brillouin zone^{54, 55} (Figure 1.3) and resulting in a spin splitting of the electronic bands. This phenomenon is

induced by a broken inversion symmetry (from $P6_3/mmc$ space group in layered 2H polytype⁵⁶ to $P\bar{6}m2$ space group in its single layer 1H form) and a strong spin-orbit coupling⁵⁷ originating from the metal d-orbitals. Ultimately, it can lead to the coexistence of both spin Hall and valley Hall effects in n-doped and p-doped systems, which can be also photo-induced for generating spin and valley accumulations on boundaries. This feature in group VI TMDCs drives new possibilities for investigating the so-called valleytronic field, in which the local extrema (valleys) can be tuned and used as information carriers⁵⁸. In 2012, using *ab initio* DFT in LDA, Kumar and Ahluwalia⁵⁹ have shown the thickness independence of the CBM positioned at the K point, while the VBM varies from the K point to the Γ point in bulk material, inducing a reduction of the electronic bandgap from 1.9 eV in monolayer to 1.2 eV in bulk MoS₂⁶⁰. This direct-to-indirect transition has been particularly studied using photoluminescence on exfoliated MoS₂ nanosheets, exhibiting a single and intense peak for monolayer, while displaying multiple emission peaks with low intensity for multilayer samples^{61, 62, 63}. The monolayer peak centered at 1.90 eV is attributed to the direct-gap luminescence, while the large and low intense peak at 1.59 eV in multilayer sample is attributed to indirect-gap luminescence. This "tunability" of the bandgap grows large interests for new generation of optoelectronic devices development, as it leads to a strong photoluminescence emission and excitonic effects⁶². Moreover, the theoretically predicted charge carrier mobility between 200 and 1000 cm²V⁻¹s⁻¹ for several group VI TMDCs, and between 2000 and 4000 cm²V⁻¹s⁻¹ for group IV TMDCs⁶⁴ appear very promising for electronic devices development, although practically limited by domain disorder and defects³⁸. In comparison, 8 nm thick silicon film for SOI MOSFETs provides a limited electron mobility of about 200 cm²V⁻¹s⁻¹ induced by local stress⁶⁵. Indeed, it has been found that 2D-materials mobility, and especially TMDC, is not degraded when the material thickness is reduced, in contrast with more mature materials (Figure 1.3e), which makes 2Ds particularly interesting for ultra-thin transistor development⁶⁶.

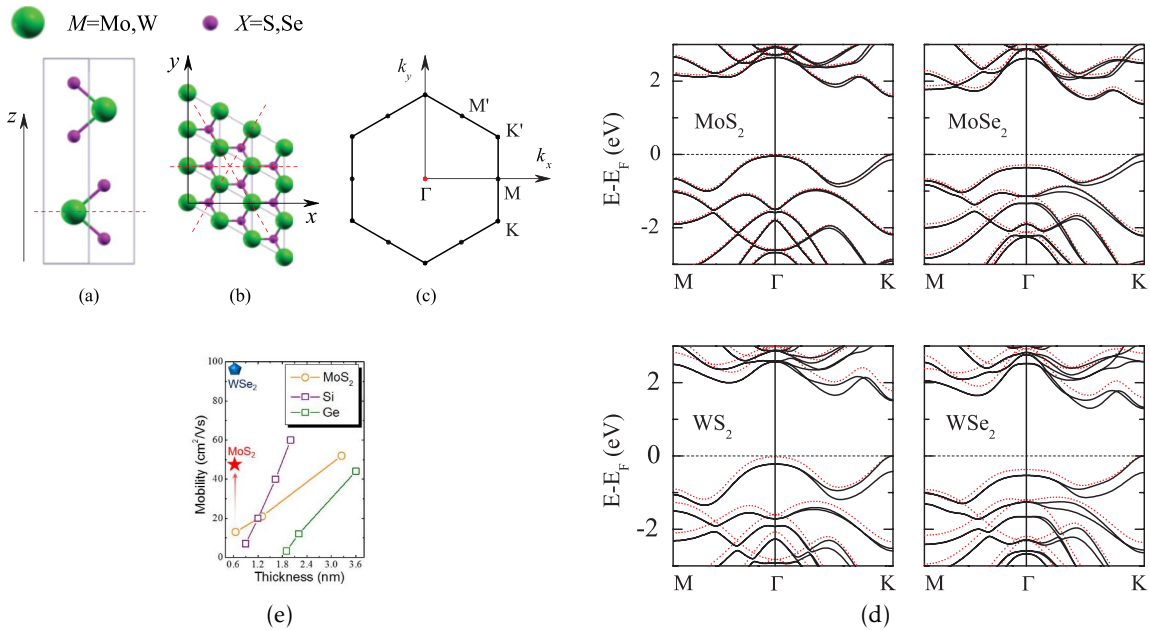


Figure 1.3: (a) Side view of the 2H-MX₂ (M=Mo, W and X=S, Se) unit cell, containing two MX₂ monolayers. (b) Top view. (c) First Brillouin zone of the MX₂ monolayer. Dashed lines indicate mirror planes. (d) Electronic band structures calculated for the MX₂ monolayer systems with (solid line) and without inclusion of the spin-orbit interaction (dotted lines). Extracted from ⁵⁵. (e) Mobility reduction with material thickness and electron mobility of grown monolayer MoS₂ and WSe₂, extracted from ⁶⁶.

Considering those promising properties and their versatility, TMDCs have been widely studied for heterojunction development that would enhance electronic, electrical and optical properties⁶⁷. For example, MoS₂/graphene hybrid system is found being a direct 2 meV band gap with high carrier mobility⁶⁸, while MoS₂/h-BN system shows indirect bandgap whose energy can be tuned with the h-BN thickness⁶⁹. It has also been shown that the band gap of h-BN/MoS₂/h-BN heterostructure undergoes an indirect-to-direct transition when applying an external increasing electric field⁷⁰ with a linear energy decrease from 0.95 to 0.45 eV, making the system very promising for optoelectronic device development. On the other hand, combining semiconducting TMDCs with different gap sizes would lead to the formation of band discontinuities, or band offsets⁷¹, which is the starting point for TMDC-based heterojunctions. As an example, it has been shown that MoX₂-WX₂ heterostructures exhibit a type-II band alignment⁷², comforted by experimental development of MoS₂-WSe₂ systems^{73, 74}. Overall monolayer MoS₂ has been the most extensively studied semiconducting TMDC, and can be used in ultrasensitive photodetectors⁷⁵, phototransistors⁷⁶ or single-layer **Metal Oxide Semiconductor Field Effect Transistor (MOSFET)**⁷⁷.

1.1.2 TMDCs synthesis

Beyond their intrinsic tremendous electronic and optical properties, the production of TMDC thin films have been widely studied by either exfoliation or synthesis. In this section, we report the different top-down and bottom-up methods, ranging from the standard mechanical exfoliation to **MBE**. A strong focus on this last technique is presented, pointing out the different thermodynamic steps of the process, highlighting the key parameters and their impact, and listing the used substrates, their applications, and limitations.

1.1.2.1 Top-down methods

Initiated by the Scotch-tape method famously used by Novoselov et al. in the production of graphene monolayer⁷⁸, the mechanical exfoliation of TMDCs from bulk material arose peculiar interests for fundamental characterization and flake-sized device development. Two mechanical methods can be distinguished: tape exfoliation, which remains until now the primary way to develop the highest quality monolayer, and metal exfoliation, which has been shortly considered because of the strong affinity of many 2D materials to metals⁷⁹. A third exfoliation method based on ionic species chemical intercalation has been widely studied since the 70s, showing promising results in photoluminescence analysis.

Li et al.⁸⁰ have summarized the MoS₂ tape exfoliation procedure, consisting in adhering a piece of scotch tape on the bulk material for a few seconds and then removing it with low angle before suppressing the excess of layered component by folding the tape. To remove the tape without altering the MoS₂ flakes, the system is transferred and gently adhered on an alumina ceramic. The adherence is maintained for a couple of hours before removing the tape and cleaning the alumina substrate with acetone to suppress adhesive residues on 20 μm large MoS₂ flakes. The exfoliation is possible because the external applied forces overcome the van der Waals adhesion between each TMDC layer (Figure 1.4). However, the angle used should be minimized to reduce as much as possible the lateral forces that are able to break the intralayer covalent bonds. Due to its simplicity, low cost and defect-free results, mechanical tape exfoliation has been widely performed for TMDC high crystal quality production. Among the first successful exfoliations and integrations of TMDCs, in 2011, Radisavljevic et al.⁷⁷ exfoliated a MoS₂ single-layer and used it as the channel material in a MOSFET, exhibiting a silicon device comparable carrier mobility of 200 cm²V⁻¹s⁻¹ and a room temperature current on/off ratio exceeding 1.108. In 2013, Li et

al. produced nanosheets of WSe_2 , TaS_2 and TaSe_2 and proposed a solution for flake thickness detection from 1 to 5 monolayers using Raman spectroscopy⁸¹, as one major drawback of tape exfoliation is its impossibility of controlling the flake size and thickness during the process. Beyond elementary physical studies, tape exfoliation has been widely used for device development. For example, it is the easiest and shortest way to produce TMDC p-n heterojunctions and homojunctions such as p- WSe_2 /n- MoS_2 ⁸², p- WSe_2 /n- MoSe_2 ⁸³ or p- MoTe_2 /n- MoTe_2 ⁸⁴ with promising results for electronic and optoelectronic applications. However, this first technique shows some major drawbacks, which are a small crystal size and an external contamination due to adhesive residues⁸⁵.

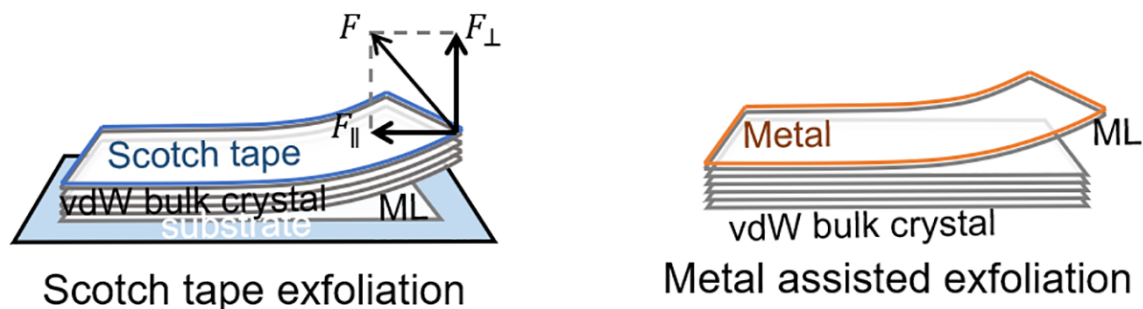


Figure 1.4: Top-down methods of tape exfoliation and metal-assisted exfoliation of 2D monolayers preparation, from ⁷⁹.

To overcome the tape pollution issue, metal-assisted exfoliation has been also considered for TMDC flake production. Particularly, it uses a 200 nm thick Au(111) surface evaporated on a mica substrate. Because of the strong chemical affinity of gold with the chalcogen atoms, it can lead to large areas (hundreds of microns) and single layer exfoliated flakes without altering the physical properties of the TMDC. It is also a totally reversible process without modifying the structure⁸⁶. Firstly developed for MoS_2 exfoliation, the method has been notably extended to MoSe_2 , MoTe_2 , WS_2 and WSe_2 , with promising results in terms of flake lateral size ($> 50\mu\text{m}$). Yet, the contamination issue remains with Au-induced defect on the surface. The metal-assisted exfoliation does not overcome the dependency to bulk crystal quality either, nor the final random localization and thickness of the flakes.

Beside these mechanical techniques, chemical exfoliation has been extensively studied since the 70s where a first method of TMDC intercalation by ionic species has been demonstrated⁸⁷. The standard procedure consists in submerging a bulk TMDC powder in a Lithium-based solution such as n-Butyllithium in order to intercalate Li atoms between the 2D layers before ultra-sonicating it with water or ethanol, which exfoliates the TMDC single-layer. During this process, intercalated Li^+ ions enlarge the space between two layers, which reduces the van der Waals interactions, and then react with water to form $\text{Li}(\text{OH})$ and H_2 gas. These two new species enlarge once more the van der Waals gap, which eventually can result in independent 2D nanosheets^{88, 89}. One major drawback of such technique is the immersion time, which is more than a day in order to intercalate sufficiently the Li^+ ions. Therefore, Zeng *et al.* have proposed a faster yet similar technique in an electrochemical cell, using the TMDC bulk material as cathode and a Lithium foil as anode for lithiation⁸⁹ (Figure 1.5). This new process appears highly reproducible, controllable and way faster than the n-Butyllithium method.

However, the increasing price of lithium compound and its flammability under ambient conditions currently leads to consider new approaches⁹⁰ like liquid phase exfoliation. This alternative process replaces the intercalated lithium source by an appropriate solvent, which should minimize the mixing

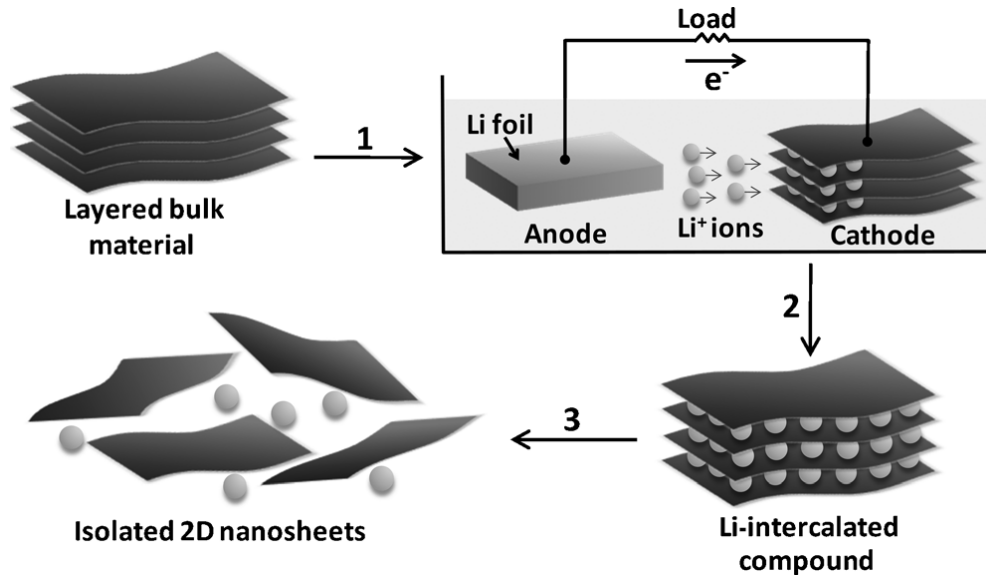


Figure 1.5: Electrochemical lithiation process for the fabrication of 2D nanosheets from the layered bulk material, from ⁸⁹.

enthalpy between the liquid and the interlayer face in order to allow the species to intercalate, and stabilize the exfoliated sheets to prevent reaggregation⁹¹. The observation of strong photoluminescence signal on the resulted freestanding TMDC nanosheets has driven huge interest of such method for optoelectronic applications^{92, 93, 94, 95}. Nevertheless, up to now liquid exfoliation has shown limited result in flake size and concentration, which makes it difficult to be considered for large-scale integration.

1.1.2.2 Bottom-up synthesis: chemical methods

Therefore, developing large-area high-quality single-crystal layers with a precise control of the electronic properties for a direct device integration remains a massive challenge using top-down methods. Bottom-up methods turn out being a suitable alternative for uniform TMDC layer development, starting with **Chemical Vapor Deposition (CVD)**. Overall, three different CVD methods have been investigated: selenization (or sulfurization) of metal layers, reaction between gaseous metal oxides and chalcogen precursors, and **MetalOrganic Chemical Vapor Deposition (MOCVD)**, which uses metalorganic precursors⁹⁶.

In 2017, Wu et al. proposed a process for MoS_2 growth using sulfurization at $750^\circ C$ of a pre-deposited 1 nm thick metallic layer on top of a sapphire substrate⁹⁷. Pure sulphur powder is evaporated at $120^\circ C$ and is chemically reacting with the Mo layer under vacuum condition. The pre-deposited metallic layer defines the thickness and the size of the final sheet, as the chemical reaction is considered as direct. However, as the metallic sheet is transferred from a sputtering system to the CVD reactor under ambient condition, a thin oxide layer is growing at the surface and is segregating into MoO_2 cluster while increasing the temperature up to $750^\circ C$. Hence, a large amount of evaporated sulphur is needed to limit this segregation and transform the whole Mo layer into MoS_2 . In the case of insufficient sulphur background pressure, the oxide layer will partially inhibit the sulfurization, resulting in Mo oxide cluster covered by thin TMDC layer. The sulfurization temperature also plays a key role in increasing the crystal quality and lateral grain size. Direct growth of metal oxide such as MoO_3 instead of Mo is one suitable possibility for controlling the formation of native oxide. Identically to the previous process, the thickness of the final TMDC layer is strongly dependent on the initial oxide layer thickness⁹⁸. The final surface

coverage and grain size also depends on the metal-oxide deposition temperature. In fact, low preparation temperature will lead to a low coverage of large grains while a high preparation temperature will exhibit the opposite behaviour⁹⁹.

A more direct and conventional CVD technique uses a combination of oxide powder (MoO_3 , WO_3 , ...) or bulk material (MoS_2 , WSe_2 , ...) and chalcogen powder or gas-source (H_2S) as precursors (Figure 1.6). The process can be summarized in four steps. At first, both sources are evaporated at high temperature into an inert gas (Ar , H_2 , N_2) carrying the species onto the substrate. A first chemical reaction takes place in this carrier gas, forming $\text{MO}_{2-x}\text{X}_x$ ($0 < x < 1$) species which are diffusing onto the target substrate. Then, those chemical species are migrating on the surface thanks to a high substrate temperature and initiate the nucleation of the TMDC¹⁰⁰. In this method, the final size of the domain is directly linked to the nucleation density, which leads to consider the impact of the growth temperature, the different species concentrations and the flow rate of the inert gas for optimizing the quality and size of the TMDC nanosheets^{101, 102}. Even though most of the studies have been performed on Si/SiO_2 substrates with promising results, the choice of a crystalline substrate with a hexagonal symmetry is needed for orienting the grown flakes and limiting the formation of grain boundaries. This can be compared to the growth of single-layer graphene on polycrystalline Cu foil resulting in a polycrystalline film with numerous grain boundaries, which are limiting the carrier mobility and thus the extraordinary graphene properties¹⁰³. Furthermore, Ago *et al.*¹⁰⁴ have demonstrated that CVD-grown MoS_2 flakes on top of such polycrystalline graphene sheet are orienting themselves with the substrate in such a way that each side of the MoS_2 grains is parallel to two of the sides of the hexagonal graphene grain. Exploiting this feature, Dumcenco *et al.*¹⁰⁵ have successfully grown large area MoS_2 nanosheet on top of well-oriented sapphire Al_2O_3 (0001) from merging single-crystalline domains with restricted lattice orientations to high-symmetry cases (0° and 60°). Moreover, they claimed that well-defined and smooth sapphire terraces encourage the diffusion of chemical species onto the nucleation sites. At this point, several other monocrystalline substrates with hexagonal symmetry have been considered for TMDC growth, such as $\text{GaN}(111)$ ¹⁰⁶ or h-BN ^{107, 108}.

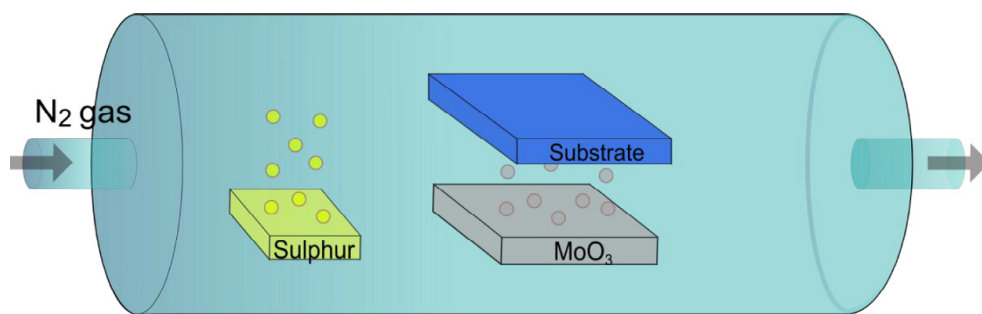


Figure 1.6: A typical powder-source CVD setup for producing 2D TMDCs nanosheets, from ¹⁰⁰.

The third chemical method is **MOCVD**, considered as one the most commonly used technique for compound semiconductor growth¹⁰⁹. In contrast to conventional CVD technique, the gaseous metal-organic precursors are placed outside the reaction chamber. One major advantage of such technique is the precise control of constant amount of precursor over the growth time, where a too small amount of powder would lead to a partial result. In 2015, Eichfeld *et al.* presented the first MOCVD process for the synthesis of WSe_2 nanosheets using tungsten hexacarbonyl $\text{W}(\text{CO})_6$ and dimethylselenium $(\text{CH}_3)_2\text{Se}$ as precursors and H_2 as the carrier inert gas¹¹⁰. They pointed out the interest of using monocrystalline substrate like sapphire as well as high growth temperatures for flake size optimization, though some

disorder at the interface was observed, suggesting a reaction during the growth process. Moreover, as MOCVD allows to control the different precursors flow rate, they analysed the impact of the Se:W ratio, pointing out a decrease in nucleation sites at high Se:W values leading to a consequent increase of the flake size. Yet, they also observed a reduction of the domain size when exceeding a ratio of 20000, suggesting the existence of an ideal precursor flux ratio. The same year, Kang *et al.*¹¹¹ developed a similar process for MoS₂ and WS₂ on 4-in silicon oxide wafer with a layer-by-layer growth mode and a high electron mobility at room temperature ($30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), increasing the interests of MOCVD for TMDC-based FETs device development. However, the technique remains slow and expensive, which encourages pushing through the research of the ideal method for manufacturing TMDC thin films.

On the other hand, **Atomic Layer Deposition (ALD)** has been quite widely studied for direct TMDC nanosheets growth. The clear advantage over CVD is the self-limitation induced by alternating a pulse and purge of the precursors. The most common material sources are transition metal chloride such as WCl₅ or MoCl₅ and hexamethyldisilathiane (HMDST)¹¹² or H₂S/H₂Se¹¹³ for sulphur/selenium source. A precise control of the thickness is obtained by counting the number of cycles. Yet, the technique has shown great limitations in grain size, in addition to a partial oxidation of the grown layer.

1.1.2.3 Bottom-up synthesis: physical methods. Focus on TMDC synthesis by Molecular Beam Epitaxy

Overall, even if those chemical-based processes have been improved over the years with now hundreds of micrometer flakes, a total coverage of the surface is hardly obtained, which leads to major difficulties in large-scale heterostructure development. Recently, alternative physical processes such as **Pulsed Laser Deposition (PLD)** or **MBE** have emerged for wafer-scale TMDC growth.

PLD is a physical process based on the formation of plasma plumes generated from bombarding a bulk material with a high-energy pulsed laser. Ions and radicals produced in the plasma are then travelling onto the substrate and crystallize. One major advantage is the use of relatively low substrate temperature, which enlarges the choice of original substrates. Because of its simplicity and efficiency, a numerous amount of 2D materials including the majority of TMDCs have been developed using PLD¹¹⁴. Moreover, the direct fabrication of TMDC heterostructures is eased. For example, Zatko *et al.*¹¹⁵ were able to develop in situ WS₂/WSe₂/WS₂ heterostructure on a Ni(111) substrate with PLD by simply switching the bulk TMDC targets during the process. They pointed out a total coverage of their substrate with homogeneous growth as well as an efficient encapsulation of the WSe₂. However, the main drawback of such technique is its too high growth rate, which makes it difficult to control precisely the thickness in the monolayer regime, and the induced small grain size, which leads to polycrystalline films.

Thus, MBE has been considered notably to address the scaling, thickness control and purity issues of the TMDC layers. The starting point was a growth technique dedicated to III-V semiconductors, with a first process established by K. G. Günther in 1958 in which group III, group V sources and the substrate were set at different temperatures in order to independently control the vapour pressure of the elements and their condensation on the substrate¹¹⁶. However, it was only in the late 60's that the "epitaxial growth" term was introduced with the use of single-crystal substrate, and in 1970 that the process was called "molecular beam epitaxy"¹¹⁷. The technique uses highly pure source materials evaporated in molecular beams in an **Ultra-high vacuum (UHV)** environment, which restricts the impurity concentration in the growing layer and allows the atomic or molecular beams to travel in collision-free paths until reaching

the substrate surface. The crystal is maintained at a moderate high temperature in order to ease the migration of the incoming atoms onto the nucleation sites¹¹⁸. The typical low growth rates ($\sim 1\text{-}100$ Å/min) associated with the use of shutters in front of the different beams leads to a precise thickness control. The interest for 2D materials growth, and notably TMDCs, is then obvious, as it could overcome the crystallinity, thickness control and purity issues faced with other techniques. In 1984, Koma *et al.* performed the first experimental growth of NbSe₂ on a cleaved 2H-MoS₂ using MBE¹¹⁹, followed in 1990¹²⁰ by a successful growth of MoSe₂ on a CaF₂(111) surface, motivated by Saiki *et al.* results on cleaved mica one year earlier¹²¹. Despite a large lattice mismatch, the in-plane crystallographic ones of the epi-layer were aligned with the substrates axes due to the presence of van der Waals forces at the interface instead of covalent bonds. Consequently, the authors named this new kind of growth "van der Waals epitaxy"¹²².

In order to understand the impact of the different factors on the epitaxial growth of TMDCs, the following section introduces growth mechanism differences between traditional and van der Waals epitaxy.

Traditional versus van der Waals MBE

In both epitaxial growths, fractions of gaseous molecules or atoms called adatoms are trapped at the surface before diffusing onto the substrate. This first mechanism named physical adsorption or physisorption is implied by the presence of van der Waals interactions at the surface, which attract close adatoms¹²³, favoured by thermal activation of the surface. In the case of conventional MBE process, a second adsorption step happens, induced by the formation of covalent bonding between surfaces atoms and adatoms, whereas the absence of dangling bonds on a van der Waals surface prohibits this so called chemisorption step¹²⁴. The second mechanism implied in molecular beam epitaxy is the diffusion of the adatoms onto the surface induced by the substrate temperature. During this process, a fraction of the adsorbed species is reacting with surfaces defects (impurities, atomic edges, local dislocations ...) and then aggregate altogether, yielding stable nucleation sites when reaching a critical size. The nucleation can also comes from the spontaneous aggregation of the adatoms. The rest of the adatoms desorb and are evacuated into vacuum. In the case of defect-free substrate, the nucleation rate depends on the homogeneous aggregation of free adatoms on the surface, driven by a thermodynamic equilibrium. In her PhD thesis, Céline Vergnaud described the thermodynamic considerations of the homogeneous nucleation step, pointing out the direct link between the increase of the substrate temperature and the decrease of the nucleation rate¹²⁴. Once the nucleation rate stabilized, the growth step starts with three possible modes in conventional epitaxy: Frank-van der Merwe or layer-by-layer mode, Stranski-Krastanov (layer-island), and Volmer-Weber (3D islands)¹²⁵. Within a thermodynamical approach, the resulting morphology of the epi-layer is determined by substrate and epilayer surface energies, the interface energy and the elastic energy due to the interface and epilayer strain in lattice-mismatched growth. Indeed, the chemical bonding of the epi-layer with the substrate can lead to a strong surface tension with strain accumulation. However, this classification does not consider the kinetic issues implied by the diffusion and the nucleation step, which leads to strong deviations between the experimental observations and the theoretical predictions. Moreover, this categorization, based on conventional 3D growth, also assumes that out-of-plane interactions and in-plane interactions are similar. Yet, such description cannot be applied to van der Waals epitaxy, where the in-plane interaction is dominant over the out-of-plane one¹²⁶. On the other hand, the covalent bonding between the substrate and the epi-layer in conventional epitaxy implies a strict selection of materials, as a strong lattice mismatch will induce strains leading to elastic deformations and/or dislocations as the growth proceeds. The weak substrate/epilayer interaction in van

der Waals epitaxy allows considering a larger amount of materials combination as soon as they exhibit a similar symmetry, as it has been notably sponsored by Koma *et al.*¹²⁷.

Therefore, the quality of the van der Waals epitaxial growth depends on three key parameters: the **Growth temperature (T_G)**, the **Transition Metal growth rate (V_M)** and the chalcogen/transition metal flux ratio (C/M), notably presented by Nie *et al.* in their **Kinetic Monte Carlo (KMC)** study on WSe₂ growth³³.

Key parameter impact

As presented above, T_G has a direct impact on the physisorption, the partial desorption of chalcogen atoms (as their sticking coefficient is lower than the transition metal ones) and the diffusion of adatoms, leading to a temperature dependence on the nucleation density¹²⁶. However, the 2D monolayer nucleation can be fully suppressed if the desorption of chalcogen adatoms driven by T_G exceeds the nucleation rate¹²⁸, inducing the formation of metallic clusters. Therefore, a practical temperature limit should be found, depending on the substrate and the grown TMDC. During the growth stage, TMDC domain morphology is also directly linked to T_G , with the formation of branched domains at low temperatures and compact triangular domains at high temperatures (Figure 1.7). In the case of branched structures, surface science conventions assume that a structure with a preserved symmetry is described as a dendrite and that without symmetry as a fractal³³. Considering a graphene substrate, **KMC** calculations show the formation of WSe₂ dendritic domains with a trigonal symmetry at low T_G (<650°C), whereas disorientated fractal structures are formed at intermediate temperatures. At T_G beyond 850°C, the adsorption rate at the WSe₂ nucleus surface is limited by the increase of Se desorption, which favours the adsorption rate at the edges of the nucleus and favours edge diffusion, leading to a slow growth of stable triangular domains with hexagonal symmetry. Experimental growth by MBE of TiSe₂, NbSe₂ and VSe₂ on **Highly Ordered Pyrolytic Graphite (HOPG)** tend to exhibit the same features, although clear formation of compact triangular domains is only obtained on NbSe₂¹²⁹, pointing out the challenge of growing TMDCs based on heavy transition metals due to their low diffusion lengths.

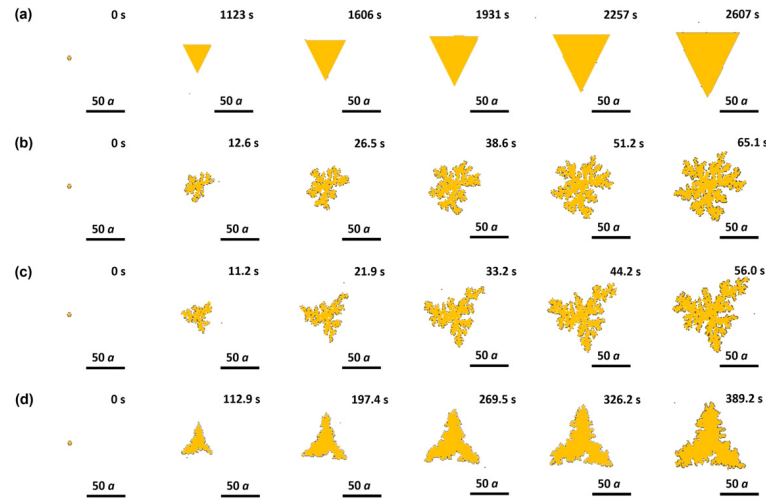


Figure 1.7: The growth process of the WSe₂ domains extracted from ³³. Under different conditions, the domain can grow from the same nucleus to different morphologies, including (a) a perfect compact triangle, (b) a fractal domain, (c) a dendritic domain, and (d) a semi-compact domain. Each pixel represents an atom. The type of the atom is represented by the color (gray: metal; yellow: chalcogen). Brightness represents the layer height. The scale bar is 50 × lattice constant a. For WSe₂, a=332 pm, 50a=16.6 nm. All the visualization of the simulation follows the same legend.

The transition metal flux V_M has a large impact on both nucleation and growth rate. Actually, since their mean free residence time and mean free path on the surface are assumed significantly longer than for chalcogens, these long lifetime species are more likely to initiate the island formation and then to set the nucleation step³³. Therefore, the flux of metal reflects the deposition rate, as a decrease of V_M would induce a decrease in adsorption rate and then nucleation density¹²⁶. As for the growth stage, KMC calculations and experimental observations show that the density of adatoms at the domain edge increases with V_M , which turns out to suppress the edge diffusion needed for large, compact triangular domains formation^{33, 126, 129}. Conversely, Rajan *et al.*¹²⁹ experimentally show that combining a low V_M and a high T_G slowly transform the triangular TiSe_2 domains into hexagons via a transitional truncated triangular shape, which can be attributed to the stability of the hexagonal morphology given high adatom mobility. Overall, they proposed a schematic phase diagram (Figure 1.8) summarizing the domain morphologies that can be obtained via MBE, encouraging the use of high T_G and low V_M for high-quality monolayer growth.

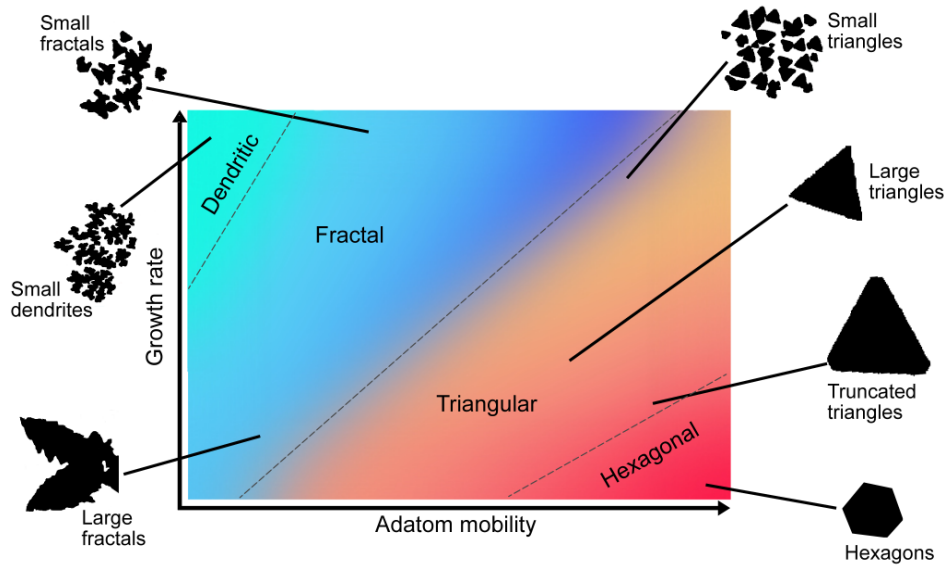


Figure 1.8: Schematic phase diagram extracted from ¹²⁹ showing the island morphologies that can be obtained via molecular-beam epitaxy growth of monolayer transition-metal dichalcogenides. The inserts show examples of the corresponding domain morphologies extracted from **Atomic Force Microscopy (AFM)** scans.

As mentioned earlier, the desorption of chalcogens adatoms during the diffusion stage is assumed to occur at lower temperature than the transition metal one, due to their smaller sticking coefficient. During their study, Nie *et al.* propose that Se adatoms would more likely influence the deposition process locally around the growing domain and reflect the transition metal chemical environment. In fact, KMC simulations revealed that a low chalcogen condition would induce a reduction of the metal sticking coefficient, implying the desorption of metallic adatoms before incorporating the crystalline domain, and inducing an artificial reduction of the growth rate. At the opposite, in a chalcogen rich condition, the majority of adatoms are passivated and crystallize within the domain edges³³, increasing their size and reducing the global nucleation density. Moreover, metal-rich pyramidal grains are observed in a deficient chalcogen condition, whereas a high C/M ratio would induce the passivation of transition metal atoms at domain edges, promoting in-plane growth (or 2D) rather than out-of-plane one (or 3D)¹²⁶.

The above discussion highlights the use of a high T_G , a low transition metal growth rate, and a high chalcogen/metal ratio for growing high quality TMDC domains with MBE.

2D substrates for van der Waals epitaxy

Since the quality of the van der Waals interface is the key parameter for obtaining a successful TMDC epitaxial growth, most of the studies have been performed on 2D substrates. The collateral advantage of using such substrate architecture is the simplicity for exfoliating the resulting epi-layer. As presented earlier, pioneering growth of NbSe₂ by Koma *et al.* in 1984 was performed on a cleaved MoS₂ substrate¹¹⁹ regardless of the massive lattice mismatch between the two materials (~10%), initiating several studies of TMDC growth on bulk or exfoliated TMDC substrates. In 1991, Ohuchi *et al.* presented the epitaxial growth of monolayer MoSe₂ on SnS₂(0001) and MoS₂(0001) substrates, with a first discussion about the triangular substructures observed in stable van der Waals epitaxy¹³⁰. It was then demonstrated that both the substrate and the epi-layer maintain their lattice constant, causing the formation of Moiré superstructures originated from an undulation of the lattice at the interfaces¹³¹. Later on, Barton *et al.* demonstrated the multilayer growth of unstrained HfSe₂ on MoS₂^{35, 132} (Figure 1.9b), while it exhibits a 41% lattice mismatch, paving the way to direct TMDC-based heterostructure development for electronic devices.

Among the different 2D substrates considered for TMDC epitaxial growth, **HOPG** has been one of the most widely studied, thanks to its high stability in vacuum and its low defect concentration. A comparative study of VSe₂ and TiSe₂ nucleation and growth on MoS₂ and HOPG substrates revealed a lower nucleation density on the graphite substrate coupled with a longer diffusion length, leading to large and compact islands formation even at low T_G⁴⁷. Using these features, Blades *et al.* have proposed an in-depth study of temperature-induced defect in WSe₂ growth on HOPG¹³³. Although tungsten vacancies are assumed to be a predominant p-type defect in this heterostructure¹³⁴, they show a 7-fold increase in defect density after a 600°C annealing step, resulting in a reduction of the bandgap from 1.6 to 1.3 eV. The crystal quality of HOPG has been also considered in order to simultaneously grow 2H and 1T'-phase MoTe₂, promoting the controllable phase growth with promising lateral homojunction electronic devices¹³⁵. Through its use as a substrate in numerous growths of MoSe₂^{136, 137}, WSe₂^{133, 138}, NbSe₂^{139, 140}, VSe₂¹⁴¹, HfSe₂ (Figure 1.9a)³⁵, HOPG has proven its versatility and its huge interest for **Scanning Tunnelling Microscopy (STM)** and **Angle Resolved PhotoEmission Spectroscopy (ARPES)**⁴⁷ measurements.

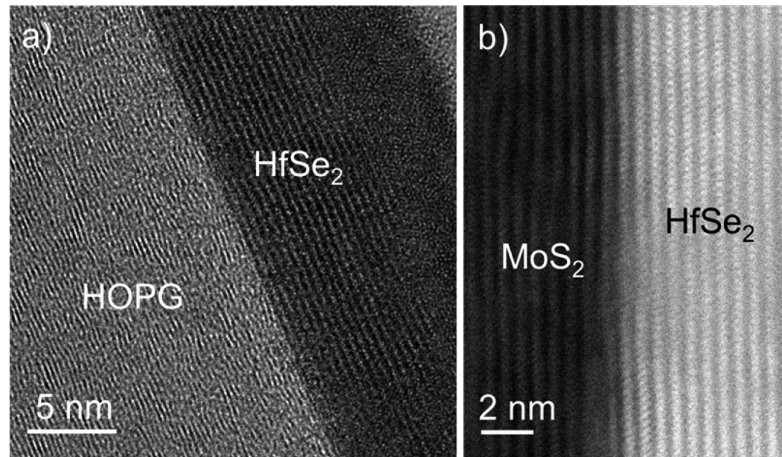


Figure 1.9: (a) TEM image of grown HfSe₂ on HOPG and (b) HAADF-STEM image of grown HfSe₂ on MoS₂ showing abrupt interfaces and layered crystalline films. Extracted from ³⁵.

Nevertheless, its polycrystalline nature makes it difficult to evaluate the epi-layer crystallographic anisotropy, with the requirement of nano-probe equipment. Thus, single crystalline substrates are

preferred. Novoselov et al. successful graphene exfoliation and characterization brought back interests on direct production of single-crystalline graphene bilayers by SiC graphitisation. Common production of bilayer graphene on 6H or 4H-SiC(0001) is performed by a high temperature annealing of the SiC substrate leading to silicon sublimation and resulting in uniform large single crystal bilayers with regular and low-defect step structures¹⁴². Among the semiconducting TMDCs, 2H-MoSe₂ growth on **Bilayer Graphene (BLG)** has been extensively studied due notably to the strong resulting photoluminescence at room temperature induced by the lowest-energy exciton transition in single-layer¹⁴³. Conductive properties of BLG also ease **Scanning Tunnelling Spectroscopy (STS)** and STM measurements, leading to observe and characterize complex phenomena such as 1D-**Charge Density Wave (CDW)** along mirror twin boundaries in MoSe₂¹⁴⁴. Recent work by Dau et al.¹⁴⁵ has revealed the MBE growth of 18 ± 10 nm wide MoSe₂ domains in the monolayer regime (Table 1.2), whose size is limited by edges or by the recurrent inversion domain boundaries. **X-Ray Diffraction (XRD)** measurements exhibit a good alignment of the in-plane lattices of MoSe₂ and graphene, with a relatively large in-plane mosaic spread of 8° (Table 1.2). In parallel, the growth of 2H-WSe₂ monolayer and multilayer on BLG was found quite promising for analysing its direct-to-indirect bandgap transition¹⁴⁶, though the main interest lies in quasi-freestanding 1T'-WSe₂ monolayer growth, which does not exist in natural bulk form¹⁴⁷ and exhibit topological field effects⁴².

From this point, lateral 1T'-1H WSe₂ heterojunctions growth has been successfully fabricated on BLG and drives huge interests for quantum nano-device development^{148, 149}. Thereafter, the study and growth of 1T'-MoTe₂¹⁵⁰ and 1T'-WTe₂¹⁵¹ on BLG have been considered due to their strong **Quantum spin Hall effect (QSH)**. Later on, a vast panel of original and challenging TMDCs have been successfully grown on BLG, including PtSe₂, VSe₂, PdSe₂ and TaS₂¹⁵². Furthermore, insulating van der Waals substrates have been also examined for TMDC growth, with early results by Ueno et al. in 1990, demonstrating the MoSe₂ and NbSe₂ growth on mica¹⁵³. More recently, Vergnaud et al. proposed a scalable epitaxial growth of WSe₂ on mica with a particular attention made on substrate preparation and growth conditions, resulting in a strong photoluminescence signal even after long air exposure²². By increasing the growth temperature and reducing the tungsten growth rate down to 0.3 Å/min, they measured a strong increase in in-plane grain size up to 100 nm and a decrease in in-plane disorientation down to 1.25° (Figure 1.10). More rarely, hexagonal BN (h-BN) has been proposed as an alternative substrate. In the case of TaS₂, it was assumed that the large charge transfer from graphene to TaS₂ would suppress an important **CDW** at room temperature, where h-BN demonstrated an enhancement in CDW due to a Moiré electrostatic modulation¹⁵⁴. Besides, FET devices can be directly fabricated when considering a h-BN substrate as shown by Mui Poh et al. with a highly-crystalline monolayer and bilayer MoSe₂ growth at 500°C under a large Se:Mo ratio, exhibiting an average grain size up to 200 nm and an electron mobility of ~ 15 cm²/(V.s)¹⁵⁵.

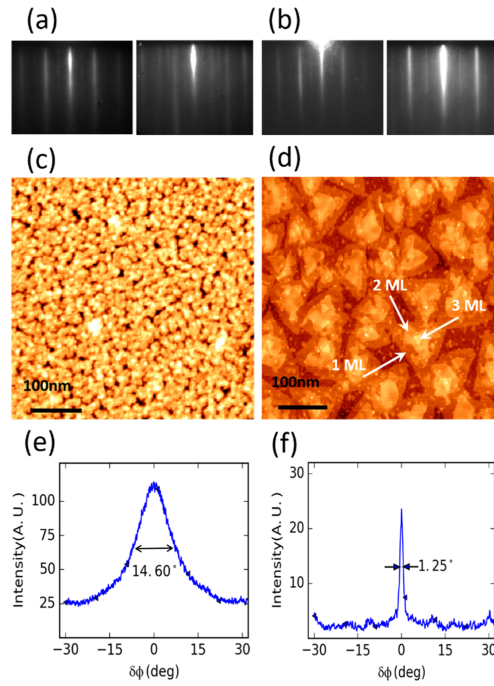


Figure 1.10: Evolution of the **Reflection High Energy Electron Diffraction (RHEED)** patterns along (100) and (110) directions (**a,b**), the Atomic Force Microscopy (AFM) images (**c,d**) and the azimuthal grazing incidence x-ray diffraction (XRD) showing the (100) peak (**e,f**) for a WSe₂ monolayer grown on mica at (T=720°C, F=1.5 Å/min) and (T=920°C, F=0.3 Å/min) respectively. Extracted from ²².

Investigations and benefits of heterojunctions from 3D substrates

Beyond van der Waals substrates (Figure 1.11b), new generations of heterojunctions have emerged using conventional 3D substrates (Figure 1.11c). In 1990, Koma *et al.* demonstrated the first so-called quasi van der Waals epitaxy of ultra-thin MoSe₂ layer on an inert F-terminated CaF₂(111) substrate, using the dangling bond-free surface for forcing the van der Waals interface formation¹²⁰. This substrate has been grown on Si(111), which paves the way for TMDC growth on silicon substrate with a CaF₂ buffer layer. From this starting point, several other conventional semiconducting or insulating substrates have been explored. The only constraint is to provide a hexagonal symmetry, generalizing the use of (111) surface orientation for cubic structures. Recently, Fragkos *et al.* proposed an extensive study of monolayer – and multilayer - TiTe₂ epitaxial growth on InAs(111)/Si(111) substrate previously prepared by MOCVD, with an observation of CDW state at room temperature¹⁵⁶. They demonstrated that the In-terminated substrate allows the formation of a sharp van der Waals interface, whose continuity is not altered by atomic edges or surface defects. In the same way, Tsoutsou *et al.* performed the epitaxial growth of TaSe₂ monolayer, TaSe₂/MoSe₂ and TaSe₂/HfSe₂ heterostructures on AlN(0001)/Si(111) substrate¹⁵⁷. The metallic behaviour of TaSe₂ coupled with its large 5.5 eV work function and its good compatibility with MoSe₂ drives new interests for epitaxial TaSe₂-based low-resistivity contacts. Besides, the use of such low-cost substrate in 300 mm wafer sizes creates tremendous interests for volume production in the industry standards. On the other hand, MOCVD-produced AlN(0001) on Si(111) was strongly considered for HfTe₂²³ and Bi₂Se₃/MoSe₂²⁴ heterostructure epitaxial growth due to its wide bandgap. In fact, it notably creates a semiconductor-on-insulator integration scheme with MoSe₂ and eases the study of non-trivial topological properties of Bi₂Se₃ and HfTe₂. Moreover, it has resulted in optimal 10 to 20 nm wide HfTe₂ grains with a mosaic spread angle of 11° (Table 1.2), while the roughness of a MoSe₂ trilayer is decreased down to 0.6 nm after a post-growth Se annealing treatment.

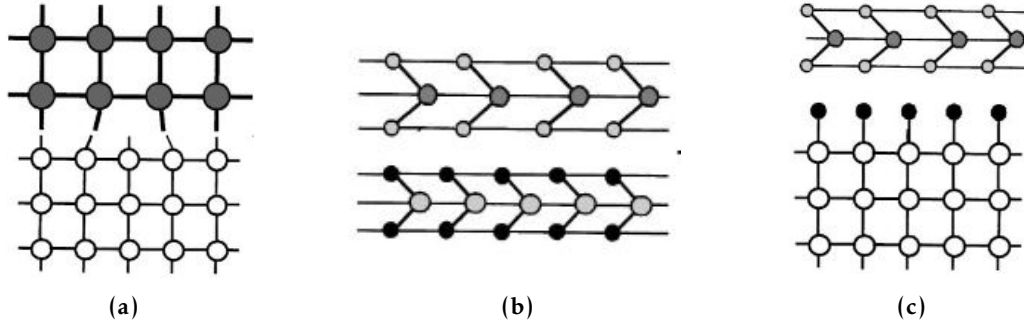


Figure 1.11: Interfaces connected by (a) dangling bonds, (b) van der Waals gap, and (c) quasi van der Waals gap. Extracted from ¹²⁷.

In parallel, insulating sapphire $\text{Al}_2\text{O}_3(0001)$ substrate has been also envisioned as it exhibits a natural hexagonal symmetry and is thermally stable up to high temperatures, not to mention its low cost and its well defined atomically flat surface. In 2017, Nakano *et al.* proposed a first epitaxial growth of WSe_2 on sapphire with great control of the thickness up to 10 monolayers and an in-plane disorientation of 8.8° (Figure 1.12)²⁷. In addition, it has been observed that the preparation temperature of the sapphire substrate would induce two preferential orientations, with a direct impact on the WSe_2 in-plane alignment as it follows directly the hexagonal lattice of the uppermost layer of surface atoms¹⁵⁸. However, the in-plane mosaic spread remains rather large regardless of the substrate preparation. The high density of 60° grains and 60° twins boundaries in this heterostructure results from the simultaneous growth of 2H and 3R WSe_2 domains, whose formation is assumed being challenging to control¹⁵⁹. As the common substrate preparation only lies in an acetone and ethanol ultrasonication followed by a 1000°C annealing step, sapphire has been widely studied for TMDC growth, with promising results in monolayer MoSe_2 growth at 550°C ²⁵, yet exhibiting small 8 nm grains with an assumed large in-plane disorientation. In 2023, the first MBE growth of 1T- PtSe_2 on sapphire has revealed a layer-dependent semiconducting-to-metallic transition with a carrier mobility maximum of $325 \text{ cm}^2/(\text{V.s})$ and a 22 nm average grain size²⁶.

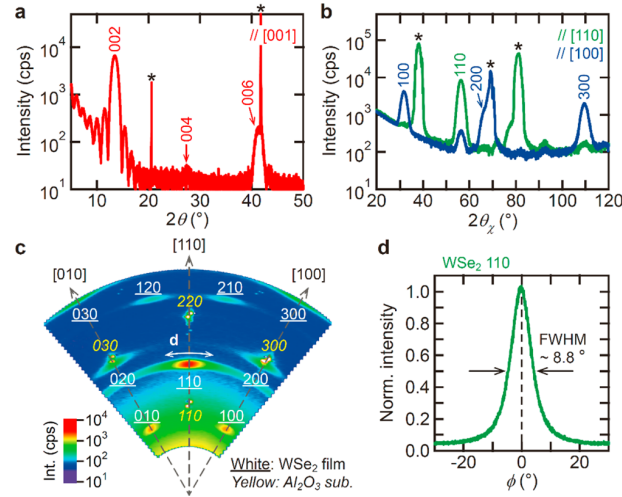


Figure 1.12: XRD patterns of 10 monolayer-thick WSe_2 epitaxial thin film, extracted from ²⁷. (a) Out-of-plane XRD pattern of the 10 monolayer-thick WSe_2 epitaxial thin film grown on $\text{Al}_2\text{O}_3(0001)$ substrate. (b) In-plane XRD patterns of the same sample along the $[110]$ (green) and $[100]$ (blue) directions of the substrates. (c) Reciprocal space mapping of the same sample within the $(hk0)$ plane. The diffraction spots labelled with white regular numbers with underlines are from WSe_2 thin film, and those with yellow italic numbers are from Al_2O_3 substrate. (d) ϕ scan near the WSe_2 (110) peak indicated in panel c.

The presence of **Mirror Twin Grain Boundaries (MTB)** is originated from the 120° symmetry of TMDCs in the monolayer regime, which implies that two mirrored grains are equivalent to two grains rotated by 60° . When coalescing, the two grains cannot be stitched together in a single lattice, resulting in the formation of a grain boundary of varying composition, generally metallic. Thus, the formation of MTB induces the appearance of electronic states lying within the TMDC bandgap, which can be used for **CDW** studies¹⁴⁴. The use of a substrate with the same symmetry as the TMDC can reduce the formation of the mirror twin domains as well as the optimisation of the growth parameters, yet strongly challenging to suppress it¹⁶⁰. In addition, recent work by Wang et al.¹⁶¹ and Li et al.¹⁶² have demonstrated the suppression of the boundaries formation when growing the TMDC on disoriented sapphire substrates, *i.e.* with a reduced cutting angle down to 0.1° . Indeed, their DFT calculations tends to highlight the role of step edges in favouring one TMDC island direction during the nucleation step.

On the other hand, conventional III-V semiconductors - notably GaAs - were soon considered for MBE growth of TMDCs due to their wide applications ranging from light emitting diodes to high power electronics¹⁶³. In fact, it was reported in 1988 that the dangling bonds on GaAs(111) surface could be terminated with sulphur after a chemical treatment using $(\text{NH}_4)_2\text{S}_x$ ^{164, 165}, forming a quasi-van de Waals surface stable up to 500°C . In 1990, Ueno et al. proposed the very first heteroepitaxy of MoSe_2 and NbSe_2 on top of a S-terminated GaAs(111)_{As} substrate with a relaxed epi-layer²⁸. Recent improvements in the sulphur or selenium termination process using MBE rather than chemical treatment drives new interests in GaAs-based heteroepitaxy. From now on, GaAs(111) surfaces are exposed to a Se or S beam prior growth at intermediate temperatures, which results in a clean passivation of the surface and suppresses the surface dangling bonds. In 2016, Ohtake et al. demonstrated that MoSe_2 islands grown on top of GaAs(111)_A (Ga terminated) are smaller and less continuous than on GaAs(111)_B (As terminated)¹⁶⁶, as the termination of the GaAs(111)_A surface by sulphur or selenium induces a reduction in the chemical reactivity of the surface¹⁶⁷. In 2020, Ohtake et al. also proposed a lattice orientation of MoSe_2 monolayer grown on GaAs(111)_B-Se study¹⁶⁸, revealing an epitaxial relationship of $[0001]_{\text{MoSe}_2} // [-1-1-1]_{\text{GaAs}}$ and $[11-20]_{\text{MoSe}_2} // [1-10]_{\text{GaAs}}$ (Figure 1.13). They pointed out the impact of the selenium surface treatment on the in-plane disorientation, with a reduction of the observed **Low Energy Electron Diffraction (LEED)** dots diameter from 24° to 14° . During the same year, bilayer 2H- MoTe_2 was successfully grown on GaAs(111)_B with 50 nm domain sizes, highlighting the versatile use of such substrate¹⁶⁹ (Table 1.2). Recently, Pierucci et al. have evidenced a continuous on terraces and step edges monolayer WSe_2 /Se-terminated GaAs heterojunction with an in-plane $[11-20]_{\text{WSe}_2} // [1-10]_{\text{GaAs}}$ and $[1-100]_{\text{WSe}_2} // [11-2]_{\text{GaAs}}$ epitaxial relation, while measuring a spread angle of 3.3° and an estimated average grain size of about 15 nm³⁰ (Table 1.2). The strong spin-orbit splitting at the K point of 0.45 eV is indicating the freestanding behaviour of the epi-layer, paving the way to new generation of optoelectronic devices in a scalable fashion.

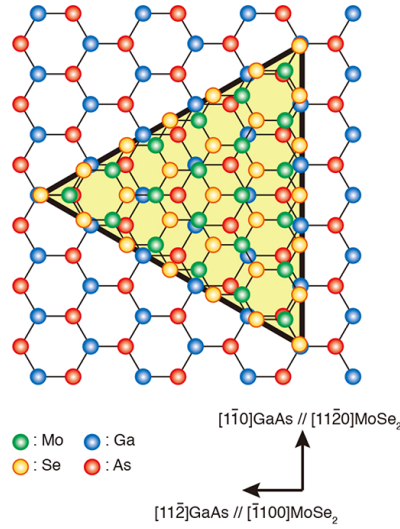


Figure 1.13: Schematic representation of the crystallographic relationships between MoSe₂ on GaAs(111)_B, extracted from ¹⁶¹.

The Table 1.2 summarizes the main results in terms of spread angle and grain size reported for TMDC layers grown by MBE up to now.

substrate	TMDC	Average grain size	Spread angle
BLG ¹⁴⁵	MoSe ₂	18 ± 10 nm	8°
Mica ²²	WSe ₂	100 nm	1.25°
AlN(0001) ²⁴	HfTe ₂	10-20 nm	11°
Al ₂ O ₃ (0001) ²⁷	WSe ₂		8.8°
Al ₂ O ₃ (0001) ²⁵	MoSe ₂	8 nm	
GaAs(111) _B ³⁰	WSe ₂	~15 nm	3.3°

Table 1.2: average grain size and in-plane disorientation for different TMDC/substrate combination

1.2 WSe₂ and HfSe₂ for devices

In this work, we will focus on the growth of WSe₂ and HfSe₂. Both materials are semiconductors with electronic bandgap energy close to 2 eV and 1.1 eV in the monolayer regime, respectively, with a predicted staggered type-II band alignment (Figure 1.14). In addition, WSe₂ is assumed to be p-type, while HfSe₂ tends to exhibit a strong n-type character. The combination of those two materials would paves the way for new generation of p-n junctions based on 2D materials.

In the following section, we highlight the structural and electronic specificities of WSe₂ and HfSe₂ before presenting the simulated projection of a heterostructure using those two TMDCs. We also discuss the WSe₂ polytypes, their characteristics, interests and drawbacks.

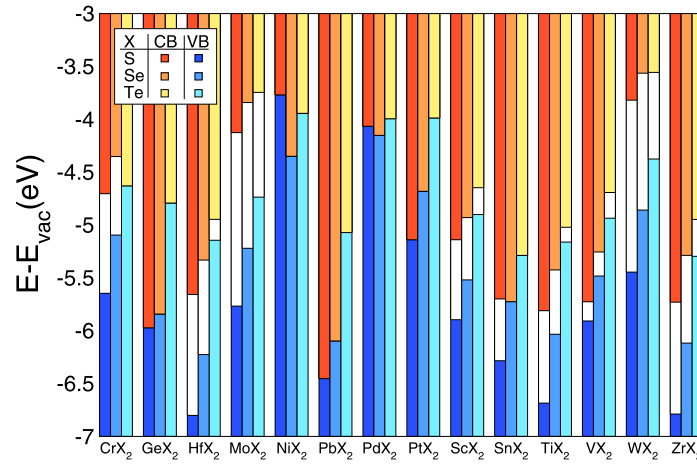


Figure 1.14: Conduction and valence band edges calculated within PBE for the 2D TMDCs. The coloured bar edges represent the valence bands (shades of blue/cyan) and the conduction bands (shades of red/yellow) for each monolayer; all energies are taken with respect to the vacuum level. Due to the band gap underestimation by PBE, the electron affinities are overestimated. Extracted from ¹⁷⁰.

1.2.1 WSe₂

1.2.1.1 2H-WSe₂

Among the different Group VI-based TMDCs, WSe₂ has been already widely studied due to its unique optical and electronic properties. As presented earlier, WSe₂ exhibits a stable and semiconducting 2H phase with a unique indirect-to-direct bandgap transition in the monolayer (1H) regime. In its bulk form, the indirect bandgap between the **VBM** at the K point and the **CBM** along the Γ -K direction has a rather low energy, assumed to slightly increase when decreasing the thickness down to a bilayer as presented by **DFT** calculation (in the generalized gradient approximation GGA) in Figure 1.15. In its monolayer form, WSe₂ exhibits a direct bandgap (K-K) with larger energy, which is assumed to induce a strong **Photoluminescence (PL)** signal at around 1.65 eV¹⁷¹. Comparative study of mono- and bilayer WSe₂ epitaxially grown on BLG¹⁴⁶ points out that the VBM shift from the K point to the Γ point in the bilayer regime is responsible to the direct-to-indirect bandgap transition, as the CBM is found out staying at the K point, while other calculations predict the CBM at Q^{55, 172}. Although bilayer WSe₂ should lead to a weak PL signal, the 40 meV difference between direct and indirect bandgaps in this case can be exploited by applying uniaxial external tensile strain on exfoliated systems. In 2014, Desai *et al.* experimentally demonstrated a direct bandgap in multilayer WSe₂ with strong PL at 1.57 eV by applying a tensile strain of 1.5%, providing promising properties for flexible optoelectronic applications¹⁷³. Experimental and DFT calculations reveal two distinct excitonic absorption peaks A and B at 760 and 600 nm in reflectance, arising from direct gap transitions at the K point^{172, 174}. The energy difference of 400 meV between the two peaks indicates on the spin-orbit interaction strength, significantly larger than MoS₂ spin splitting (~160 meV). Tanabe *et al.* experimental work on exfoliated WSe₂ nanosheet shows a VBM splitting of 0.49 eV induced by a strong spin-orbit coupling, in agreement with DFT predictions¹⁷⁵.

Aside from these optical properties, the intrinsic hole mobility in bulk WSe₂ **FETs** is estimated up to 500 cm²V⁻¹s⁻¹¹⁷⁶ when exfoliated monolayer WSe₂ **FETs** has revealed a 250 cm²V⁻¹s⁻¹ peak hole effective mobility as well as an electrostatic conductance modulation¹⁷⁷. The electronic bandgap measured by **STS** on monolayer WSe₂ grown by MBE on BLG amounts to 1.95 eV¹⁴⁶, while it is reduced to 1.83 eV on a bilayer grown on HOPG by MBE¹³⁸, revealing a thickness-dependent parameter. The difference

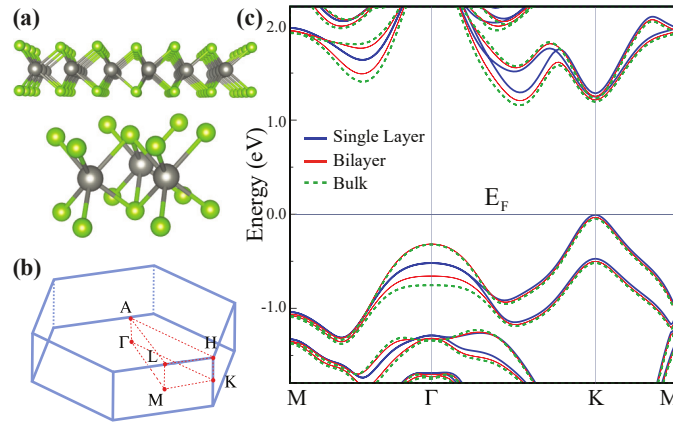


Figure 1.15: (a) Side and titled view of single-layer WSe₂. (b) Brillouin zone of WSe₂ and (c) **Generalized gradient approximation (GGA) + spin-orbit** band structures. The Fermi level is set to zero. Blue, red, and green colors are for single-layer, bilayer, and bulk structures, respectively. Extracted from ¹⁷¹

between the electronic and optical bandgap energies lies in the exciton binding energy, sensitive to differences in the dielectric environment, especially different substrates^{73, 178}. 2H-WSe₂ is a promising candidate for p-type FETs thanks to an exceptional saturation hole current of 3.07×10^{-4} A with Pt contacts on exfoliated ultra-thin films with a clean van der Waals interface¹⁷⁹. Pure p-type behaviour has been also obtained on monolayer WSe₂ grown by CVD with Pt contacts, resulting in a saturation hole current of $7.6 \mu\text{A}/\mu\text{m}$ and a mobility rising up to $40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Recently, Oberoi et al. proposed a p-type 2H-WSe₂ FET grown on Sapphire by MOCVD¹⁸⁰. As Pierucci et al. have demonstrated an intrinsic p-type behaviour in monolayer 1H-WSe₂ grown on Se-terminated GaAs(111)_B coupled with a strong spin-orbit coupling³⁰, monolayer-based heterostructures developed by MBE is now suitable and scalable for opto- and nanoelectronic devices production. Considering its thermodynamic stability, the 2H phase is assumed being grown at reasonably high temperatures in MBE, mainly between 400°C and 550°C^{146, 181, 182}.

1.2.1.2 3R-WSe₂

In addition of this "natural" stable 2H stacking, WSe₂ can exhibit the rhombohedral 3R stacking in the bilayer/trilayer regime. Both phases can be described from their stacking sequences AA' (2H), AB or AC (3R bilayer), as presented in Figure 1.16.

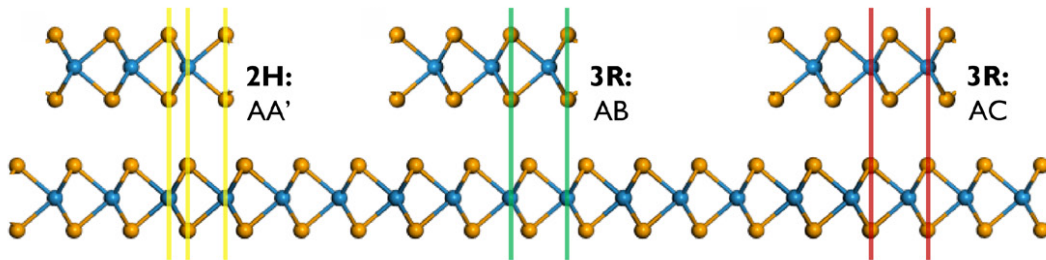


Figure 1.16: cross-sectional schematic representations of respectively the 2H:AA', 3R:AB and 3R:AC bilayer stacking configurations. Extracted from ¹⁸¹.

In the 2H:AA' configuration, the chalcogen and metal atoms of the top monolayer are simultaneously stacked on the metal and chalcogens atoms of the bottom monolayer, respectively. On the opposite, the 3R:AB bilayer stacking configuration has the chalcogen atoms of the top monolayer stacked on the metal atoms of the bottom monolayer, whereas the 3R:AC configuration has the metal ones stacked

on the chalcogens¹⁸³. The 2H results from a 60° in-plane rotation of one monolayer, when 3R bilayer stacking lacks this relation as evidenced in Figure 1.17. In the cross-sectional representation (Figure 1.16), the WSe₂ sequence can be described as herringbones which are rotated in the 2H phase, while being translated in the 3R phase. As the formation energy difference between those two polytypes is rather low (1 meV/at)¹⁸⁴, it is most likely to observe the coexistence of both phases in synthesized films by CVD or MBE.

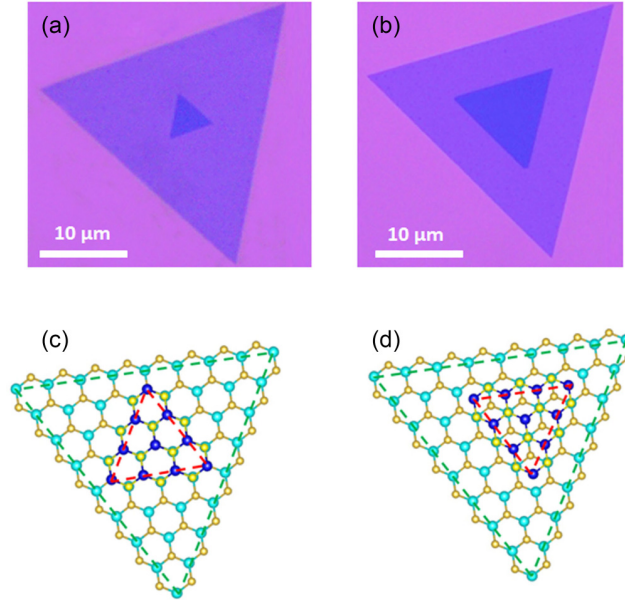


Figure 1.17: Optical image of (a) hexagonal AA' (2H) and (b) rhombohedral AB (3R) WSe₂ homo-bilayers, as grown on a SiO₂/Si substrate by CVD. (c), (d) Corresponding atomic arrangements (Se yellow, bottom W cyan, top W blue). The dashed cyan and red lines mark the zigzag Se edges. The 3R configuration is characterized by matching edge orientation between subsequent layers. Extracted from ¹⁸⁵.

This broken inversion symmetry leads to the formation of parallel in-plane nonlinear dipoles, making the 3R-WSe₂ crystal a good candidate for 2D nonlinear optics^{186, 187}. The lack in inversion symmetry is also reflected in the band structure of 3R-WSe₂, where the conduction and valence band are split, due to the different atomic environment of the tungsten atoms in each layer¹⁸⁸. However, both phases exhibit a semiconducting behaviour with similar bandgap energies. Recently, Liu *et al.* demonstrated the presence of a ferroelectric behaviour in bilayer 3R-WSe₂ stacking with a Curie temperature of 353 K, further evidenced as a first-order phase transition¹⁸⁹.

1.2.1.3 1T-WSe₂

Last, as many other group VI TMDCs, WSe₂ can exhibit a metastable octahedral phase 1T, which spontaneously distorts itself into a more stable 1T' phase, with a metal-metal covalent bonding³⁸. The energy barrier between 1H and 1T' is more than 1 eV/at, which enables the growth of single-crystal 1T'-WSe₂.

Due to its metallic bonding, the 1T'-WSe₂ bandgap energy is drastically reduced to ~120 meV¹⁴⁸, driving huge interests for electrocatalytic hydrogen evolution and energy storage applications¹⁹⁰. The presence of such small yet positive bandgap is also one crucial and necessary feature to realize QSH effect with long decoherence length at rather high temperatures, as the effect should combine a 2D bandgap

within two layers and 1D metallic edge states bridging the bandgap¹⁴⁷. Therefore, this effect is called a non-trivial topological phenomenon, with tremendous interests in spintronic devices.

The MBE growth of 1T'-WSe₂ on BLG has been recently considered because of the great control in thickness provided by the technique, with promising results at T_G=230°C¹⁴⁸. Upon thermal annealing, the 1T' phase undergoes an irreversible 1H phase transition at around 400°C¹⁹¹.

1.2.2 HfSe₂

Up to now, most of the studies have been devoted to Group VI TMDCs, where group IV metal dichalcogenides have been partially considered. Among them, HfSe₂ is predicted to be an intrinsic n-type semiconductor¹⁹² with an indirect electronic bandgap of ~1.1 eV, assumed to persist from bulk to single layer^{43, 193, 194} and a large work function of 5.5 eV^{157, 195}. At room temperature, Zhang et al.⁶⁴ have calculated a high phonon-limited carrier mobility of around 3500 cm²V⁻¹s⁻¹. Unlike Group VI TMDCs, HfSe₂ exhibits a unique 1T polytype. In its monolayer form, the VBM is located at the Γ point, while the CBM is at the M point¹⁹⁶, as presented in Figure 1.18d.

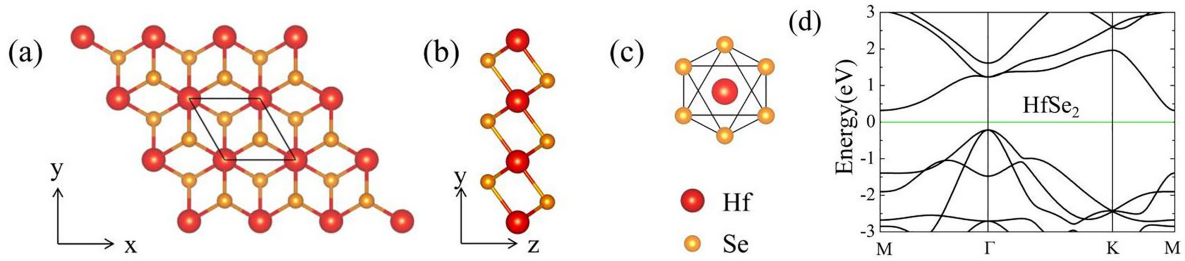


Figure 1.18: Atomic configurations of HfSe₂ monolayer. (a) Top view. (b) Side view. The rhombus in (a) denotes the primitive cell of HfSe₂ monolayer. (c) The stacking shape of HfSe₂ monolayer is octahedron. (d) The band structure of HfSe₂ monolayer. Extracted from ¹⁹⁶

Due to these promising features, exfoliated HfSe₂ multilayer has been used for FETs on SiO₂/Si substrate fabrication. However, the extracted carrier mobilities were far from the ones expected with values up to 1 and 4 cm²V⁻¹s⁻¹ for back-gated¹⁹⁷ and top-gated¹⁹⁴ FETs, respectively. Therefore, bottom-up methods appeared more suitable for device fabrication, with only a few studies using CVD^{198, 199}, and a clear trend towards MBE growth.

To date though, direct MBE growth of HfSe₂ have only been performed on HOPG and AlN(0001)/Si(111) substrates^{35, 195}, both confirming the n-type feature and ~1 eV bandgap of the TMDC. Driven by the promising prediction of a type II band alignment formation in group IV/group VI TMDC heterostructures⁴³, several studies proposed a MBE growth of HfSe₂ on MoSe₂ epitaxial thin films and MoS₂ substrate, resulting in p-n heterojunction configuration with prospective applications in opto-electronics. All of these MBE growths have been performed at a substrate temperature between 400°C and 500°C.

1.2.3 WSe₂/HfSe₂ heterostructure

Based on their band alignment, three types of heterojunctions can be distinguished as presented in Figure 1.19: straddling (type I), staggered (type II) and broken gap (type III)²⁰⁰. Commonly, optical emitting devices are developed from type I band alignments, as they provide a spatial carrier confinement enhancing the recombination needed for **Light Emitting Diode (LED)** fabrication. In the case of

photoconductors or solar cells, type II band alignment turns out being attractive for separating the carriers. Type II and type III are also particularly interesting in TFETs development, as the resulting engineering of the conduction-to-valence band transition energy enhances drastically the tunnelling current density²⁰¹. Last, atomically thin p-n diodes based on type II band alignment have been proposed using 2D materials, and especially TMDCs. One major advantage of van der Waals heterostructures is the possibility of dropping the applied potential across the van der Waals gap, allowing the bands of the two materials to move freely at the junction, with respect to each other.

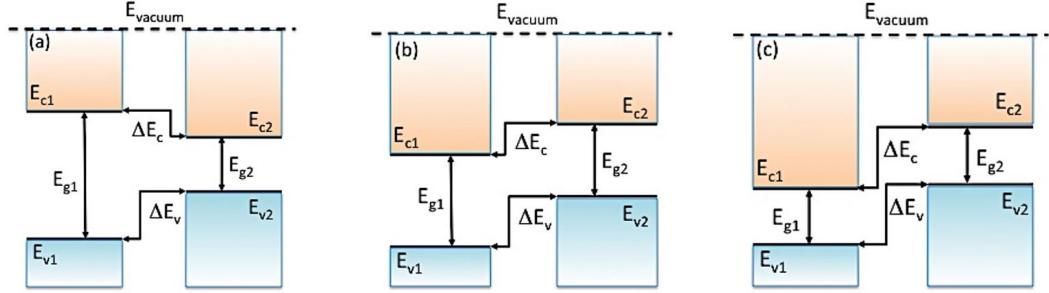


Figure 1.19: Schematics of the possible band alignment encountered in TMDCs heterostructures: (a) straddling, (b) staggered, (c) broken gap. Adapted from²⁰⁰

In 2019, Kashiwabara *et al.* have developed a WSe₂/HfSe₂ heterojunction on insulating sapphire substrate by MBE²⁰², resulting in rather high experimental hole carrier density of $2 \times 10^{14} \text{ cm}^{-2}$ and a carrier mobility of $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. A 5 monolayer-thick WSe₂ layer was grown on a sapphire substrate before growing 5 new monolayers of HfSe₂ on top. Each epitaxial TMDC was grown at 450°C and then annealed at 900°C for 30 minutes. Despite the 11% lattice mismatch between WSe₂ ($a=3.30 \text{ \AA}$) and HfSe₂ ($a=3.74 \text{ \AA}$)²⁰³, they observed negligible strain in the heterojunction, indicating on the good quality of the van der Waals interface. In addition, a 30° rotation of the WSe₂ layers with respect to the substrate orientation is spotted while the HfSe₂ layers are well aligned with the Al₂O₃(0001) surface. This 30° rotation between both TMDCs is assumed to spontaneously happen in order to reduce the lattice mismatch, with the formation of a 2×2 WSe₂ supercell and a $\sqrt{3} \times \sqrt{3}$ HfSe₂ supercell, as presented by Ju *et al.* in their *ab initio* study¹⁹⁶ (Figure 1.20a). Simulated band structures of each stacking possibility revealed the B stacking as the most stable one, with an indirect bandgap of 0.21 eV between the VBM at the point K, contributed by WSe₂, and the CBM at the M point, contributed by HfSe₂ (Figure 1.20b). Therefore, it exhibits a type-II band alignment with electrons and holes localized in HfSe₂ and WSe₂, respectively. The conduction band offset (ΔE_c) and the valence band offset (ΔE_v) are predicted to be 1.35 eV and 0.45 eV, which width should increase the carrier separation performances.

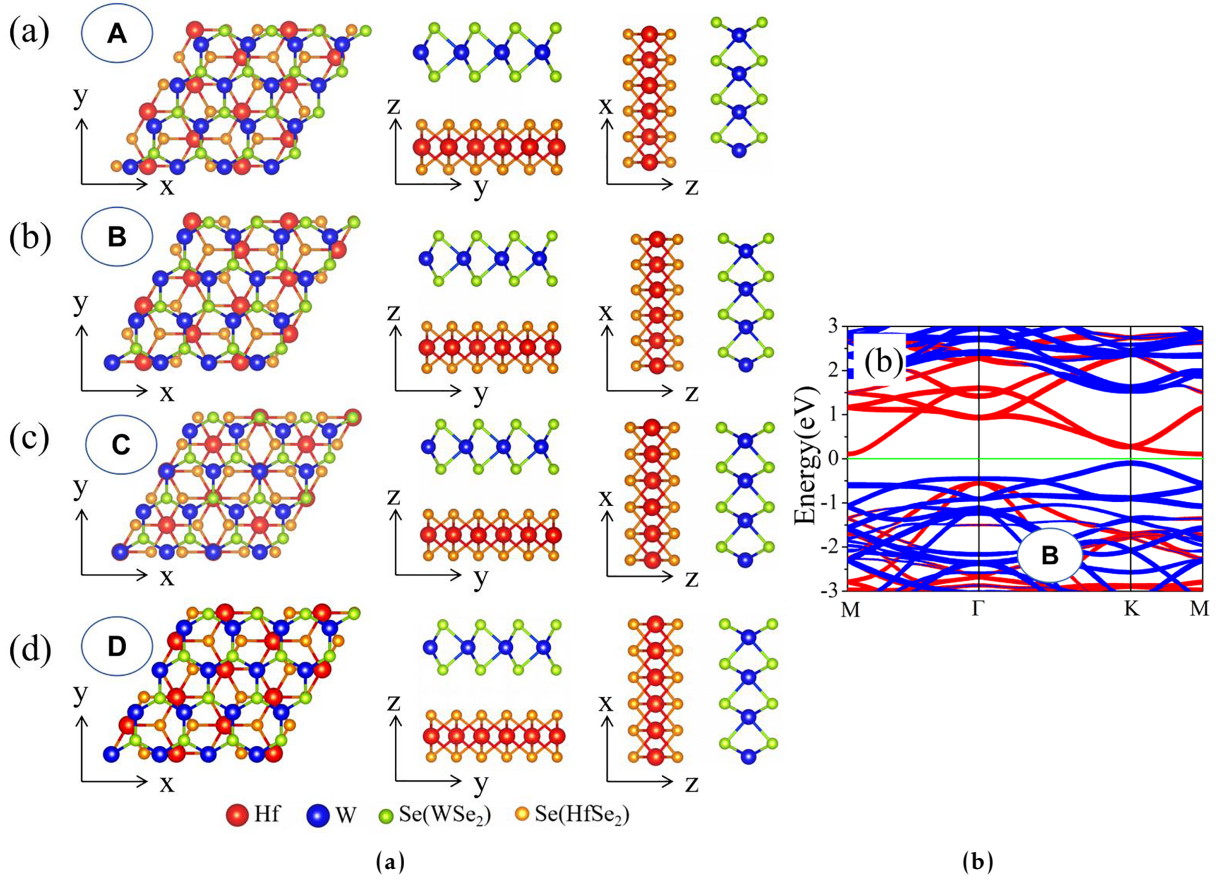


Figure 1.20: (a) The top and side views of non-equivalent four stacking patterns named as A, B, C, and D for the $\text{WSe}_2/\text{HfSe}_2$ vdW heterostructures. The optimized lattice constants for A, B, C and D are all 6.54 Å. (b) The projected band structure of B. The contributions of WSe_2 and HfSe_2 are shown with the blue and red lines, respectively. Extracted from ¹⁹⁶.

1.3 PhD work: MBE growth of $\text{WSe}_2/\text{HfSe}_2$ based tunnel diodes

1.3.1 Why tunnel diodes ?

In the last two decades, the number of studies on tunneling devices for **High Frequency (HF)** source and detectors development has drastically increased. In fact, band-to-band carrier tunneling is mostly determined by the band alignment and intrinsic semiconductor properties of the material heterostructure, and does not suffer from limitations due to thermal activation, in contrast with conventional thermionic-based devices. Moreover, it can lead to **Negative Differential resistance (NDR)**, which is a unique and key feature for HF devices development^{204, 205}.

Three types of tunnelling diodes can be referenced for HF applications: **Esaki Diode (ED)**, **Resonant Tunnelling Diode (RTD)** and **Backward Diode (BD)**. As presented in Figure 1.21a & 1.21b, EDs and RTDs both exhibit an "N-like" shape $I(V)$ characteristics with a NDR region expressed by a peak current density (J_{peak}) as well as a **Peak-to-valley current ratio (PVCR)**, and are both expected being particularly suitable as oscillators for HF sources and detectors²⁰⁶. Furthermore, as they do not exhibit a clear NDR, BDs (Figure 1.21c) are only considered for detection, with the curvature coefficient at zero bias expressed as $\gamma = \frac{d^2I}{dV^2} / \frac{dI}{dV}$ (A/W).

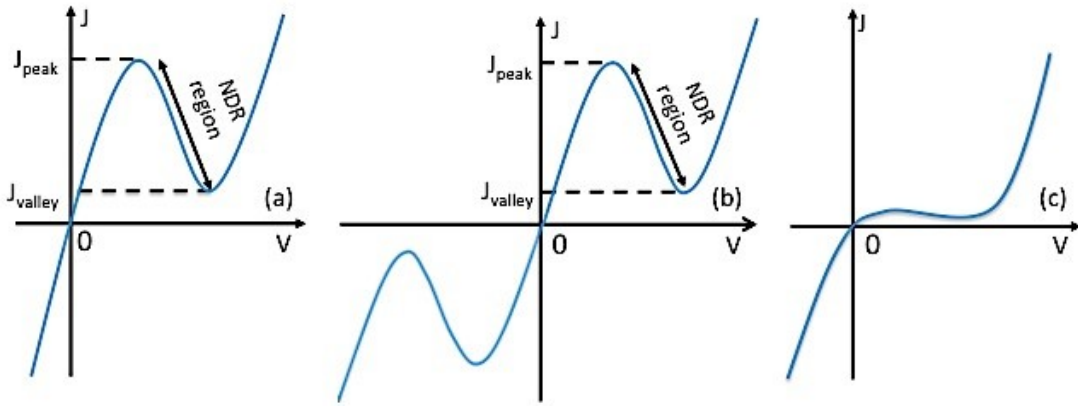


Figure 1.21: Typical I(V) characteristics of Esaki (a), RTD (b) and backward diodes (c).

Until now, the best performances for tunneling diodes have been obtained using III-V 3D compounds. For example, standard BD with an InGaAs/GaAsSb staggered interface²⁰⁷ can provide a relatively high curvature value of 43 A/W. Furthermore, RTDs based on InP materials²⁰⁸ has exhibited a J_{peak} of 5×10^6 A/cm² and PVCR of 1.7 at room temperature, leading to oscillations up to 1.92 THz, while EDs based on broken gap InAs/GaSb heterojunction²⁰⁹ led to a J_{peak} of 2.2×10^6 A/cm² and a PVCR of 3.9. Those remarkable results are yet exhibiting a common weakness, *i.e.* that the increased J_{peak} goes along a reduction in PVCR²¹⁰, and vice versa. This is induced by an undesirable increase of the valley current (J_{valley}), which originates from a barrier width fluctuation induced by interface roughness, alloy and impurity scattering, and imperfections in the quantum well.

This sensitivity of the tunneling interface leads to several major issues using conventional 3D materials like III-V compounds, mainly due to the covalent bonding at the interface. Besides the lattice matching requirements, chemical species inter-diffusion and band offset pinning irrespective of the doping levels and applied voltage, are also detrimental to the overall device performance^{211, 212}. Therefore, the improvement of the tunnelling interface by exploiting the unique van der Waals features of TMDCs, coupled with their wide bandgap range and the variety of possible band alignments^{200, 213} are of great interest for new generation of tunnel diode development.

These properties make TMDCs some ideal candidates for tunnelling devices, and a certain amount of studies have now established band-to-band tunnelling for different heterostructures. Recently, Fan *et al.*²¹⁴ proposed an ED based on a vertical WSe₂/SnSe₂ type III heterostructure with Pd contacts, combining CVD and exfoliation methods. The very low Schottky barrier of Pd/WSe₂ contact supresses the thermionic emission current, enabling the observation of NDR at room temperature. Due to the high sensitivity of SnSe₂ to air oxidation, the heterojunction was developed in a glovebox, highlighting the influence of the fabrication process on the interface quality. It led to a considerable 14600 A/cm² tunnelling current density and a strong PVCR of 4, which stands in the magnitude of conventional III-V based EDs. Regarding BDs, WSe₂/SnS₂ diodes have shown great results with a high photoresponsivity of 244 A/W using exfoliated TMDCs²¹⁵ and 227 A/W using CVD grown flakes²¹⁶. However, as presented earlier, the exfoliation of TMDCs is still a challenge in producing large scale, atomically thin layers, and is particularly sensitive to external pollution. Furthermore, CVD have shown clear limitations in scaling, while the use of MBE appears clearly suitable for wafer-scale heterostructures development. As the WSe₂/HfSe₂ p-n junction is predicted to exhibit a strong type II structure, it is of great interest for tunnelling device development.

1.3.2 Choice of the substrate: GaP(111)_B

Gallium Phosphide is a wide bandgap III-V semiconductor ($E_G=2.26$ eV at 300 K²¹⁷) with a cubical zinc-blend crystallographic structure of lattice constant $a=5.45$ Å²¹⁸, exhibiting a polar axis in the (111) direction, which results in either A or B polarity. The two polarities are associated to surface termination, either gallium or phosphorus, respectively²¹⁹, leading to different surface reconstructions after thermal deoxidation in UHV (Figure 1.22). Although the 2×2 reconstruction of GaP(111)_A is well documented and reproducible²²⁰, the reconstruction of GaP(111)_B is more controversial. Early observations suggested a 1×1 surface reconstruction^{221, 222}, while Hattori *et al.* pointed out a much more complex structure with the coexistence of six equivalent domains and two reconstruction units²²³. Recently, Kleinschmidt *et al.* showed the formation of a P-rich 2×2 reconstruction when cleaning the GaP(111)_B surface in UHV under hydrogen flux²²⁴. Because of its low lattice mismatch ($\sim 0.4\%$) with silicon, GaP/Si virtual substrate has been strongly considered for linking nonpolar silicon substrates and polar III-V epilayers, replacing GaAs and its larger lattice parameter ($a=5.65$ Å). GaP has been also predicted being a potential high band gap solar cell due to its ability to produce microns-scale diffusion lengths and its high absorption coefficient²²⁵. The epitaxial growth of gallium phosphide on Si(100) and GaP(100) for planar devices is well documented, with a nominal growth temperature at 525°C and 600°C, respectively²²⁶, while the growth on Si(111) remains challenging due to the formation of rotational twins, reducing the surface quality^{227, 228}. To date, there has been only one investigation on the GaP(111) homoepitaxy, which revealed a growth very sensitive to T_G and gallium growth rate²²⁹.

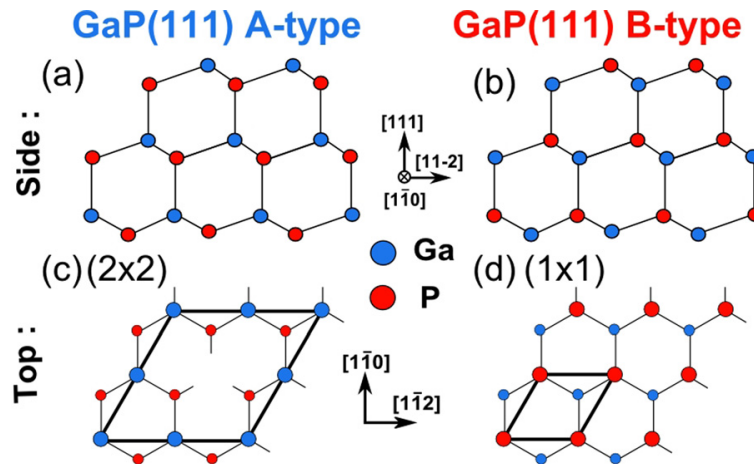


Figure 1.22: (a) and (b) side view of lattice model of GaP(111)_A and GaP(111)_B, (c) and (d) top view of lattice model of GaP(111)_A with (2×2) surface reconstruction, and GaP(111)_B with (1×1) surface reconstruction. Extracted from ²¹⁹.

In this work, GaP(111) has been selected as a substrate for WSe₂ and HfSe₂ MBE growth, replacing the earlier use of GaAs(111), due to its significantly higher thermal stability³⁴. In fact, its congruent sublimation temperature at 675°C²³⁰ instead of 625°C²³¹ is of great interest for attaining higher T_G , which is one key parameter for grain size optimization and carrier mobility enhancement³³. However, this 3D/2D heteroepitaxy is only possible after a selenium termination of the III-V substrate in order to favour the formation of a Van der Waals gap²⁸. It has been displayed that the uptake of Se is greater in (111)_A – to the fifth layer in GaAs – than in (111)_B, and that its desorption is also occurring at a lower temperature²³². The formation of an extreme surface Se passivation is favoured in order to prevent carrier traps induced by the formation of a thin layer of GaSe, which promotes the choice of a P-terminated GaP(111) substrate. It is also assumed that group-V components are more easily desorbed than group-III

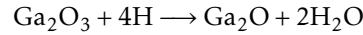
components under thermal activation, which paves the way to a better Se passivation on a (111)_B surface rather than on a (111)_A one.

1.3.3 The challenges

The development of a GaP(111)_B-Se/WSe₂/HfSe₂ heterostructure grown by MBE for tunnelling devices fabrication is yet to be explored. In this dissertation, each step of the whole process is investigated, revealing four main challenges, *i.e.* the substrate preparation, the optimisation of both WSe₂ and HfSe₂ direct growth on GaP(111)_B, and the development and characterization of the WSe₂/HfSe₂ vertical heterojunction.

1.3.3.1 The substrate preparation

The preparation of the GaP(111)_B surface is divided in two main steps: its deoxidation, and the selenium termination. The first step is performed in a MBE chamber dedicated to III-V compound growth using a combination of cracked **Phosphine (PH₃)** and **Atomic Hydrogen (H_{at})**. In fact, removal of the native oxide surface by a simple thermal annealing in UHV would lead to exceed the GaP congruent sublimation temperature up to 690°C, resulting in the condensation of surface gallium into droplets^{233, 234}. The use of H_{at} has successfully shown a decrease of the deoxidation temperature of GaAs and GaSb down to 400°C, as it favours the transition of native Ga₂O₃ into volatile Ga₂O, as indicated by the following reaction²³⁵:



However, the high reactivity of H_{at} also induces a slight etching of the GaAs surface, increasing the roughness and the step density. The excessive As desorption can be compensated by applying a high overpressure of As during the oxide removal stage²³⁶. As the H_{at} and PH₃ deoxidation process of GaP(111)_B has not been yet investigated, the first study of this manuscript deals with the determination of the best combination of key parameters, *i.e.* the **oxide removal temperature (T_{DEOX})**, the H_{at} exposition time and the PH₃ flux. The surface morphology and the deoxidation efficiency are specifically considered, as a low-defect surface is required for limiting the nucleation density of WSe₂ or HfSe₂.

The second step of the substrate preparation is performed in a second MBE chamber dedicated to TMDC growth. As presented earlier, the formation of a high quality van der Waals interface is only possible after removing the dangling bonds of the deoxidized GaP(111)_B substrate by a Se-termination. The surface is heated under a selenium overpressure at a minimal temperature of 450°C, following the Yamamoto *et al.* procedure^{29, 237}. To date, the only study on GaP(111) passivation under partial vapour pressure of selenium led to the formation of a 1-2 nm thick surface phase of Ga₂Se₃(111), unpinning the Fermi level and lowering the surface electronic states density in the band gap²³⁸. Therefore, the second study of this manuscript focuses on preventing the formation of sub-surface GaSe while obtaining an electronic Se passivation and keeping a smooth morphology prior TMDC growth. In that aim, we investigate the impact of the different key parameters, *i.e.* the passivation temperature and the partial pressure of selenium, on the termination.

1.3.3.2 The TMDC growth optimization

Based on the previous results obtained on GaAs(111)_B³⁰, the growth of WSe₂ as well as the post-growth annealing temperature impact on the nucleation, the polytype formation, the morphology and the

structural properties is studied. The effect of the growth rate V_W on the overall layer quality is also discussed, and a probable relationship between polytypism and layer thickness is highlighted. The use of WSe_2 in tunnelling device leads to search for a pure 2H-phase epi-layer with a high carrier mobility and a strong p-doping behaviour, which implies to maximize the average grain size. The high-quality of the $GaP(111)_B$ -Se/ WSe_2 interface is also one crucial parameter to consider, as well as the continuity of the epi-layer and the band alignment with the substrate.

Prior to the development of a $WSe_2/HfSe_2$ heterojunction, the direct growth of $HfSe_2$ on $GaP(111)_B$ -Se is investigated, focusing on the impact of T_G , T_A and V_{Hf} on the quality of the interface and the epi-layer. Once more, the optimization of the TMDC layer structural properties is one major consideration, coupled with the band alignment with the substrate.

Last, a first trial of a $GaP(111)_B/HfSe_2/WSe_2$, as well as its opposite $GaP(111)_B/WSe_2/HfSe_2$ heterostructure are performed, with one great challenge of obtaining a strong type II structure between the two TMDC, while preventing an in-plane and out-of-plane disorientation induced by the natural van der Waals interface.

Instrumentation

2.1 Molecular Beam Epitaxy

2.1.1 General presentation of the system

The **Institute of Electronic, Microelectronic and Nanotechnology (IEMN)** clean room is equipped with an ultra-high vacuum tube linking two **MBE** reactors manufactured by **Riber** and **Vinci Technologies**, which are dedicated to the **III-V** and **TMDC** growth, respectively, and a surface analysis chamber (Figure 2.1). The base pressure in the tube is in the low 1×10^{-10} Torr range. Both introduction chambers are pumped using a primary and a turbo-molecular pumps. For this work, 2-inch GaP(111)_B substrates from **Ensemble3 Ltd. Poland** are cleaved into sixths or smaller, which are glued on 3-inch unpolished silicon wafers with indium before being placed on 3-inch molybdenum carriers. Transport carts with eight slots are used to carry the samples along the vacuum tube to the different reactors. Prior the deoxidation process, samples are baked out at 100°C for twelve hours in the introduction chamber, and then outgassed at 200°C for 90 minutes in the degassing chamber.

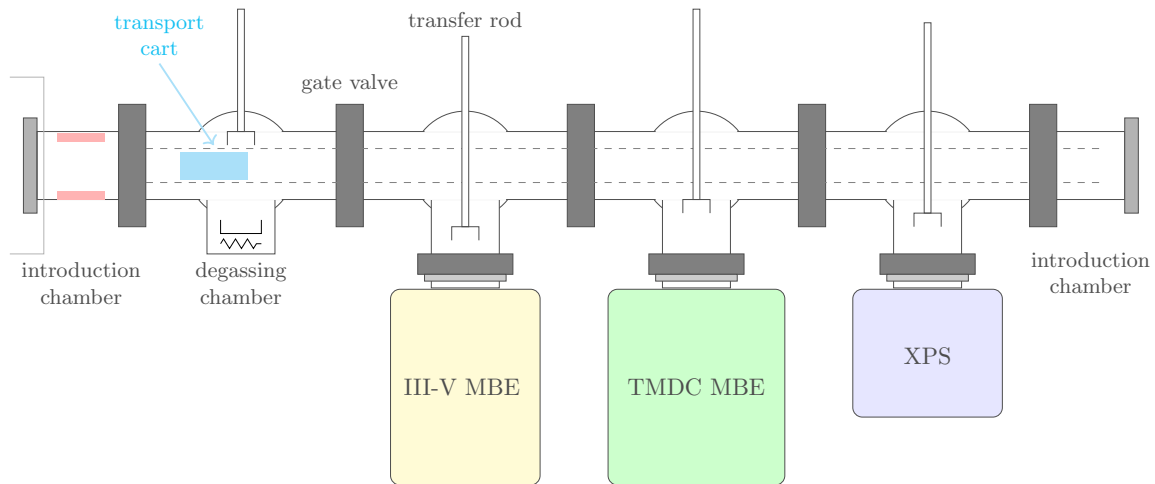


Figure 2.1: Schematic of the IEMN setup linking two MBE reactors and one surface analysis chamber

Both MBE chambers are constantly maintained under **UHV** – down to a few 1×10^{-10} Torr – with a combination of an ionic pump, a cryogenic one and the cryogenic panels cooled down to 77 K using

liquid nitrogen. A Bayart-Alpert ion gauge and a quadrupole residual gas analyser are used to measure and analyse the residual pressure. During the growth process, the substrate is rotating on itself to achieve thickness homogeneity and is heated thanks to a tantalum filament placed backside. The temperature is regulated through a thermocouple located backside the sample holder whereas an infrared pyrometer calibrated against the melting point of InSb (525°C) measures the sample surface temperature. Both reactors are fitted with a RHEED system, which provides a real-time control of the growth process.

2.1.2 III-V reactor

The III-V MBE reactor *Riber C21* (Figure 2.2) contains effusion cells for group-III elements (gallium, indium, aluminium), two valve cracker cells for arsenic and antimony, two gas lines for phosphine and arsine cracked through a high temperature injector, effusion cells for dopants (Be, Si, Te) and a CBr_4 line for carbon doping. Finally, it is also equipped with a RF plasma cell used to produce atomic hydrogen through a remote hydrogen plasma generated at 600 W with a nominal 3 sscm flow rate. The growth rate is calibrated from RHEED specular intensity oscillations. The phosphine gas is cracked in the high temperature injector at 900°C, resulting in a phosphorus flux mainly composed of P_2 species. The PH_3 flow rate is monitored at the entry of the injector with a mass-flowmeter, with a maximum flow rate of 10 standard cubic centimetres per minute (sccm).

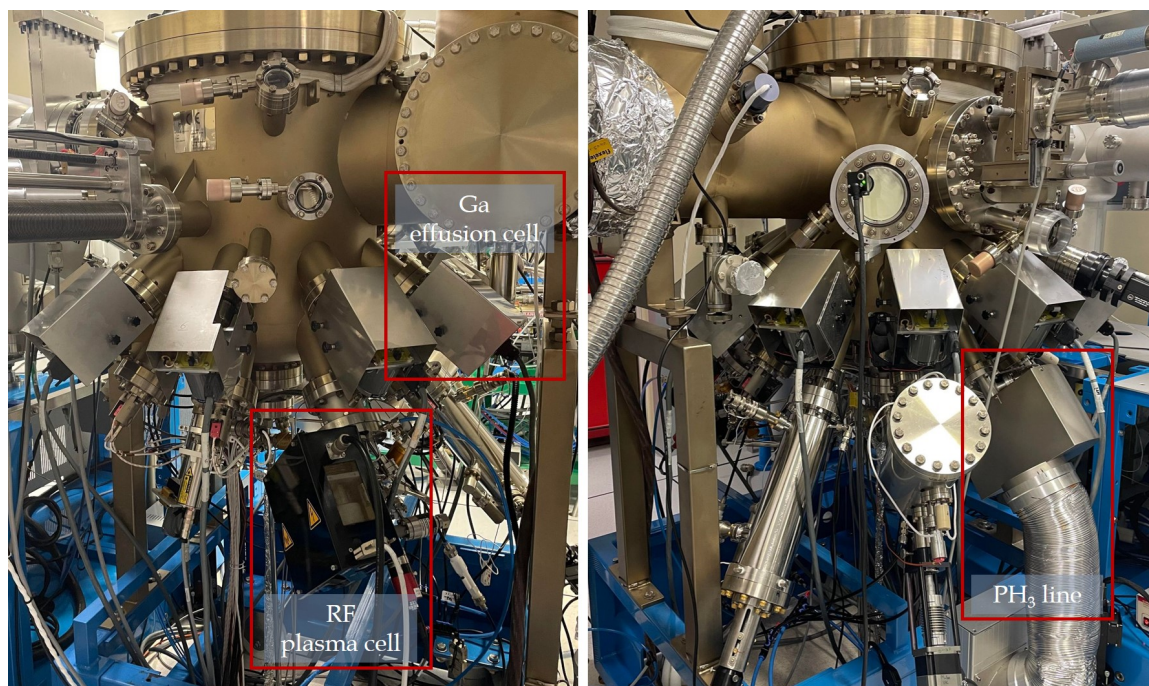


Figure 2.2: III-V reactor specificities

2.1.3 TMDC reactor

The TMDCs system is fitted with a *Riber VCOR110* valve cracker cell and a standard Knudsen effusion cell for selenium sublimation, and a *Telemark 575* electron gun with 6 crucibles for transition metal evaporation (Figure 2.3).



Figure 2.3: TMDC reactor specificities

The selenium valve cracker cell, added during the time of this work, is composed of an evaporator linked to a thermal cracker (tip). The evaporator temperature is maintained between 135 and 200°C while the tip temperature located 30 cm away is maintained between 325 and 450°C. At a fixed set of temperatures, the aperture of a valve prior the shutter monitors the selenium flux, allowing varying it during the growth. The selenium **beam equivalent pressure (BEP)** and the associated growth rate ($\text{\AA}/\text{s}$) are measured using simultaneously a Bayart-Alpert ion gauge and a quartz microbalance placed near the sample position. We target Se equivalent pressure in the range $1 \times 10^{-7} - 5 \times 10^{-6}$ Torr, corresponding to growth rates in the 0.02-2.2 $\text{\AA}/\text{s}$ range. Since for similar temperature conditions on the selenium cell the BEP measurements were more reproducible from day to day than the growth rate ones, we mainly refer to the selenium BEP for the experiments described in this work.

The different transition metal solid sources used in this work are placed in several refractory crucibles fitted with the appropriate liner. The metal evaporation is performed thanks to a 10 kV scanning electron beam deflected by 270°. The electron current defines the tungsten or hafnium growth rate, which is measured with the quartz microbalance at the sample position. As the melting point of tungsten and hafnium are at 3387°C and 2222°C, the desired growth rates are experimentally obtained for currents between 160 and 190 mA, and between 47 and 66 mA, respectively. However, this measure should be made after a degassing process, which is conducted by scanning the source at higher currents for 20 minutes. The current is then decreased down to desired value with a constant ramp of 3 mA/min, aiming to growth rates between 0.001 $\text{\AA}/\text{s}$ and 0.02 $\text{\AA}/\text{s}$.

The growth time estimation is based on the transition metal growth rate measured in $\text{\AA}/\text{s}$ converted in terms of number of TMDC monolayers per seconds (ML/s). The proportionality factor between those two values is calculated as a ratio between the number of M atoms deposited on the quartz microbalance for a thickness of one angstrom and the number of M atoms composing one TMDC monolayer, both expressed in terms of $\text{at}\times\text{M}/\text{cm}^2$. Table 2.1 summarizes the parameters used in this work. Therefore, the

WSe₂ and HfSe₂ growth times are estimated from the expression:

$$t(s) = \frac{\text{ML number}}{\alpha} \times \frac{1}{V_M}$$

	WSe ₂	HfSe ₂
a (Å)	3.28	3.75
1ML (at×M/cm ²)	1.035 × 10 ¹⁵	8.233 × 10 ¹⁴
M _{vol} (g/cm ⁻³)	19.3	13.28
M _{mol} (g/mol)	183.84	178.49
1Å(at×M/cm ²)	6.32 × 10 ¹⁴	4.48 × 10 ¹⁴
α=Å/ML	0.611	0.544

Table 2.1: conversion ratio calculation summary

We point out the difficulty we have faced to control efficiently the grown thickness, as we have generally obtained samples thinner than expected. The origin of this systematic difference between the estimated thicknesses calculated prior the process and the effective ones observed with scanning transmission electron microscopy or calculated with X-ray photoemission spectroscopy intensities ratio is twofold. First, for tungsten, we did not succeed in regulating the growth rate and therefore used a constant current determined by calibration before growth. It is likely that the growth rate decreases with time at constant current. Second, the electron beam used for metal sublimation also evaporates the selenium species accumulated within the electron gun environment by thermal radiation, inducing an undesired increase of the measured growth rate, which is difficult to quantify.

To prevent surface oxidation, the samples devoted to ex-situ characterizations (apart for atomic force microscopy analysis) are capped using a 30-50 nm thick amorphous selenium layer grown below 20°C. As the different microscopy characterization techniques analysis require sample sizes of approximatively 0.5 × 0.5 cm², the GaP/TMDC heterostructures are removed from the Si wafers by heating the system up to 170°C on a hot plate. The potential desorption of the selenium species at this temperature imposes a short execution time estimated around 20 seconds. The samples are then cleaved following the primary directions of the substrate in order to select a central zone.

2.2 Diffraction characterization methods

2.2.1 Grazing incident X-Ray Diffraction (GIXRD)

Grazing incident **XRD** is a strong characterization technique for quantifying the in-plane disorientation and estimating the average grain size of the TMDC films. The Bragg's law leads the diffraction condition of the X-ray incident beam^{239, 240}, according to $n\lambda = 2d \sin \theta$. This allows determining the inter-planar spacing d_{hkl} between a set of crystal planes with Miller indexes h , k and l . The theoretical Bragg reflections of the different materials involved in this work are presented in Annex A. The calculation is based on the relation:

$$2\theta_{th} = 2 \arcsin \frac{\lambda}{2d_{hkl}} \quad (2.1)$$

where λ is the radiation wavelength. The general equation of d_{hkl} for a hexagonal lattice stands as:

$$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3} \frac{h^2 + k^2 + hk}{a^2} + \frac{l^2}{c^2}}} \quad (2.2)$$

with a and c the mesh parameters summarized in Table 2.2, The d_{hkl} equation for a cubic lattice with mesh parameter a is simplified into:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2.3)$$

2H-WSe ₂ P6 ₃ /mmc	1T-HfSe ₂ P-3m1	GaP F-4 ₃ m	GaSe P6 ₃ /mmc
a 3.33Å	a 3.77Å	a 5.45Å	a 3.77Å
c 15.07Å	c 6.41Å	c 16.53Å	c 16.53Å

Table 2.2: mesh parameters of hexagonal WSe₂, HfSe₂, GaSe and cubic GaP

2.2.1.1 X-ray generation and equipment

In the monochromatic mode, the most common source is Cu $K\alpha$ X-rays. To this end, an electron beam produced by heating a filament and accelerated in vacuum by a 20-60 kV electric field bombards a Cu-metallic rotating anode. A Nickel filter is then used in order to absorb the Cu $K\beta$ wavelength, resulting in the generation of a Cu $K\alpha_{1,2}$ monochromatic beam of wavelength $\lambda=1.542$ Å. One alternative for increasing the selectivity is to produce a beam with a narrower wavelength distribution by using a single-crystal monochromator placed before the sample. However, the induced intensity reduction prevents from using it in grazing incidence. Several slits and parabolic mirrors are placed after the anode in order to reduce the beam natural divergence, generally around 6°. The sideways divergence of the incident or scattered beams can also be controlled using Soller slits inserted in the X-ray beam path, resulting in less asymmetric and narrower peak shapes.

The XRD equipment used for this work is a **SmartLab RIGAKU** located at the Chevreul Institute in Villeneuve d'Ascq with the help of Pascal Roussel and Lydia Karmazin. We use a generator slit of 0.1 mm, a sideways Soller slit of 0.114° before the sample, and a detector slit of 10 mm. The grazing incidence condition is set by incident and exit angles ω and θ equal to 0.5° (Figure 2.4), just above the total reflection angle.

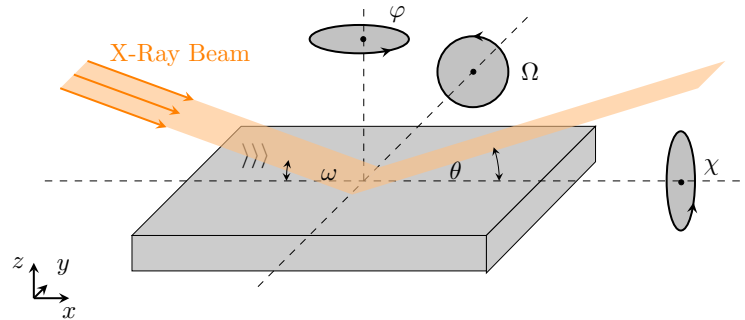


Figure 2.4: SmartLab RIGAKU in grazing incidence schematic

2.2.1.2 Experiments

The use of grazing incident XRD for this work aims at measuring the in-plane angular spread and estimating the average grain size of the grown films. At first, the detector is moved to the substrate Bragg reflection, also called inter-planar angle $2\theta_\chi$, which is set at 47.13° and corresponds to the (2-20) GaP reflection. Then, we perform a full rotation of the sample on itself (φ scan), leading to a succession of diffraction peaks attributed to the GaP substrate. A series of $2\theta_{\chi/\varphi}$ scans between 10 and 115°, implying

the rotation of the detector with the sample (Figure 2.5), are then performed after defining the starting point of the sample rotation on the most intense φ_{GaP} peak. These scans reveal several TMDC Bragg reflections attributed to specific Miller indexes h, k, l . The (110) TMDC peak is further used as reference for a second $360^\circ \varphi$ scan which leads to a succession of diffraction peak attributed to the TMDC layer only.

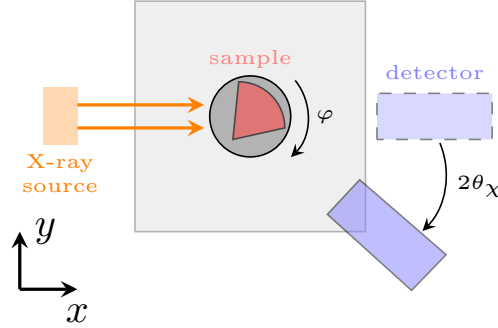


Figure 2.5: SmartLab RIGAKU in grazing incidence top view schematic, $2\theta_{\chi/\varphi}$ scan acquisition

The in-plane angular spread is directly measured from extracting the integral breadth of the most intense φ_{TMDC} peak. On the other hand, the average grain size estimation is extracted from the Scherrer equation:

$$L = \frac{k\lambda}{\beta \cos \theta} \quad (2.4)$$

where L is the grain size, λ is the incident wavelength ($1.54 \text{ \AA}$), k is the Scherrer constant²⁴¹ set at 1, β is a $(h \ k \ l)$ $2\theta_{\chi/\varphi}$ peak integral breadth after the suppression of the instrumental contribution and $\theta = 2\theta_{\chi/\varphi}/2$ is the experimental position of the selected $[h \ k \ l]$ TMDC Bragg reflection.

As a further improvement, Williamson and Hall²⁴² have added the contribution of the microstrain to the peak width under the form $\beta_e = C\varepsilon \tan \theta$, which then becomes $\beta = \frac{k\lambda}{L \cos \theta} + \beta_e$, transforming the equation 2.4 into:

$$\beta \cos \theta = C\varepsilon \sin \theta + \frac{k\lambda}{L} \quad (2.5)$$

Considering the TMDC (100), (110), (200) and (300) Bragg reflections, Equation 2.5 can be used as a linear regression for extracting the average grain size. For this work, the experimental φ peaks are fitted using a Gaussian lineshape with *Origin2023*[®], while $2\theta_{\chi/\varphi}$ peaks are fitted with a pseudo-Voigt (Gauss-Lorentz) lineshape with *WinPLOTR- fullprof*[®].

2.2.2 Reflective High Energy Electron Diffraction (RHEED) and Low-energy Electron Diffraction (LEED)

In Situ **RHEED** is used to control the evolution of the surface crystallography and morphology during the growth. In addition, *ex situ* **LEED** placed in the XPS reactor completes this analysis.

The RHEED method consists in focusing an electron beam generated with a few kV onto the sample surface in grazing incidence, as presented in Figure 2.6. The crystalline lattice diffracts the electron beam whose diffraction pattern defined by the intersection of the Ewald sphere with the reciprocal

lattice is projected on a fluorescent screen. The penetration depth is around 1 nm due to the strong epi-layer/electron interaction. The longitudinal coherence length due to the beam wavelength is estimated around 15 nm whereas the lateral coherent length arising from the angular dispersion of the incident beam is around 5 nm²⁴³. Therefore, the RHEED pattern will be sensitive to surface morphology changes at a length scale below these coherent lengths, *i.e.* in a range of a few tenths of nanometers.

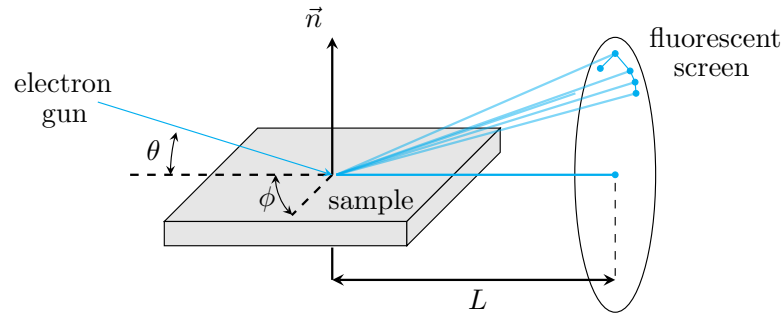


Figure 2.6: RHEED schematic

In the case of an epitaxial growth, four different diffraction patterns are referenced. The presence of anisotropic vertical lines characterizes a good alignment of the crystallites in the plane (Figure 2.7a & 2.7b), whereas isotropic vertical lines represent randomly oriented crystallites in the plane. The presence of isotropic points indicates a 3D growth behaviour with well-oriented crystallites (Figure 2.7c & 2.7d), whereas isotropic rings would define randomly oriented crystallites with a high roughness. The azimuthal rotation of the sample induces an evolution of the diffraction pattern, which enables the determination of the epitaxial relationship between the substrate and the grown layer in the case of anisotropic vertical line observation.

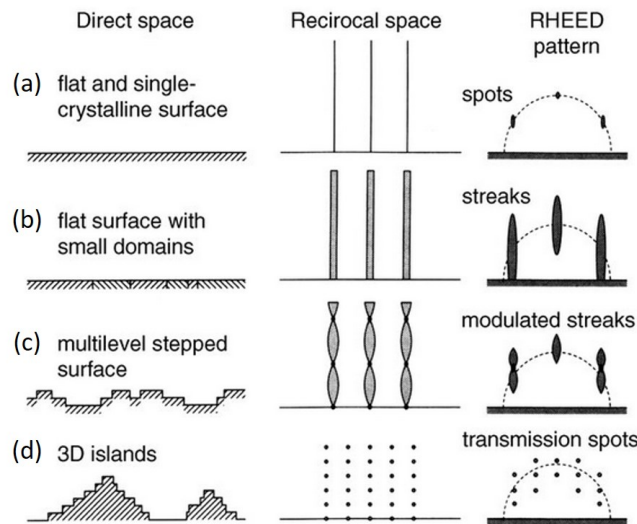


Figure 2.7: Schematic of various kinds of real surfaces, in real-space morphology, in reciprocal space, and their RHEED pattern, extracted from ²⁴³.

The **Low Energy Electron Diffraction** technique uses a low energy electron beam (50-200 eV) in normal incidence. The resulting pattern produces a direct representation of the pseudo-2D surface reciprocal lattice but information about surface roughness is hardly obtainable.

2.3 Spectroscopic characterization methods

2.3.1 Raman spectroscopy

The Raman spectroscopy is a non-destructive technique based on the frequency shift induced by the inelastic scattering of incident photons after interacting with an atom electron cloud. A laser illuminates the surface, scattering photons exhibiting a frequency shift representative of the excited vibration mode energy, generally expressed in cm^{-1} . In this work, the vibration modes of WSe_2 induced by intra-planar atomic vibrations are exploited to qualify the various polytypes. The **Full Width at Half Maximum (FWHM)** measurement of WSe_2 and HfSe_2 Raman peaks is also indicative on the crystal quality. However, as the intensity of the signal is directly linked to the thickness of the sample, the observation of a Raman shift signal for monolayer samples has been challenging. Moreover, due to the large probed depth (~ 100 nm), the spectra presented in this manuscript have been adjusted after subtracting all the GaP substrate contribution. The resulted peaks are fitted with Lorentzian components.

Dominique Vignaud and Flavie Braud have performed the Raman spectroscopy in the IEMN clean room on a *Horiba Scientific LabRAM HR* instrument with a laser wavelength of 473.1 nm. The spectral resolution is 0.5 cm^{-1} for a grating with 1800 grooves per mm. The analysed range stands between 100 cm^{-1} and 700 cm^{-1} .

2.3.2 X-ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) is by many means the main characterization method employed in this work, as it is first directly linked to the MBE reactors through the **UHV** line, preventing any oxidation of the sample. The main purpose of XPS is to identify, quantify the different elements and analyse their chemical state and stoichiometry at the sample surface thanks to a maximum probed depth of around 10 nm. Besides, the different features of the technique are exploited to calculate the thickness of the TMDC film and characterize the band structure by measuring the valence band discontinuity and estimating the band bending of deoxidized and Se-passivated samples.

2.3.2.1 Operating principle and system used

During the measurement, a monochromatic X-ray beam of energy $h\nu$ illuminates the sample. The generated photons penetrate the analysed material and excite the different core level electrons. The induced photoelectric effect excites electrons, which are extracted from their initial energy state E_i to a final state E_f above the vacuum level while the energy conservation law implies that $E_f - E_i = h\nu$ as presented in Figure 2.8. The extracted electron, called photoelectron, is carried out of the surface, behaving as a free electron. When reaching the spectrometer, it possesses a kinetic energy E_k , which can be expressed as:

$$E_k = h\nu - E_b - \phi_s \quad (2.6)$$

Where E_b is the binding energy of the extracted electrons, and ϕ_s is the spectrometer work function. During the measurement, the sample and the spectrometer are electrically contacted, which implies that their respective Fermi level are aligned. The determination of ϕ_s is performed during the spectrometer calibration using metallic gold samples for which the $4f_{7/2}$ core level binding energy is well documented and set at 84 eV.

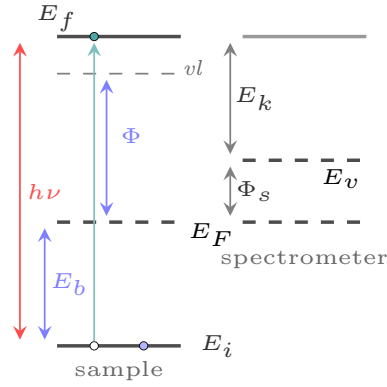


Figure 2.8: photoemission principle in XPS

For this work, XPS measurements are performed on a *Physical Electronics PHI 5600* system as presented in Figure 2.9. The analysis chamber is equipped with an ionic pump and a turbomolecular one, which maintain a pressure in the low 10^{-10} Torr range. It is fitted with a non-monochromatic magnesium source used for photoelectron diffraction measurements and a monochromatic Al $K\alpha$ X-ray source of energy 1486.6 eV for which the ultimate overall resolution as measured from the FWHM of the Ag $3d_{5/2}$ line is 500 meV. X-rays are produced by bombarding an aluminium anode with a high-energy electron beam and diffracted onto the sample by a quartz crystal monochromator. A series of electrostatic extraction lenses collect the emitted photoelectrons further sent into the analyser made of two polarized hemispheres designed to select electrons with a specific energy E_{pass} . They are further detected by a multichannel plate detector, while photoelectrons with a different energy are attracted by the hemispheres and do not contribute to the measurement. The energy resolution ΔE of such analyser is related to the pass energy E_{pass} as:

$$\Delta E = E_{\text{pass}} \times \left(\frac{W_1 + W_2}{2R} + a^2 \right) \quad (2.7)$$

where W_1 is the input slit width in the radial direction, W_2 is the exit slit width or effective element slit width in the radial direction, R is the mean radius of the analyser, and a is the half-angle in the radial direction of the input particle distribution²⁴⁴.

The angle between the incident monochromatic X-Rays source and the analyser is 90° and the acceptance angle of the hemispherical analyser is set to 14° . The direction of photoelectrons is given by the polar angle θ , as referenced to the sample surface and the azimuth angle φ . The result is a $I=f(E_b)$ spectrum where I is the intensity of the photoelectron current for a defined binding energy measured in count per second (c/s). The background signal is attributed to secondary electron emission produced by the inelastic diffusion of the photoelectrons before reaching the surface of the sample.

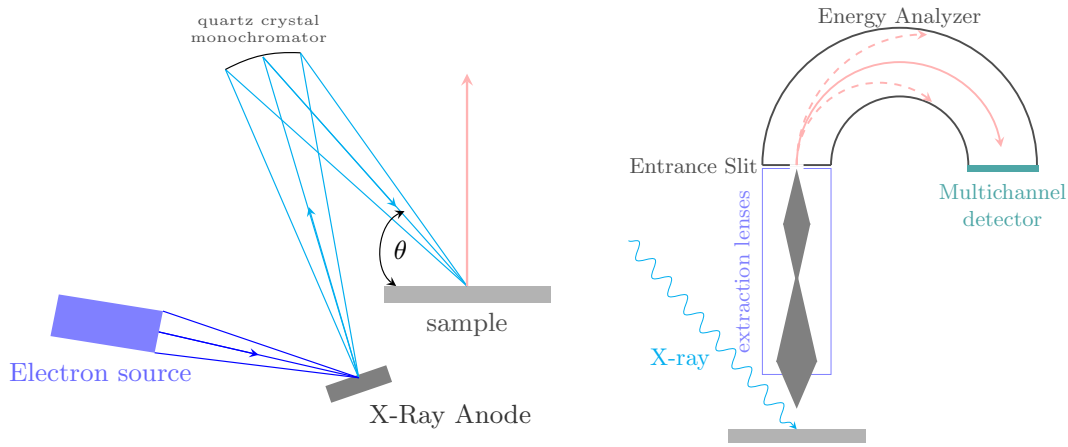


Figure 2.9: XPS schematic

2.3.2.2 Experimental details

A large binding energy scan between 1400 and 0 eV is systematically performed at the beginning of the analysis with a pass energy of 58.7 eV. The main identified peaks on this spectrum are then independently analysed at higher resolution with a lower pass energy of 11.75 eV. To obtain depth dependent measurements, three polar angles, *i.e.* 25, 45, 75° are chosen whereas the azimuth angle is fixed along the [11-2] sample direction. The analyser half acceptance angle is 7°. The analysed **Core levels (CLs)** are Ga 3d, Ga 2p, P 2p, Se 3d, W 4f and Hf 4f. The presence of several components within one XPS CL can be attributed to the doublet separation of the p, d and f levels induced by the coupling between the electrons orbital kinetic and spin moments. The splitting energies²⁴⁵ are fixed at 0.44 eV between Ga 3d_{5/2} and Ga 3d_{3/2}, 0.86 eV between P 2p_{3/2} and P 2p_{1/2}, 0.86 eV between Se 3d_{5/2} and Se 3d_{3/2}, 2.16 eV between W 4f_{7/2} and W 4f_{5/2}, and 1.67 eV between Hf 4f_{7/2} and Hf 4f_{5/2}. The intensity of the various XPS are measured as the peak area after standard background subtraction according to the Shirley procedure^{246, 247}. Core level decomposition is achieved using pseudo-Voigt functions within the *PHI Multipak*TM software²⁴⁸.

2.3.2.3 Thickness calculation

The following method has been adapted from Tran Minh Duc synthetic work on quantitative XPS²⁴⁹, Jawad Hadid²⁵⁰ and Adrian Hemmi²⁵¹ PhD manuscripts. The Beer Lambert differential equation law 2.8 gives the XPS emission intensity from an infinitely thin layer dz at depth z from the surface, with a take-off angle θ . It is proportional to the atomic density of the analysed material N , the photoemission cross section σ , the transmission factor of the spectrometer T , the photon flux ϕ_θ , the analysed area A_θ and the emission anisotropy L . This last parameter is defined by the asymmetry parameter β depending on the kinetic energy of the analysed photoelectron x , the orbital type (s, p, d,...), and the angle between the incident X-Rays and the analyser γ ($\gamma=90^\circ$ here), leading to $L_x = 1 + \frac{\beta_x}{2} \cdot \left(\frac{3}{2}(\sin \gamma)^2 - 1 \right) = 1 + \frac{\beta_x}{4}$ for this work. We consider that the probability of a photoelectron to escape from the solid is limited by its **Inelastic Mean Free Path (IMFP)** λ_x , which depends directly on the kinetic energy of the electrons.

$$dI_x(z) = N \cdot \sigma \cdot T \cdot \Phi_\theta \cdot A_\theta \cdot L_x \cdot e^{\frac{-z}{\lambda_x \sin \theta}} dz \quad (2.8)$$

Therefore, the measured XPS signal intensity for a homogeneous sample of thickness d is obtained by integrating $dI(z)$:

$$I_x(z) = N \cdot \sigma \cdot T \cdot \Phi \cdot A_\theta \cdot \sin \theta \cdot L_x \cdot \lambda_x \cdot \left(1 - e^{-\frac{d}{\lambda_x \sin \theta}}\right) \quad (2.9)$$

Considering a bulk material of infinite thickness, the integration of expression 2.8 would yield to the photoemission intensity I_x° .

$$I_x^\circ = N \cdot \sigma \cdot T \cdot \Phi_\theta \cdot A_\theta \cdot \sin \theta \cdot \left(1 + \frac{\beta_x}{4}\right) \cdot \lambda_x \quad (2.10)$$

For simplification, the thickness isolation procedure presented in the next paragraph will focus on the intensities of the W 4f and Ga 3d peaks. The calculation remains identical considering Hf 4f or Se 3d and P 2p. From the last equation, the standards intensities for infinite thicknesses of WSe₂ and GaP are presented in relations 2.11 and 2.12, respectively. λ_{W-WSe_2} and λ_{Ga-GaP} are the IMFP values of a photoelectron emitted from W 4f and Ga 3d going through WSe₂ and GaP, respectively.

$$I_{W-WSe_2}^\circ = N_W \cdot \sigma_W \cdot T \cdot \Phi_\theta \cdot A_\theta \cdot \sin \theta \cdot \left(1 + \frac{\beta_W}{4}\right) \cdot \lambda_{W-WSe_2} \quad (2.11)$$

$$I_{Ga-GaP}^\circ = N_{Ga} \cdot \sigma_{Ga} \cdot T \cdot \Phi_\theta \cdot A_\theta \cdot \sin \theta \cdot \left(1 + \frac{\beta_{Ga}}{4}\right) \cdot \lambda_{Ga-GaP} \quad (2.12)$$

Moreover, the experimental XPS signal intensity of W 4f for an undetermined WSe₂ thickness d is defined from equations 2.9 and 2.11, as:

$$I_{W-WSe_2} = I_{W-WSe_2}^\circ \cdot \left(1 - e^{-\frac{d}{\lambda_{W-WSe_2} \sin \theta}}\right) \quad (2.13)$$

Considering an electron emitted from Ga 3d and going through WSe₂, a change in IMFP should be accounted for through the following equation:

$$I_{Ga-GaP} = I_{Ga-GaP}^\circ \cdot e^{-\frac{d}{\lambda_{Ga-WSe_2} \sin \theta}} \quad (2.14)$$

By dividing equation 2.13 and 2.14, the unknown parameter T , Φ_θ and A_θ are suppressed, leading to:

$$\frac{I_{W-WSe_2}}{I_{Ga-GaP}} = \alpha_{W/Ga} \times \left[e^{\frac{d}{\lambda_{Ga-WSe_2} \sin \theta}} - e^{\frac{d}{\sin \theta} \left(\frac{1}{\lambda_{Ga-WSe_2}} - \frac{1}{\lambda_{W-WSe_2}} \right)} \right] \quad (2.15)$$

The parameter $\alpha_{W/Ga}$ is the ratio between standard intensities, which must be calculated before isolating the thickness:

$$\alpha_{W/Ga} = \frac{I_{W-WSe_2}^\circ}{I_{Ga-GaP}^\circ} = \frac{N_W \cdot \sigma_W \cdot (4 + \beta_W) \cdot \lambda_{W-WSe_2}}{N_{Ga} \cdot \sigma_{Ga} \cdot (4 + \beta_{Ga}) \cdot \lambda_{Ga-GaP}} \quad (2.16)$$

From this point, the thickness can be extracted by means of a solver for a fixed angle value, or by exploiting the three polar angles with a linear regression calculation after estimating the different IMFPs. It is only doable if considering that λ_{Ga-WSe_2} and λ_{W-WSe_2} values are similar, which simplifies the relation 2.15 into:

$$\ln \left[\frac{I_{W-WSe_2}}{I_{Ga-GaP}} \cdot \frac{1}{\alpha_{W/Ga}} + 1 \right] = \frac{d}{\lambda_{Ga-WSe_2}} \cdot \frac{1}{\sin \theta} \quad (2.17)$$

However, the simplification of the model, which is not considering elastic scattering effects (Figure 2.10), can induce a considerable deviation for thin layer thicknesses calculations. One convenient procedure

to overcome this issue is to consider the **Effective Attenuation Length (EAL)** rather than IMFP in the formula, though ISO warns that EAL values may be different depending on the analytical applications²⁵².

The EAL calculated for bulk materials with uniform surface region is generally identified by the index QA, with a value L_{QA} defined by the equation 2.18, estimated from Si, Cu, Ag and Au photoelectron lines excited from Mg $K\alpha$ and Al $K\alpha$ by Jablonski and Powell²⁵³. The so-called single-scattering albedo ω characterizes the inelastic and elastic scattering properties of a solid as $\omega = \frac{\lambda_{in}}{\lambda_{in} + \lambda_{tr}}$, with λ_{in} the IMFP of the analysed photoelectron, and λ_{tr} the associated Transport Mean Free Path (TRMFP)^{252, 254}.

$$L_{QA} = \lambda_{in}(1 - 0.147\omega - 0.164\omega^2) \quad (2.18)$$

On the other hand, considering a finite thickness d would induce a change in EAL identified by the index TH designed for overlayer thickness measurement. The implied L_{TH} value defined by the equation 2.19, with $Z = \frac{a \cdot Z_a + b \cdot Z_b}{a+b}$ the average atomic number for a binary compound, is considerably differing from L_{QA} . When developing this equation, Jablonski and Powell confronted the calculated EALs for different excitation rays between 321 eV and 4.4 keV to the ones obtained from Monte Carlo simulations and transport approximation (TA) approach, highlighting a slight divergence of 1.71%²⁵⁵.

$$L_{TH} = 0.979\lambda_{in}[1 - \omega \cdot (0.955 - 0.077 \ln Z)] \quad (2.19)$$

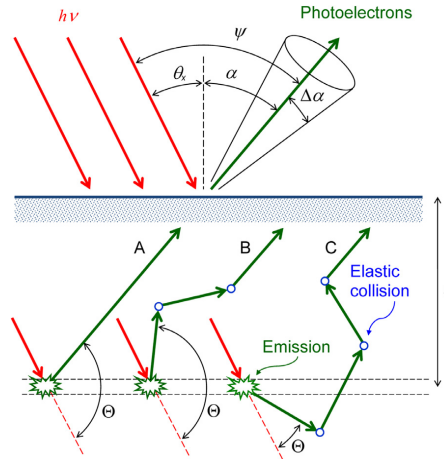


Figure 2.10: Outline of a typical experimental configuration for XPS measurements, extracted from ²⁵².

By substituting the different values of IMFP by EAL ones, equations 2.15 and 2.16 evolve into:

$$\frac{I_{W-WS_{e2}}}{I_{Ga-GaP}} = \frac{I_{W-WS_{e2}}^0}{I_{Ga-GaP}^0} \times \left[e^{\frac{d}{L_{TH}^{Ga-WS_{e2}} \sin \theta}} - e^{\frac{d}{\sin \theta} \times \left(\frac{1}{L_{TH}^{Ga-WS_{e2}}} - \frac{1}{L_{TH}^{W-WS_{e2}}} \right)} \right] \quad (2.20)$$

$$\alpha_{W/Ga} = \frac{I_{W-WS_{e2}}^0}{I_{Ga-GaP}^0} = \frac{N_W \cdot \sigma_W \cdot (4 + \beta_W) \cdot L_{QA}^{W-WS_{e2}}}{N_{Ga} \cdot \sigma_{Ga} \cdot (4 + \beta_{Ga}) \cdot L_{QA}^{Ga-GaP}} = \frac{N_W \cdot S_{WSe_2}}{N_{Ga} \cdot S_{GaP}} \quad (2.21)$$

with S the different sensitivity factors that can be deduced for Se:W or Se:Hf intensity ratios estimation, presented in Annex B.

In Table 2.3, we point out the clear difference between IMFPs and EALs for a finite thickness, whereas both values are rather similar if considering an infinite one. The lower L_{TH} values tend to correct a

potential over evaluation of the film thickness, justifying our choice to select this more complex model *a priori*.

However, the **Scanning Transmission Electronic Microscopy (STEM)** observation of the samples grown during this work highlighted a significant and systematic understate of the calculated thickness using EAL, while the use of IMFP lead to a better convergence between both values. We assume that this underestimation using EAL comes from the low film thickness close to the limit of the model.

For this work, the photoemission cross-section values σ are extracted from J. H Scofield calculations²⁵⁶, while the different asymmetry parameters β are obtained from J.J Yeh and I. Lindau ones in the dipole length approximation²⁵⁷. The atomic densities N of GaP, HfSe₂ and WSe₂ and the different values of IMFP, TRMFP and EAL calculated from the **National Institute of Standards and Technology (NIST)** database^{258, 259, 260, 261} are presented in Annex B.

$\lambda_{in}^{W-WSe_2}$		$\lambda_{in}^{Ga-WSe_2}$	λ_{in}^{Ga-GaP}
26.07 Å		26.25 Å	30.41 Å
$L_{TH}^{W-WSe_2}$	$L_{QA}^{W-WSe_2}$	$L_{TH}^{Ga-WSe_2}$	L_{QA}^{Ga-GaP}
21.22 Å	24.81 Å	21.37 Å	29.44 Å

Table 2.3: IMFPs, L_{TH} and L_{QA} comparison for WSe₂ on GaP

2.3.3 X-Ray Photoelectron Diffraction (XPD)

Considering the equations 2.11 or 2.12 earlier expressed, the XPS intensity for a homogenous sample in depth is expressed in terms of the polar angle θ and the transmission factor T . The intensity should vary gently as a function of θ , following the variation of T . However, this is clearly not the case, especially for monocrystalline samples, as presented in Figure 2.11a where the intensity profiles of Ga 3d and P 2p from a deoxidized GaP(111)_B substrate exhibit strong variations along the [11-2] direction. These modulations are induced by an interference phenomenon called photoelectron diffraction^{262, 263}, which is directly linked to the scattering of the emitted wave by neighbouring atoms. For high kinetic energies of 1 keV or more, the electron-atom scattering is dominated by a strong and narrow peak in the forward direction²⁶⁴. Considering a simple diffusion model in straight line, there is a non-zero probability for the emitted wave to be diffused by the neighbouring atoms during the propagation step along crystallographic rows, leading to a beam focalization for high kinetic energies (Figure 2.11b) and inducing an increase of the XPS CL intensity. By varying the polar angle, the interferences conditions are changed, resulting in different peaks observed on intensity profiles along specific crystallographic directions, which can be exploited to determine the different positions of the atoms at the crystal surface.

X-Ray Photoelectron Diffraction (XPD) measurements have been performed on deoxidized GaP(111)_B substrates and Se-passivated samples in order to test the penetration depth of the Se atoms from the surface, using a Mg K α X-ray source (1253.6 eV). In this case the half acceptance angle of the analyser has been set to 2°. The polar angle θ is varied from 25° to 155° with a 2° step and the sample is aligned along the [11-2] direction or along the 30° rotated [110] direction. The Ga 3d, P 2p and Se 3d peaks area are extracted at each iteration for intensity profile construction. The peaks positions are then compared to a simple theoretical calculation of the diffracted photoelectron angles based on a 2D projection along the [11-2] and [110] directions.

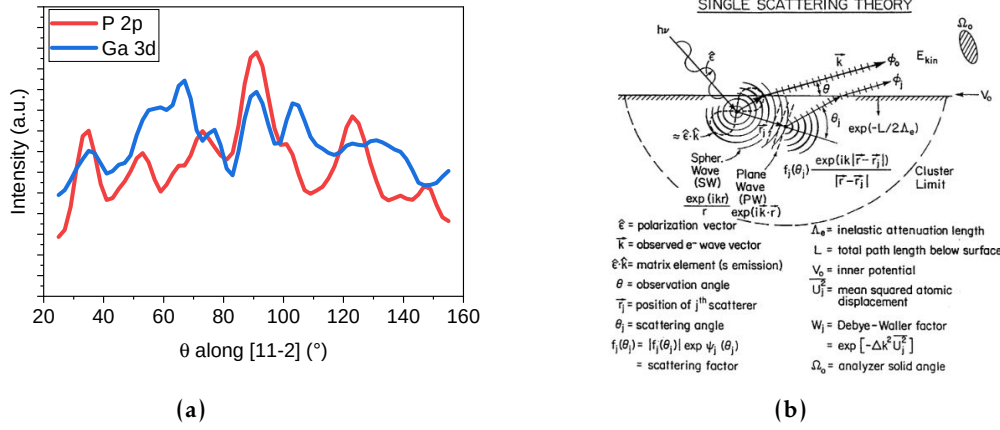


Figure 2.11: (a) intensity profile example for a GaP(111)_B substrate. (b) Schematic drawing of the processes involved in photoelectron diffraction, extracted from ²⁶⁵.

2.3.4 UV Photoelectron Spectroscopy (UPS)

In addition to XPS and XPD measurements, the IEMN surface analysis chamber is equipped with a UV photon source consisting in a helium discharge lamp, whose generated plasma emits two lines: He I $K\alpha$ (21.2 eV) and He II $K\alpha$ (40.8 eV) for **Ultra-violet Photoelectron Spectroscopy (UPS)**. The interests of such low excitation energies is a larger ionization effective cross-section for valence electrons and a thinner excitation line than in XPS. Therefore, UPS is performed for two purposes: the work function determination and the valence band acquisition, which can also be measured in XPS with a lower precision and a lower surface sensitivity²⁶⁶.

As expressed earlier, the XPS and UPS spectra are referenced to the Fermi level (E_F) whose binding energy is equal to zero. Therefore, as illustrated in Figure 2.12, the intersection between the baseline and the decreasing valence band signal at low binding energy determines the position of the material **VBM** compared to E_F . For most of the analysed materials in this manuscript, the VBM is predicted to lie at the Γ point, with the exception of the single layer WSe₂ whose direct bandgap exhibits a VBM at the K point.

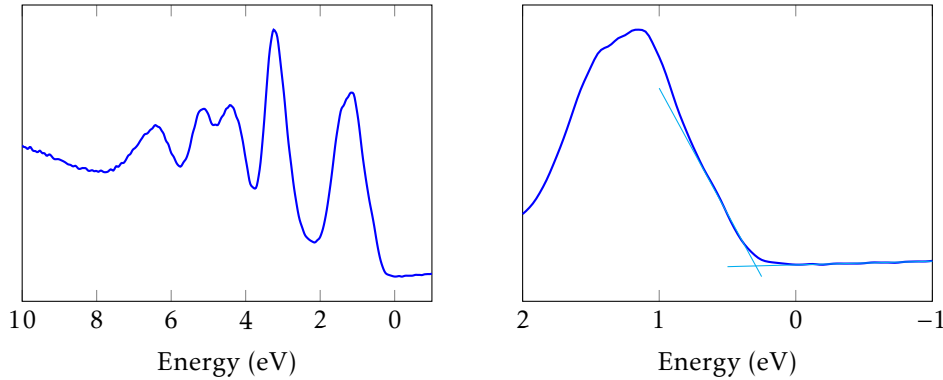


Figure 2.12: Example of $E_F - E_V$ determination using UPS

Considering a hexagonal lattice in the reciprocal space as schematized in Figure 2.13, the distance between the centre of the Brillouin zone Γ and one of its edge K is equal to $\frac{4\pi}{3a}$. In the case of a WSe₂ crystal of in-plane lattice parameter $a=3.34 \text{ \AA}$, this distance is equal to $\Gamma K=1.25 \times 10^{10} \text{ m}^{-1}$.

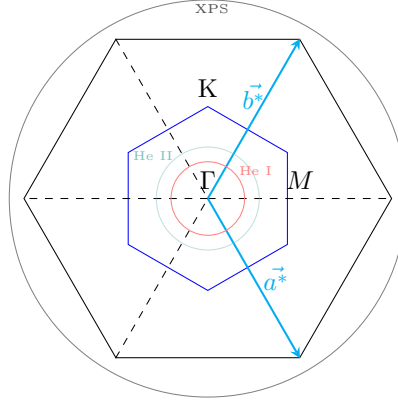


Figure 2.13: Schematic of a hexagonal reciprocal space lattice with the representation of the Brillouin zone. The circles represent the analysed zone in the reciprocal space for XPS Al K α , UPS He I K α and UPS He II K α in the case of an analysis around the Γ point.

In general, the emitted beam can be described by means of its maximum kinetic energy $E_{k,\max}$ and its related wave vector near the Fermi level $k_{\max}$.

$$E_{\text{kin},\max} = h\nu - \Phi_{\text{analyzer}} \text{ and } k_{\max} = \sqrt{\frac{2mE_{k,\max}}{\hbar^2}}$$

Therefore, for a given half acceptance angle α , the in-plane and out-of-plane components of the wave vector can be described as $k_{\parallel\max} = k_{\max} \sin \alpha$ and $k_{\perp\max} = k_{\max} \cos \alpha$, whose values depending on the beam source are summarized in Table 2.4 for α equals 2° and 7°. The $k_{\parallel\max}$ value represents the analysed zone radius in the reciprocal space, which does not cover the whole Brillouin zone of WSe₂ when using UPS ($\Gamma K_{\text{WSe}_2} > k_{\parallel\max\text{He II}} > k_{\parallel\max\text{He I}}$). In order to reach a specific point of the Brillouin zone, we need then to vary the polar angle θ and azimuthal angle φ . Therefore, to probe the VBM at the K point for WSe₂ monolayer band structure analysis, a first 30° rotation along φ is applied with respect to the [11-2] direction before setting the polar angle θ to 54.3° for He I and to 66.4° for He II. In the case of multilayer WSe₂, HfSe₂, deoxidized and Se-terminated GaP(111)_B samples, the VBM lies at the Γ point and θ is set at 90°. We align the sample along the primary direction [11-2].

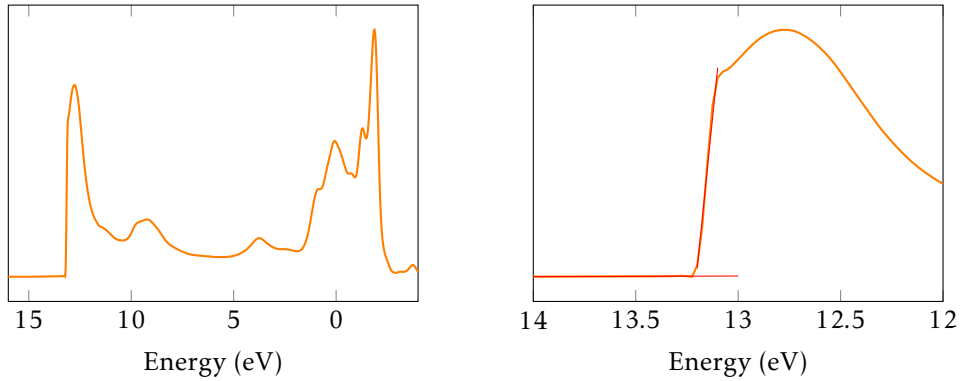


Figure 2.14: Example of ϕ determination using UPS with a -3V polarization

The work function Φ_s is indirectly calculated from the experimental threshold voltage E_{th}^F measurement at high energy using the He I K α source (Figure 2.14). As the analyser and the sample work functions lie in the same energy range, a -3 V negative polarization is applied to the sample, which shifts the UPS

spectrum by 3 eV for all the analysed materials in standard UPS configuration with $\theta=90^\circ$. The sample work function is then deduced from the equation:

$$\phi_s = h\nu + eV_{\text{polar}} - E_{\text{th}}^F \quad (2.22)$$

with $h\nu=21.2$ eV and $eV_{\text{polar}}=-3$ eV.

Source	$E_{\text{kin,max}}$	k_{max}	$k_{\parallel\text{max}} (7^\circ)$	$k_{\perp\text{max}} (7^\circ)$	$k_{\parallel\text{max}} (2^\circ)$	$k_{\perp\text{max}} (2^\circ)$
Al (1486.6 eV)	1482.9	1.97×10^{11}	2.40×10^{10}	1.96×10^{11}	6.88×10^9	1.97×10^{11}
He I (21.2 eV)	17.5	2.14×10^{10}	2.61×10^9	2.13×10^{10}	7.47×10^8	2.14×10^{10}
He II (40.8 eV)	37.1	3.12×10^{10}	3.80×10^9	3.10×10^{10}	1.09×10^9	3.12×10^{10}

Table 2.4: values of $k_{\parallel\text{max}}$ and $k_{\perp\text{max}}$ at different angle α and 3 different beam sources

2.3.5 Angle Resolved PhotoEmission Spectroscopy (ARPES)

Beyond standard XPS and UPS, **ARPES** is simultaneously measuring the emitted photoelectron kinetic energy and their wave vector with both high energy and angular resolutions, leading to characterize the electron energy dispersion depending on the in-plane wave vector component $k_{\parallel}$. The incident beam produced by synchrotron radiation allows tuning the photon energy to maximize the surface sensitivity.

For this work, Abdelkarim Ouerghi, Aymen Mahmoudi and Meryem Bouaziz from C2N have performed the ARPES measurements at the CASSIOPEE beamline of the SOLEIL synchrotron light source. The CASSIOPEE beamline is equipped with a *Scienta R4000* hemispherical electron analyser whose angular acceptance is $\pm 15^\circ$ (Scienta Wide Angle Lens). The experiments were performed at $T=[30-70]$ K with a pressure of 10^{-10} mbar and a spot size of 600 nm. The total angle and energy resolutions were 0.25° and 16 meV.

2.4 Microscopic characterization methods

2.4.1 Atomic force Microscopy (AFM) in "tapping" mode

The morphological surface characterization after the deoxidation process, the Se passivation and the TMDC growth was performed using **AFM**. The conventional AFM setup consists in a silicon tip placed at the end of a cantilever mechanically excited by a piezoelectric element while a laser beam focused at its apex is reflected toward a photodetector as represented in Figure 2.15a. The piezo-scanner moves the sample relative to the probe position. Depending on the tip-sample distance, the interactions forces can be either repulsive or attractive, generally linked to van der Waals, electrostatic or capillary forces (Figure 2.15b). AFM measurement includes three different scanning modes: contact, tapping and non-contact, which are all carried by specific interactions. The tapping mode, or intermittent resonant contact mode, is selected for this work in order to reduce the damage of the sample that can happen in the contact mode and prevents loss of lateral resolution due to lateral forces. The non-contact mode is not considered because of the difficulties in implementation at ambient conditions. In the intermittent resonant contact mode, the cantilever is driven at frequency near its resonance frequency. In a simple picture, the forces damp the oscillations amplitude while the cantilever approaches the surface. Thus, the oscillations amplitude of the cantilever, measured by the photodetector, decreases with the distance

between the probe and the surface. The topographic image of the selected area is obtained by maintaining constant this signal amplitude with the piezo-system and monitoring the height position of the probe. The oscillations amplitude variation at a near resonance frequency is used as an error signal corrected by the probe z-movement induced by the piezo-scanner. The environment mechanical vibrations directly limit the vertical resolution, while the tip curvature radius limits the lateral resolution.

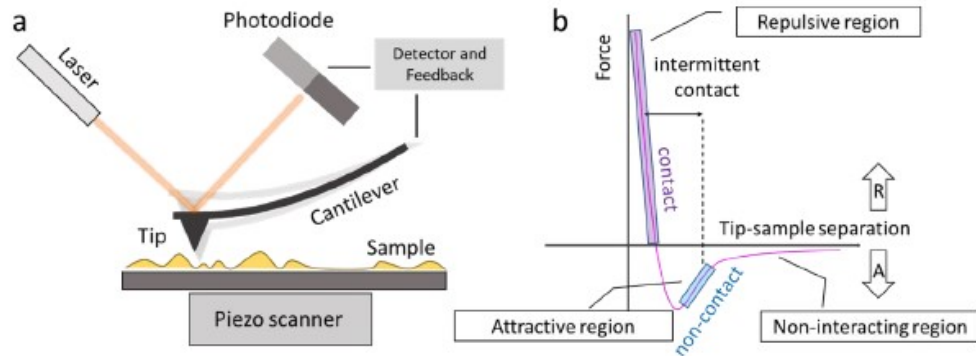


Figure 2.15: The working principle behind AFM. (a) Main parts comprising a typical AFM system. (b) Illustration of a typical force-separation curve, where R and A arrows represent the directionality of the repulsive and attractive force. Extracted from Nemanja Peric PhD manuscript²⁶⁷, p. 61.

The AFM measurements are performed on the scanning probe microscopy unit of the **multi-physics characterization platform (PCMP-PCP)** at IEMN on a *Multimode* model from Bruker monitored with a *Bruker NS4a controller*, and using standard *NCHVA-A* probes from Bruker with a resonance frequency at 320 kHz. We extract three main features: a topographic image, an error image correlated to the variations of amplitude with respect to the setpoint, and a phase image linked to the visco-elasticity, adhesion or stiffness variation on the surface. This last image enables observing chemical environment changes on the surface, helping to identify grain boundaries or surface defects.

2.4.2 Transmission Electronic Microscopy (TEM)

STEM is used to identify the different polytypes encountered in this work and to provide direct observation of the selenium passivation and epitaxial relationship. David Troadec processes the preparation of thin slabs along the substrate cleaving direction [11-2] using **Focus Ion Beam (FIB)** etching at the IEMN **PCMP-PCP**. The current applied for monitor the slab fabrication with the coupled **Scanning Electronic Microscope (SEM)** should not exceed 16 nA in order to prevent the selenium cap degradation. Gilles Patriarche at C2N, Paris, performed STEM studies in a *Titan Themis 200 (FEI)* microscope with an accelerating voltage of 200 kV. The system is equipped with a spherical aberration corrector on the probe and an **Energy-dispersive X-ray Spectroscopy (EDX)** system super X (0.7 srad solide angle of collection). The (half) convergence angle of the probe is 17.6 mrad and the probe current 40-45 pA. The inner and outer semi-angles of the Dark Filed detector are respectively 69 mrad and 200 mrad, detecting inelastically scattered electrons at high angles (HAADF-STEM images). The system is coupled to an **Energy-dispersive X-Ray Spectrometer (EDXS)** used for elemental determination.

2.4.3 Scanning Tunneling Microscopy (STM)

STM is a surface imaging technique at atomic scale thanks to the tunnel effect between the last atoms of a tip shaped probe and the observed surface atoms^{268, 269}. Compared to AFM, the tunnel effect is less

dependent on long distance effects and the resulting image is less affected by tip-induced artefacts as soon as the tip is sufficiently sharp. Besides imaging, the tip-surface electrical bias can be tuned and the resulting current can be recorded in order to estimate locally the density of electronic states on metallic and semiconducting surfaces^{270, 271, 272, 273}.

In conventional STM analysis, a piezoelectric tube is used as an actuator to control the position of a tungsten tip at approximatively 1 nm from the semiconducting surface. At this distance, electrons can cross the dielectric barrier by tunnel effect. While the piezoelectric tube is driving the tip to maintain a constant tunnel current setpoint at a fixed bias, the height variations of the surface are recorded as a function of the lateral position.

Another mode of operation, called **Scanning Tunnelling Spectroscopy (STS)**, measures the tunnel current as a function of the bias sweep at a fixed tip-sample distance. The differential conductance (dI/dV) can as well be recorded, it is proportional to the local density of electronic states after some treatment^{270, 271, 272}. A lock-in amplifier is often used to decrease the noise level of this measurement by directly recording the variations of the current as a function of a bias modulation.

The instrumental setup (*Scienta-Omicron Nanoprobe* coupled with a *Nanonis controller*) is a UHV multiple-probe-STM coupled with a SEM for global navigation. The SEM allows selecting the area to be studied and a precise positioning of the STM probes. Each probe can move independently and can be used as electrical probe for interprobe transport measurements (Keithley SMUs).

The two WSe_2 samples for this study, grown on semi-insulating and n-doped GaP(111)_B substrates, were fixed with a metallic clamp. The use of semi-insulating substrate prevents the injected electron to penetrate the substrate, inducing surface measurements yet with limited current. On the other hand, the measurement with the doped GaP allows using stronger current with only a few proportion of current passes in the surface.

For this work, Zeinab Issa, Maxime Berthe and Louis Biadala have performed STM and STS measurements on the scanning probe microscopy unit of the **PCMP-PCP** at IEMN.

GaP(111)_B surface preparation for TMDC growth

The substrate preparation is a crucial step before the growth of WSe₂ and/or HfSe₂. In this chapter, we discuss the GaP(111)_B surface deoxidation and passivation under selenium flux, the optimisation of both processes as well as the evolution of the band structure. We aim for a complete suppression of the native oxide layer along with favouring the formation of a quasi van der Waals gap at the substrate/TMDC interface without altering the surface morphology. In complement, we study the homoepitaxial growth of GaP(111)_B before the selenium passivation step in order to control the morphology of the atomic steps, which might influence the TMDC nucleation.

3.1 GaP deoxidation

In this section, we present the preparation of the GaP(111)_B surface in the III-V dedicated MBE reactor, starting with the optimization of the deoxidation process and followed by its surface characterization. The goal is to totally remove the native oxide layer without altering the surface morphology. The phosphorus flux, mainly composed of P₂ species is produced through the thermal cracking of PH₃ whose flow rate is controlled by a mass-flow meter. For simplicity, we express the P₂ flux in terms of the PH₃ flow rate.

3.1.1 Process optimization

The first trial of GaP(111)_B deoxidation was based on GaAs conventional preparation process using thermal annealing under As flux monitored by RHEED. The initial P₂ flux was set at 2 sccm and increased up to 8 sccm with the temperature. The initial faint 1 × 1 RHEED pattern was progressively reinforced, while starting to get slightly spotty at 670°C, indicating a surface roughening. When decreasing the temperature under P₂ flux, the 1 × 1 pattern was evolving into a 2 × 2 one that we link to the B-termination, as already observed on GaP(111)_B cleaned in UHV under hydrogen flux²²⁴. However, the reconstruction of GaP(111)_B remains controversial, with observations ranging from 1 × 1 pattern^{221, 222} to more complex 17 × 17^{220, 274, 275} or $\sqrt{247} \times \sqrt{247} - R22.7^\circ$ superstructures²⁷⁶. The observation of such 2 × 2 pattern tends to suggest a P-rich surface, as presented by Kleinschmidt et al.²²⁴.

The AFM image of the resulting surface in Figure 3.1 reveals a textured surface with a RMS roughness of 0.4 nm, while the associated phase image shows circular domains with well-defined grain boundaries. It appears clearly that a lower deoxidation temperature is preferable in order to prevent this roughening.

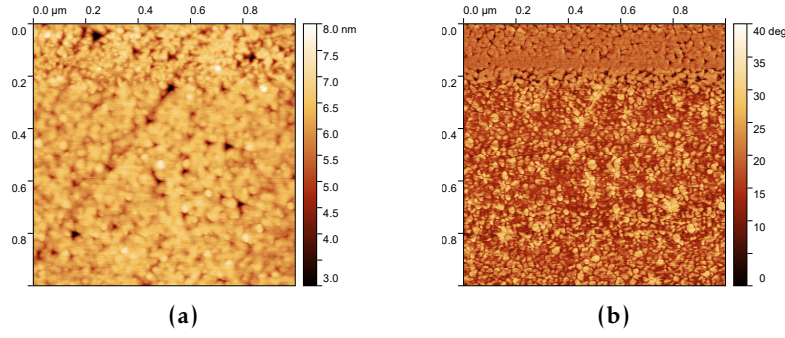


Figure 3.1: $1 \times 1 \mu\text{m}^2$ AFM imaging of a GaP(111)_B surface after a thermal deoxidation at 670°C with its associated phase scan.

Since the deoxidation of GaAs has been optimized using atomic Hydrogen flux (H_{AT})²³⁵, we propose to use a combination of P_2 and H_{at} flux in two steps as the substrate temperature is ramped up. The sample is first heated up to 450°C under H_{at} flux only before shutting it off and increasing the substrate temperature under P_2 flux only. The optimization of the process relies on the variation of the hydrogen exposure time and the final substrate temperature, while the residual traces of oxygen on the surface are tracked using XPS measurements (Figure 3.2a). We point out the need of a minimum H_{at} exposure time of 10 minutes above 250-300°C to reduce the O 1s CL signal below the XPS detection limit. On the other hand, a shorter exposure time induces an increase of the final substrate temperature to suppress the residual native oxide. We use the subsequent P_2 flux exposure to heal the surface, as H_{at} also slightly etches the P surface. Therefore, a minimum P_2 flux of 2 sccm is required, further increased up to 4 and 8 sccm.

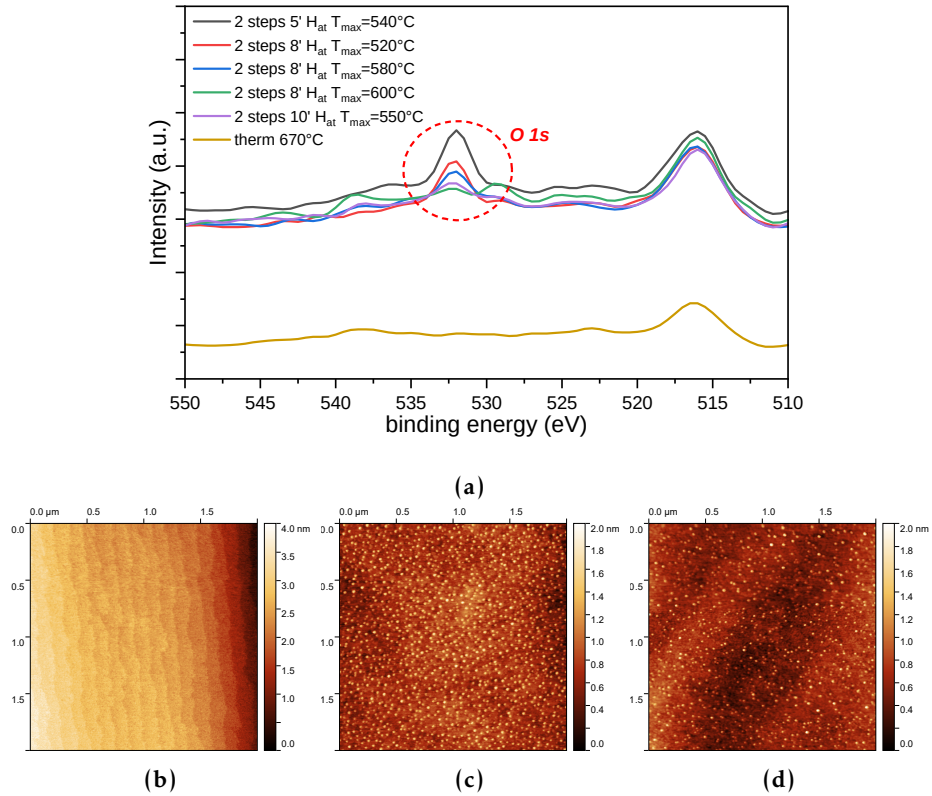


Figure 3.2: (a) XPS survey measurements captured with a take-off angle of 45° for several deoxidation processes in two steps. $2 \times 2 \mu\text{m}^2$ AFM imaging after a deoxidation process using (b) $t_{\text{AH}}=8$ min and $T_{\text{F}}=580^\circ\text{C}$, (c) $t_{\text{AH}}=8$ min and $T_{\text{F}}=600^\circ\text{C}$ and (d) $t_{\text{AH}}=10$ min and $T_{\text{F}}=550^\circ\text{C}$.

However, when looking at the associated AFM images, it appears that a partially deoxidized surface exhibits clear GaP atomic steps (Figure 3.2b), while surfaces treated at higher temperatures or under longer H_{at} exposure times present rough surface with small dots covering the whole surface (Figure 3.2c & 3.2d). Those dots are associated with the formation of Gallium droplets induced by the partial desorption of surface phosphorus, as already observed for GaAs surfaces deoxidized at high substrate temperatures. In addition, the density of the droplets is reduced by a factor 2 when increasing the H_{at} exposure time from 8 minutes to 10 minutes and reducing the final temperature from 600°C to 550°C. We propose to change the current deoxidation sequence in order to maximize t_{AH} and to increase the P_2 exposure time, which is assumed to heal the surface. Therefore, a third step is inserted into the process, where both H_{at} and P_2 are simultaneously injected after the first H_{at} exposure.

The new sequence can be summarized as: H_{at} only from 250-300°C to 450°C, then $H_{at} + P_2$ (2-4 sccm) up to 500°C, and finally P_2 only (4-8 sccm) up to 550°C/560°C. The overall 10 to 11 minutes H_{at} exposure time is spread into two equal parts, as we assume the hydrogen to alter the surface at rather high temperatures. The RHEED pattern evolves from a faint 1×1 to a well-defined one during the two first steps, before turning into a clear 2×2 shortly after the shutdown of H_{at} , further corroborated by the LEED measurements (Figure 3.3).

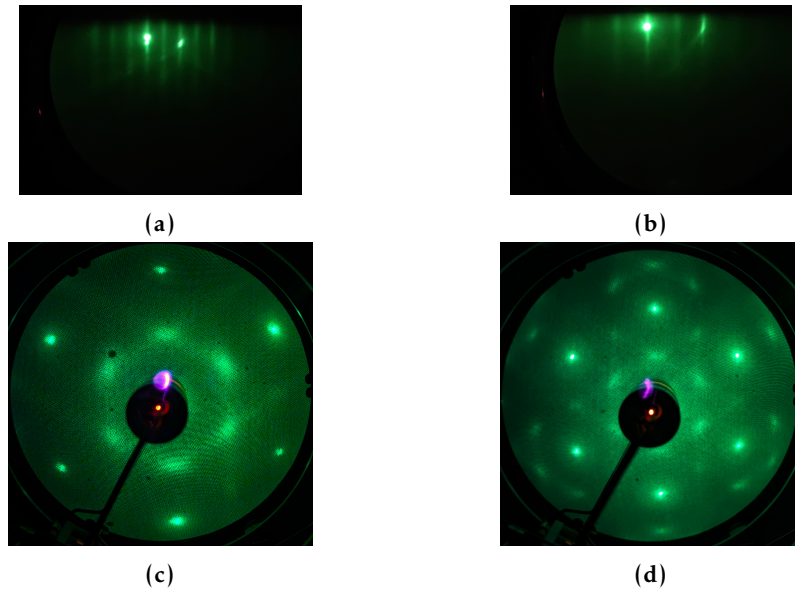


Figure 3.3: 2×2 RHEED pattern along (a) $\langle 1-100 \rangle$ and (b) $\langle 11-20 \rangle$ obtained after a deoxidation process in three steps with a final temperature of 550°C, with the associated LEED pattern recorded at (c) 40 eV and (d) at 80 eV.

When increasing the temperature up to 580°C under a 8 sccm P_2 flux, the 2×2 reconstruction vanishes and gives rise to a faint $\sqrt{19} \times \sqrt{19}$ diagram around 600°C, in a rather similar way to what is observed on GaAs(111)_B^{277, 278}. The XPS measurements presented in Figure 3.4a shows the efficiency of the new deoxidation process, with the total suppression of the O 1s CL for a final temperature of 540°C. Besides, $2 \times 2 \mu m^2$ AFM image of a well deoxidized GaP surface with the new sequence exhibits a smooth surface with an RMS roughness of 0.15 nm, with clear atomic steps yet serrated and tiny dots over the surface with a mean diameter of 9 nm (Figure 3.4b). When increasing the final temperature up to 650°C, the dot density is decreasing while their size is increased up to 20 nm (Figure 3.4c). We assume reaching a critical point where the P_2 flux is not sufficient to keep a 2D surface, further confirmed by the Figure 3.4d, where a final temperature of 730°C induces a strong surface roughening and the destruction of the surface.

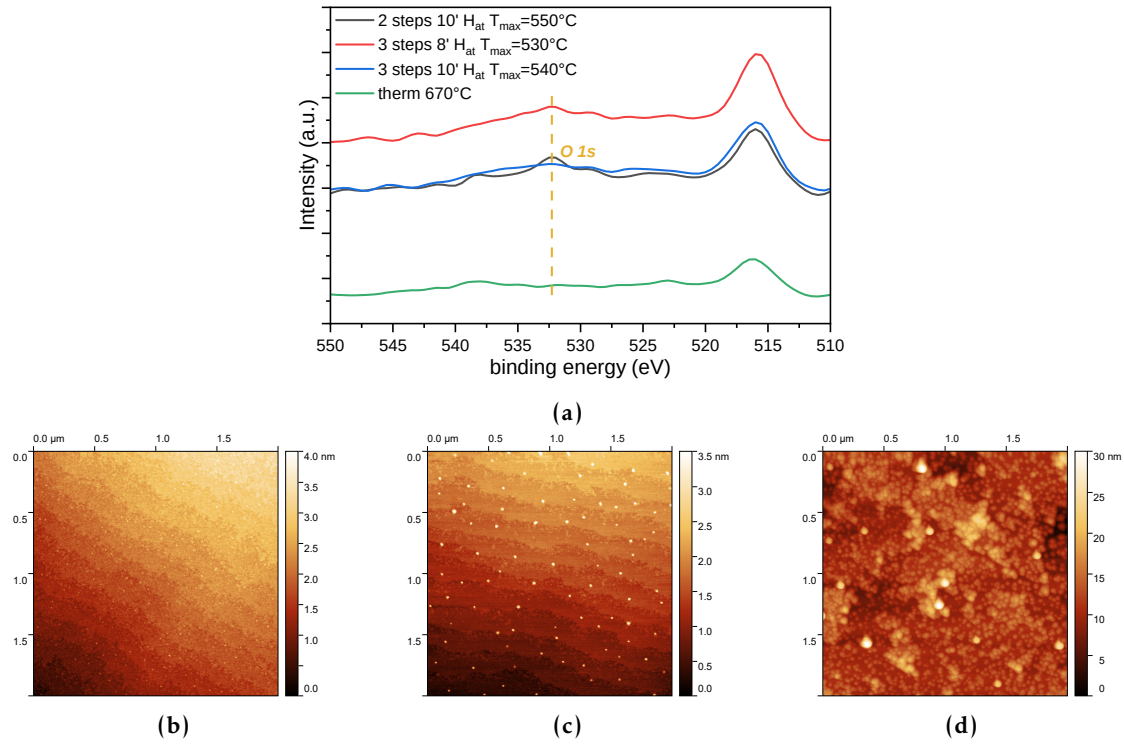


Figure 3.4: (a) XPS survey measurements captured with a take-off angle of 45° for several deoxidation processes. $2 \times 2 \mu\text{m}^2$ AFM imaging after a deoxidation process in 3 steps using (b) $t_{\text{AH}}=11$ min and $T_{\text{F}}=560^\circ\text{C}$, (c) $t_{\text{AH}}=11$ min and $T_{\text{F}}=650^\circ\text{C}$ and (d) $t_{\text{AH}}=11$ min and $T_{\text{F}}=730^\circ\text{C}$.

3.1.2 GaP(111)_B 2×2 surface characterization

Once the deoxidation process optimized, the surface is yet to be characterized. The following section will explore the surface electronic states of GaP(111)_B with XPS and UPS measurements. The normalized XPS Ga 3d and P 2p CLs recorded on an n-type GaP surface for two electron takeoff angles are shown in Figure 3.5a and 3.5b. The spectra recorded at $\theta=25^\circ$ is surface sensitive, while the one recorded at 75° is bulk sensitive. The Ga 3d CL shape is not altered by the detection angle, while exhibiting a slight shift that we attribute to band bending. It is composed of one single doublet at 19.98 eV associated to the Ga-P bonds (Figure 3.5c). On the other hand, the P 2p CL exhibits two clear surface components beside the main doublet at 129.63 eV associated to P-Ga bonds. The decomposition of the spectra (Figure 3.5d) highlights a rather strong component S1 at 130.34 eV and a smaller one S2 at 128.88 eV, already observed on some GaP or InP(001) reconstructions²⁷⁹, while a surface component comparable to S1 has also been reported on GaAs(111)_B surfaces prepared under hydrogen^{280, 281, 282}. We tentatively interpret the surface components in terms of the trimer model of the GaAs(111)_B (2×2) surface²⁸¹, assuming the observed GaP(111)_B (2×2) reconstruction is close to the GaAs(111)_B (2×2) one. Therefore, the surface component S1 can be associated to P-P bonds formed on the surface by the excess P atoms, while S2 might be correlated to the outermost P atoms on the surface bonded to three Ga atoms. The XPS analysis of p-type GaP(111)_B surfaces exhibits a similar behaviour.

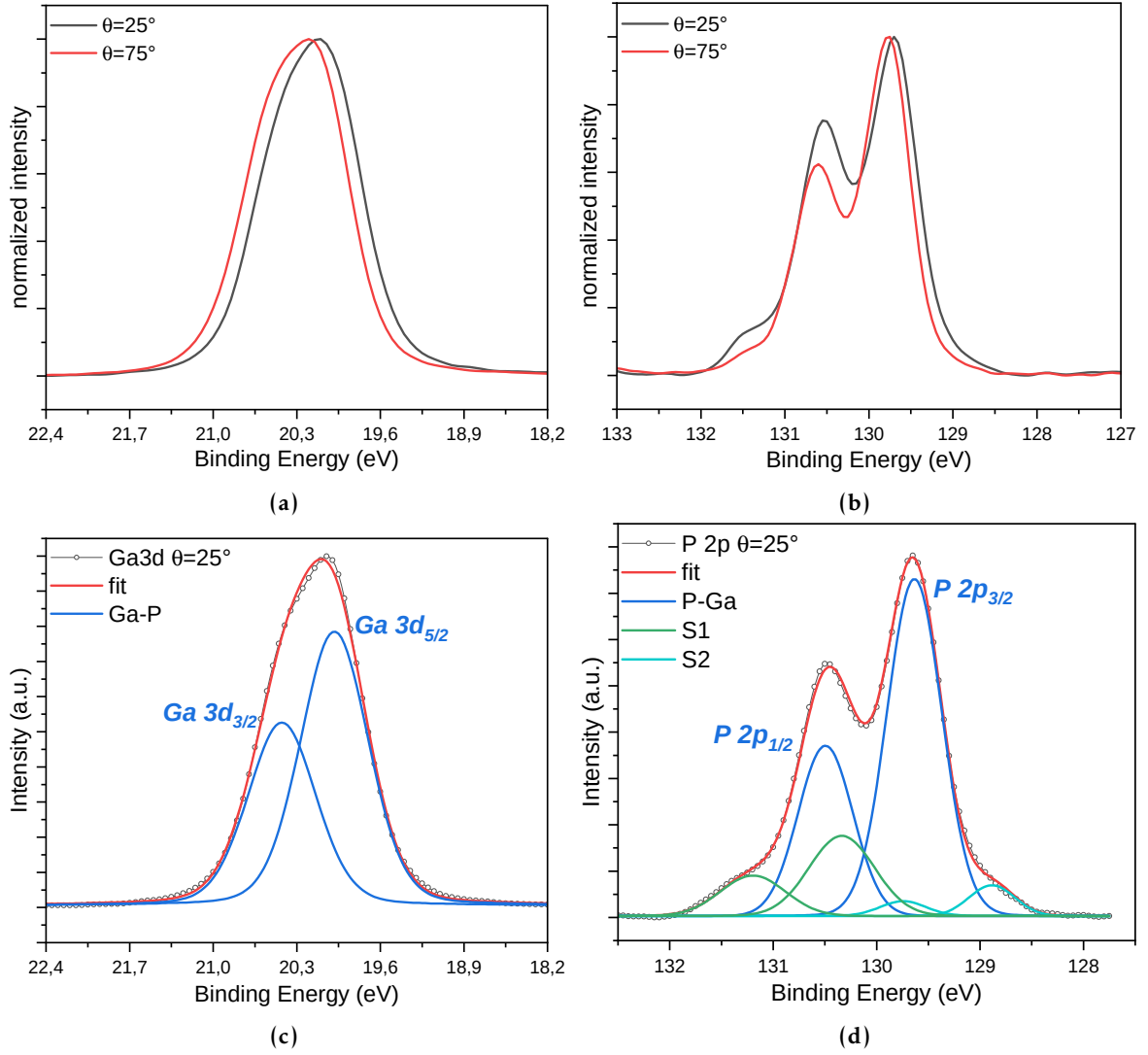


Figure 3.5: (a) Normalized Ga 3d CL and (b) P 2p CL recorded for two take-off angles on a deoxidized n-type GaP(111)_B surface. (c) and (d) the associated Ga 3d and P 2p CLs decompositions for a take-off angle $\theta=25^\circ$. S1: P-P bond at the surface; S2: P-Ga bond at the surface.

Moreover, UPS measurements have been performed on three surfaces with different doping types and levels whose carrier density are summarized in Table 3.1. For convenience, we will call those surfaces n+, n⁻ and p in the following discussion. As presented in Figure 3.6a, the intersection of a linear extrapolation of the low binding energy part of the valence band with the background determines the energy of the VBM in Γ with respect to the Fermi level at the surface $E_F - E_{\text{vsurf}}$. On the other hand, the position of the VBM in the bulk $E_F - E_{\text{vbulk}}$ is calculated from the different doping level considered, the effective densities of states $N_C = 1.77 \times 10^{19} \text{ cm}^{-3}$ and $N_V = 1.87 \times 10^{19} \text{ cm}^{-3}$, and the bandgap energy $E_G = 2.26 \text{ eV}$, from the equations:

$$n = N_C \times e^{\frac{E_F - E_C}{kT}} \quad \text{and} \quad p = N_V \times e^{\frac{E_V - E_F}{kT}} \quad (3.1)$$

The differences between the measured $E_F - E_{\text{vsurf}}$ and the calculated $E_F - E_{\text{vbulk}}$ is a measure of the downward and upwards band bending for the p and n samples (Table 3.1), respectively.

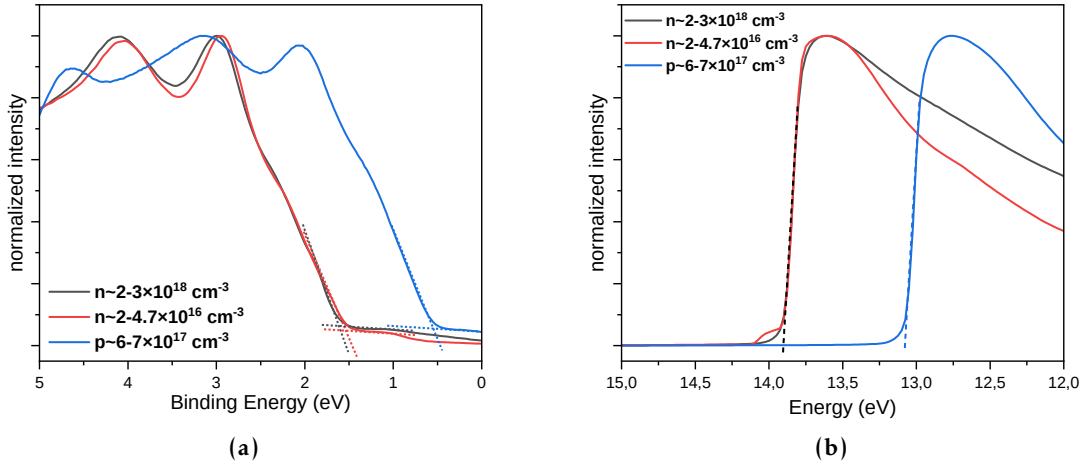


Figure 3.6: UPS measurement with He I of three GaP(111)_B surfaces with different doping levels. (a) Valence band spectra recorded in Γ and (b) threshold energy determination.

These results suggest the existence of two surface state bands within the bandgap centered around 0.68 eV and 1.58 eV above the bulk VBM. In addition, the work function ϕ is extracted from the threshold energy measurement (Figure 3.6b), which can lead to the determination of the surface dipole (Table 3.1) if considering the electron affinity of GaP ($\chi=3.8$ eV) as:

$$\phi = E_G - (E_F - E_{V\text{bulk}}) + \chi + \phi_b + \phi_s \quad (3.2)$$

with E_G the bandgap energy, ϕ_b the band bending and ϕ_s the surface dipole associated with the dipole between the two terminal surface atoms²⁸³.

Sample	Carrier density (cm ⁻³)	$E_F - E_{V\text{surf}}$ (eV)	$E_F - E_{V\text{bulk}}$ (eV)	ϕ_b (eV)	ϕ (eV)	ϕ_s (eV)
n ⁺ GaP	n~2–3×10 ¹⁸	1.59	2.2	0.61	4.31	-0.16
n ⁻ GaP	n~2–4.7×10 ¹⁶	1.53	2.1	0.57	4.29	-0.24
p GaP	p~6–7×10 ¹⁷	0.57	0.09	-0.48	5.12	-0.37

Table 3.1: surface (measured) and bulk (calculated) VBM, induced band bending, work function and surface dipole energy for three GaP(111)_B surfaces with different doping levels.

The final arrangement of the deoxidized n⁺, n⁻ and p samples studied in this section are presented in Figure 3.7 with their respective band bending and surface dipoles.

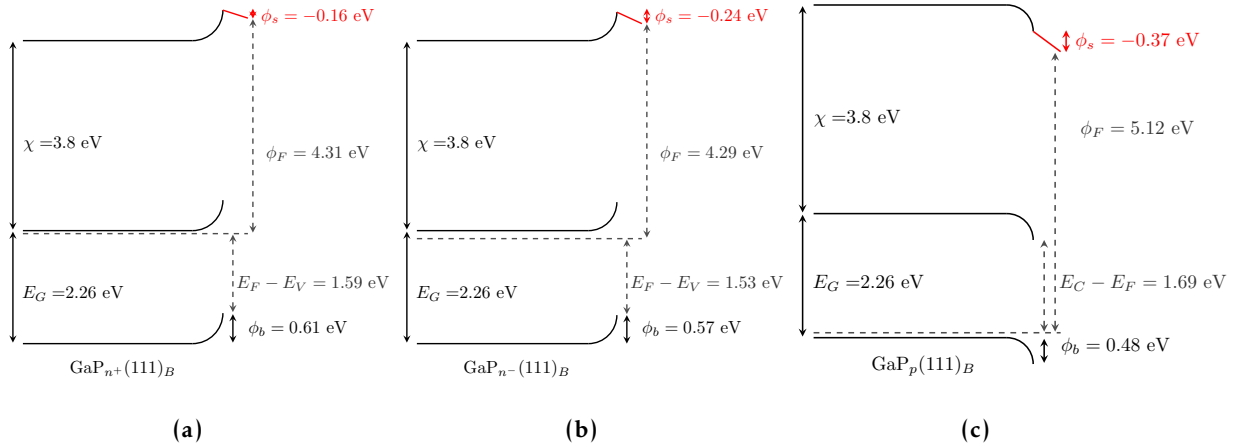


Figure 3.7: Band structure schematic of deoxidized (a) n⁺ GaP, (b) n⁻ GaP and (c) p GaP.

To summarize, the deoxidation process of the GaP(111)_B surface has been extensively studied, pointing out the need of using a combination of H_{at} and cracked phosphine rather than thermal deoxidation. We have emphasized the need for a 3-step sequence, summarized as H_{at} only from 250-300°C to 450°C, then H_{at} + P₂ (2-4 sccm) up to 500°C, and finally P₂ only (4-8 sccm) up to 550°C in order to obtain a clean and smooth deoxidized surface. We point out the observation of serrated atomic step edges by AFM. On the other hand, XPS measurements reveal a slight excess of P atoms on the surface, while the combination of XPS and UPS measurements allows us to determine the band bending and the surface dipole for three different doping types and levels.

3.2 GaP(111)_B homoepitaxy

Even if the resulted surface state after deoxidation is sufficient for TMDC growth, the observation of serrated atomic steps in Figure 3.4b remains a concern as the nucleation of WSe₂ and HfSe₂ might preferentially occur at the step edges. Therefore, we have carried out a GaP(111)_B homoepitaxy study with the goal of improving the morphology of the step edges, whose results are presented in the following section.

After the deoxidation at 550°C, the substrate temperature is ramped up to the growth temperature under 8 sccm P₂ flux. We observe a transition in the RHEED pattern at around 620°C from 2×2 to $\sqrt{19} \times \sqrt{19}$, which remains stable until a critical temperature of around 670°C, where the RHEED pattern evolves into a faint 1×1 reconstruction. As this evolution of the surface reconstruction is similar to that reported for GaAs(111)_B²⁸⁴, the following study uses the results of the GaAs homoepitaxial growth as a starting point. A perfect morphology of GaAs is obtained for a growth performed at the end of the $\sqrt{19} \times \sqrt{19}$ plateau^{277, 285}. In this section, we will discuss the impact of the temperature, the gallium growth rate V_{Ga} , the P₂ flux and the film thickness on the morphology.

3.2.1 Effect of the growth temperature on the morphology

Under 620°C, the growth of 50 nm thick GaP layers with a V_{Ga} of 0.4 ML/s and a P₂ flux of 8 sccm results systematically in the formation of small pyramids (Figure 3.8a) whose size is increased with the growth temperature. The optical microscopy image in Figure 3.8d shows the uniformity of the pattern formation over the whole surface, as a bright dot represents the top of a pyramid. We point out that the RHEED reconstruction was remaining stable during the growth with a clear $\sqrt{19} \times \sqrt{19}$ pattern. On the other hand, the increase of the temperature up to 650°C under the same growth conditions (V_{Ga} =0.4 ML/s and P₂=8 sccm) induces the reduction of the pyramids density and their increase in size (Figure 3.8e), allowing the observation of rather wavy atomic steps with irregular sizes (Figure 3.8b). In an attempt to suppress the remaining pyramids, the temperature is further increased until the $\sqrt{19} \times \sqrt{19}$ pattern evolves into a 1×1 one, *i.e.* 670°C. However, the resulting optical microscopy image in Figure 3.8f clearly shows the formation of 10 μm large pyramids, leading to a rough surface. Moreover, $2 \times 2 \mu\text{m}^2$ AFM image in Figure 3.8c reveals the presence of 40 nm large triangular nano-holes with a mean depth of 6 nm. In a similar way as the Local Droplet Epitaxy (LDE) method for Quantum dots fabrication on GaAs surfaces^{286, 287}, the presence of these holes could be induced from the formation of gallium droplets during the temperature rise after deoxidation, which would stand as local growth inhibitors.

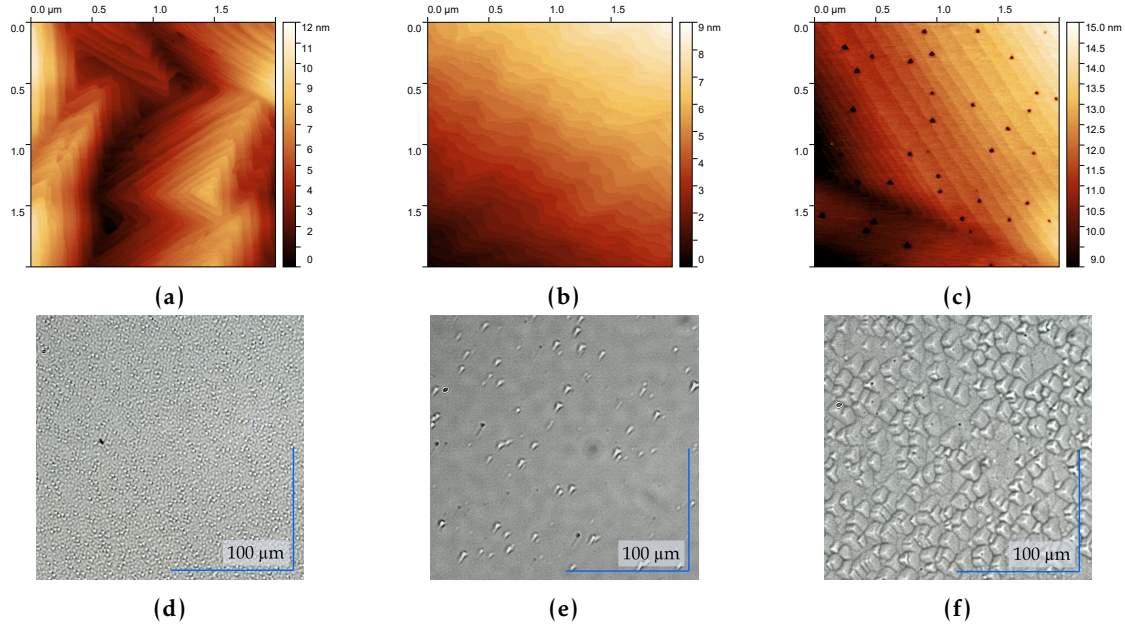


Figure 3.8: $2 \times 2 \mu\text{m}^2$ AFM and the associated optical microscopy images after a 50 nm GaP growth at (a, d) $T=620^\circ\text{C}$, (b, e) $T=650^\circ\text{C}$ and (c, f) $T=670^\circ\text{C}$. The P_2 flux is set at 8 sccm and $V_{\text{Ga}}=0.4 \text{ ML/s}$.

The systematic formation of pyramids and the strange evolution of the morphology with the temperature lead us to consider varying V_{Ga} and the P_2 flux for each growth temperature exceeding 640°C . We assume that the formation of pyramids is partially induced by a too high gallium growth rate.

3.2.2 Effect of the gallium growth rate and the P_2 flux on the morphology at temperature above 650°C

At 650°C , the reduction of V_{Ga} from 0.4 ML/s to 0.16 ML/s does not change the density of pyramids but even increases their size, as presented in Figure 3.9d. On the other hand, the AFM image (Figure 3.9a) shows atomic steps with fewer irregularities. A reduction in P_2 flux from 8 to 6 sccm leads to lower the 2×2 to $\sqrt{19} \times \sqrt{19}$ and the $\sqrt{19} \times \sqrt{19}$ to 1×1 RHEED pattern transition temperatures down to 600°C and 640°C , respectively. However, optical microscopy images (Figure 3.9e & 3.9f) do not reveal any impact of this reduction on the pyramids density and shape, while AFM images tend to show more irregular atomic steps for a strong V_{Ga} (Figure 3.9b) than for a lower one (Figure 3.9c). Even if there is no perfect growth condition at this temperature, the morphology seems slightly better when using a lower growth rate. Yet, the reduction of the P_2 flux appears useless. Moreover, it could favour a deterioration of the surface at higher temperatures.

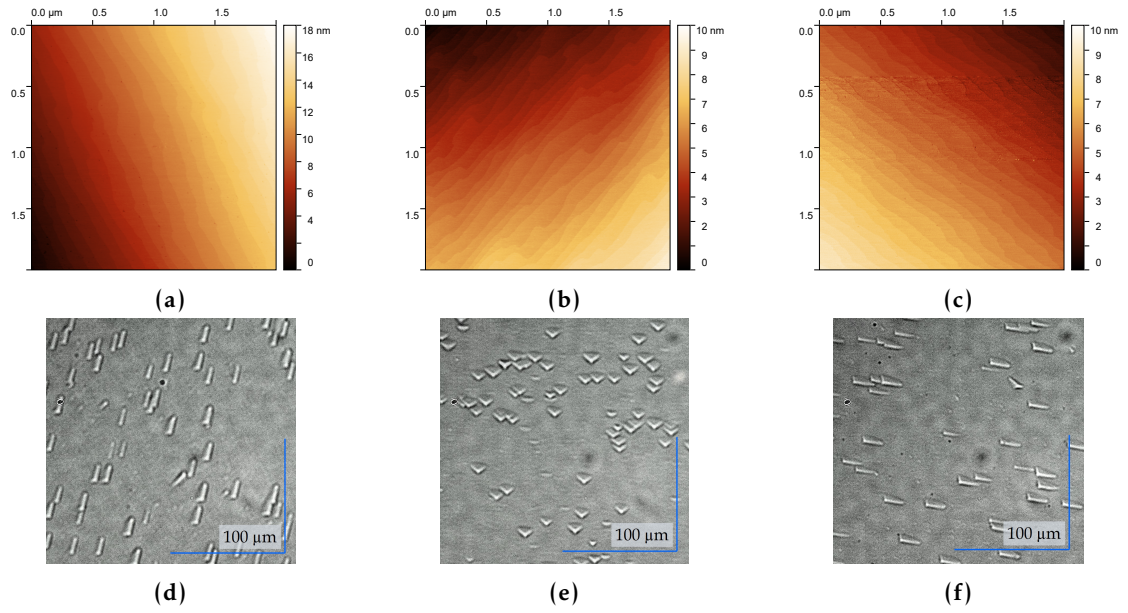


Figure 3.9: $2 \times 2 \mu\text{m}^2$ AFM and the associated optical microscopy images after a 50 nm GaP growth at 650°C with (a, d) $P_2 = 8$ sccm and $V_{Ga} = 0.16$ ML/s, (b, e) $P_2 = 6$ sccm and $V_{Ga} = 0.4$ ML/s, and (c, f) $P_2 = 6$ sccm and $V_{Ga} = 0.16$ ML/s.

When reaching 670°C, it is obvious that a low P_2 flux is not sufficient for GaP growth. Indeed, a precise control of the temperature in this range is necessary, as an increase up to 675°C induces the desorption of the phosphorus species, changing the 2D RHEED pattern into a 3D one even under 8 sccm of P_2 . Therefore, we focus on the impact of the growth rate on the morphology. First, considering the optical images in Figure 3.10d to 3.10f, it appears that the formation of pyramids can be prevented when using a growth rate lower than 0.2 ML/s, while AFM images (Figure 3.10a to 3.10c) show a systematic presence of nano-holes, confirming the main impact of the temperature in their appearance. In addition, the AFM images at low V_{Ga} exhibit well-defined and regular atomic steps, which globally supports our previous observations at 650°C of the need for a low growth rate.

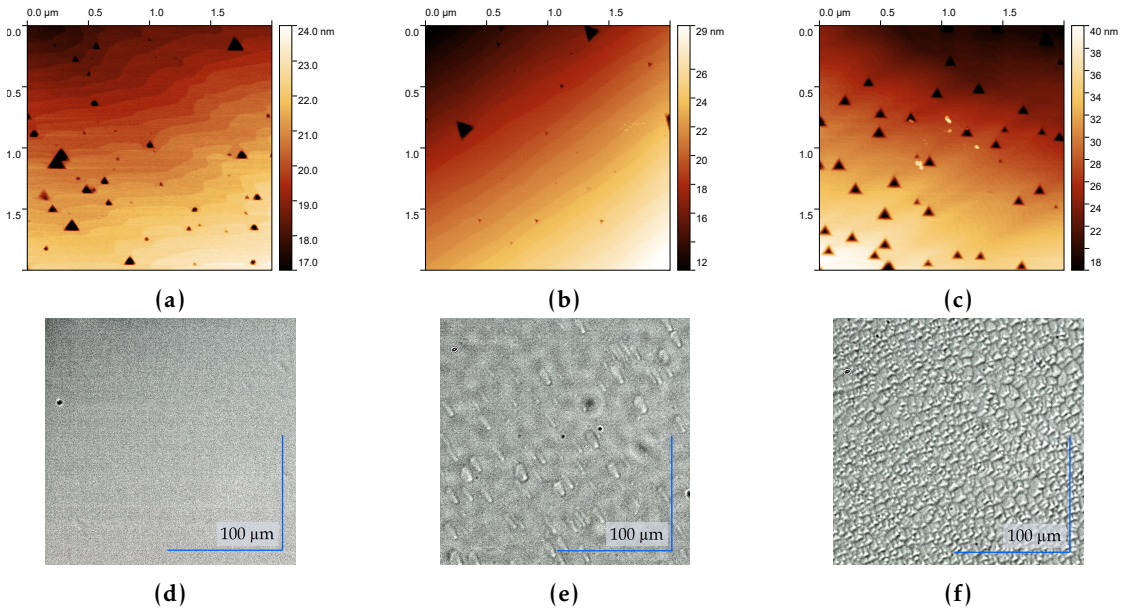


Figure 3.10: $2 \times 2 \mu\text{m}^2$ AFM and the associated optical microscopy images after a 50 nm GaP growth at 670°C with $P_2 = 8$ sccm and (a, d) $V_{Ga} = 0.08$ ML/s, (b, e) $V_{Ga} = 0.16$ ML/s, and (c, f) $V_{Ga} = 0.56$ ML/s.

In an attempt to simultaneously suppress the pyramids and the nano-holes, we propose to reduce the temperature down to an intermediate value of 660°C. However, for both growth rates (0.08 and 0.16 ML/s), the optical microscopy images show the presence of large and well defined pyramids (Figure 3.11c & 3.11d), while nano-holes with a reduced density are spotted on the AFM image at low V_{Ga} (Figure 3.11a).

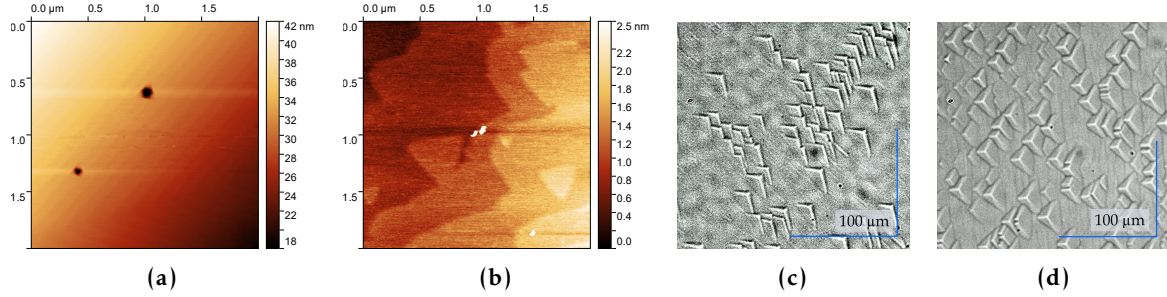


Figure 3.11: $2 \times 2 \mu\text{m}^2$ AFM and the associated optical microscopy images after a 50 nm GaP growth at 660°C with $P_2 = 8$ sccm and (a, c) $V_{\text{Ga}} = 0.08$ ML/s and (b, d) $V_{\text{Ga}} = 0.16$ ML/s.

Overall, we are facing a dilemma where a too low growth temperature favours the formation of pyramids, whereas a too high one induces the formation of triangular holes, and where the reduction or increase of the growth rate does not have a simultaneous impact on these two issues. Up to now, the homoepitaxial growth of a 50 nm thick layer on GaP(111)_B with a smooth morphology has been impossible in our configuration.

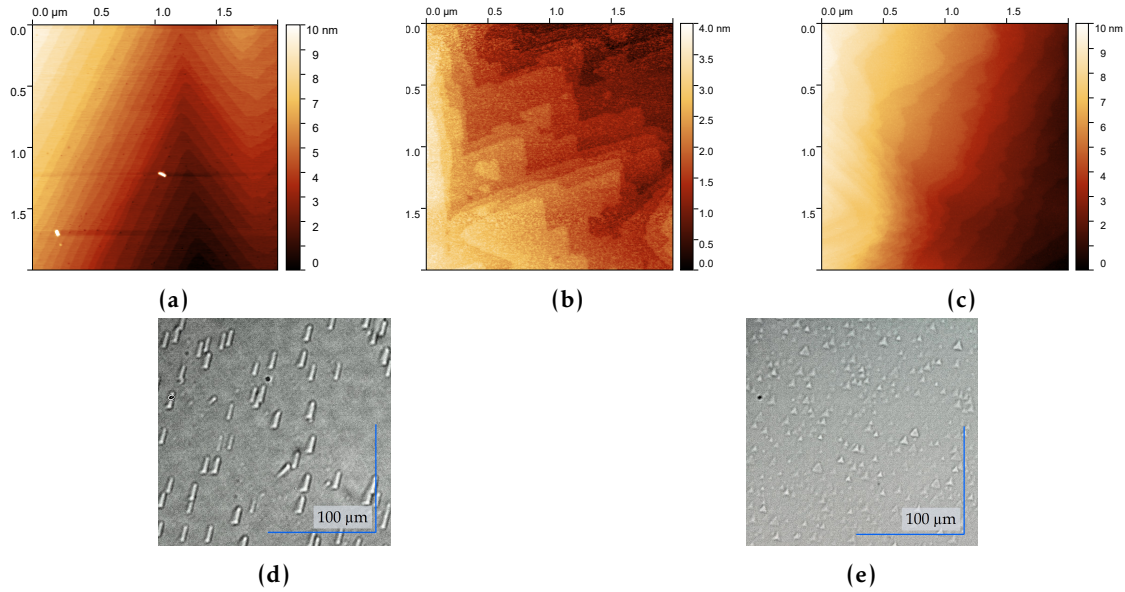


Figure 3.12: $2 \times 2 \mu\text{m}^2$ AFM and the associated optical microscopy images after a (a, d) 50 nm, (b, e) 20 nm and (c) 5 nm GaP growth at 650°C with $P_2 = 8$ sccm and $V_{\text{Ga}} = 0.16$ ML/s.

Last, as the goal of this study is to improve the surface morphology before a TMDC growth, we investigate the effect of the homoepitaxial film thickness on the morphology. In Figure 3.12 are presented the morphology of GaP(111)_B samples grown with a growth rate of 0.16 ML/s and a P_2 flux of 8 sccm for three film thicknesses: 50 nm, 20 nm and 5 nm. The temperature is set at 650°C in order to get a reduced density of large pyramids and to prevent the appearance of triangular holes. As expected, the density of the pyramids and their size are reduced with decreasing thickness. However, even for a 5 nm thick layer

(Figure 3.12c), it appears rather difficult to remove them totally. More, the atomic steps shape are less suitable for TMDC growth than those observed on the deoxidized surface.

In this section, we have tried to overcome the morphology issue induced by serrated atomic step edges after deoxidizing the GaP(111)_B surface by attempting a homoepitaxial growth. As the surface reconstruction observed by RHEED looks very similar to GaAs(111)_B when the temperature is increased above 550°C, we have based our study on early results obtained on this surface. We emphasize the systematic formation of small pyramids on the surface for temperatures below 620°C, where an increase up to 650°C is inducing a strong reduction of the density of these pyramids, coupled with an increase in size. We also show the systematic formation of 40 nm large triangular nano-holes when attaining 670°C, which is the only temperature allowing the suppression of the pyramids if using a low gallium growth rate. Up to now, it has been impossible to grow a GaP(111)_B homoepitaxial buffer with a satisfying morphology. Therefore, in the following, the Se-termination, the WSe₂ and HfSe₂ growth have been performed only on well-deoxidized GaP surfaces without any buffer regrowth.

3.3 Se passivation

After the GaP(111)_B surface deoxidation presented in section 3.1 of this chapter, the sample is transferred under UHV in the second MBE reactor dedicated to Se-based materials. Then, it is annealed to 250°C before being exposed to a selenium flux F_{Se} while increasing the temperature to a maximum value T_{Se} . The substrate is maintained for 3 minutes at this temperature before cooling down. As presented in the section 1.1.2.3, the goal of this selenium passivation is to favour the formation of a quasi van der Waals gap between the GaP(111)_B substrate and the TMDC layer by removing the dangling bonds of the deoxidized surface.

3.3.1 Evolution of the substrate surface after the Se-termination

As soon as the GaP(111)_B surface is exposed to the Se flux at 250°C, the 2×2 RHEED pattern turns instantly into a 1×1 one (Figure 3.13a & 3.13b), characterized by the suppression of the intermediate streaks and remains unchanged up to 700°C. Actually, this 1×1 pattern is stable up to more than 750°C, a strong degradation appearing around 800°C. In addition, the LEED pattern obtained after deoxidation and after the Se-treatment show the same evolution of the surface reconstruction (Figure 3.13c & 3.13d).

AFM images captured before (Figure 3.13e) and after a Se-passivation at 700°C (Figure 3.13f) do not reveal any changes of the surface morphology, with clear atomic steps of identical height (~ 3.5 Å), width (~ 200 nm), depending on the disorientation angle of the substrate), serrated shape and same mean roughness (~ 0.2 nm). Besides, the XPS survey spectrum of both surfaces exhibit the characteristic CLs of selenium besides those of gallium and phosphorus (Figure 3.13g), confirming a reaction of the Se species with the substrate.

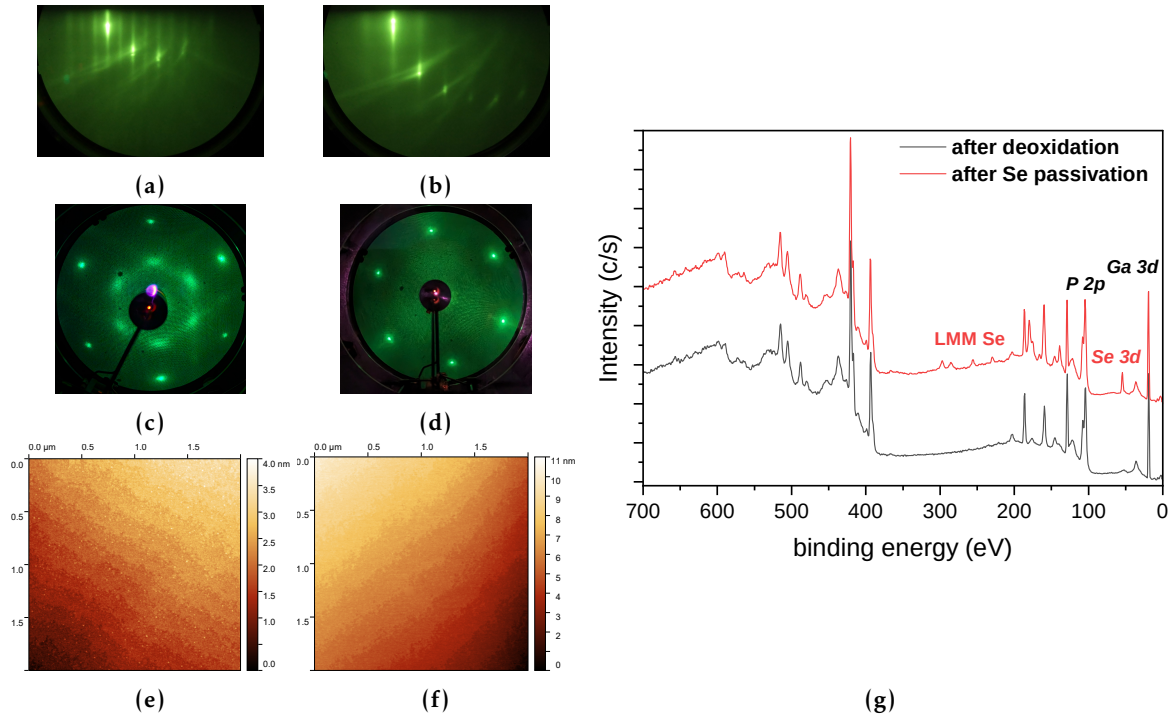


Figure 3.13: RHEED pattern along <1-100> and the associated LEED pattern at 40 eV of the GaP(111)_B surface after the deoxidation (a, c) and after the Se-passivation treatment at 700°C (b, d). 2 × 2 μm² AFM images of the GaP(111)_B surface (e) after the deoxidation and (f) after the Se-passivation treatment. (g) The associated XPS surveys recorded with a take-off angle of $\theta=25^\circ$.

The decomposition of the different CLs after a Se passivation at 700°C with F_{Se} of 4.4×10^{-6} Torr ($V_{\text{Se}}=0.79$ Å/s) shows the suppression of S1 in the P 2p CL (Figure 3.14a), previously linked to excess P atoms in surface, while the S2 component (outermost P atoms bonded to three Ga atoms) intensity decreases by a factor 2. Thus, we assume that the selenium atoms are mainly reacting with the P-surface, though some P atoms remains in the outermost layer, probably giving rise to a mixed P-Se layer as discussed in the case of GaAs(111)_B-Se²³². Moreover, the Ga 3d CL after Se-passivation (Figure 3.14b) exhibits an additional component at higher binding energy (20.95 eV), corresponding to 14% of the peak area, that we ascribe to the formation of surface Ga-Se bonds as the Se electronegativity is larger than that of P. The 0.2 eV energy shift observed for both P 2p and Ga 3d CLs after Se-passivation is further associated to a decrease of the band bending as later presented in Table 3.6. Finally, the Se 3d CL in Figure 3.14c is composed of two doublets Se1 and Se2 at binding energies of 55.38 eV and 54.38 eV, respectively. As proposed by Scimeca *et al.* in the case of the GaAs(111)_B surface exposed to Se²³², we interpret Se1 as resulting from the Se-Ga bonds on the top surface whereas Se2 is related to some Se atoms present in the sub-surface layer. Figure 3.14d presents the evolution of the Se3d/Ga3d CL intensity ratio as well as the Se3d/P2p CL ratio with the take-off angle. The clear reduction of both ratios with the angle supports that selenium lies mainly on the top surface of the substrate in a similar way to what was observed on GaAs(111)_B-Se, while the Se2/Se1 ratio of 0.2 is slightly smaller in the case of GaP(111)_B.

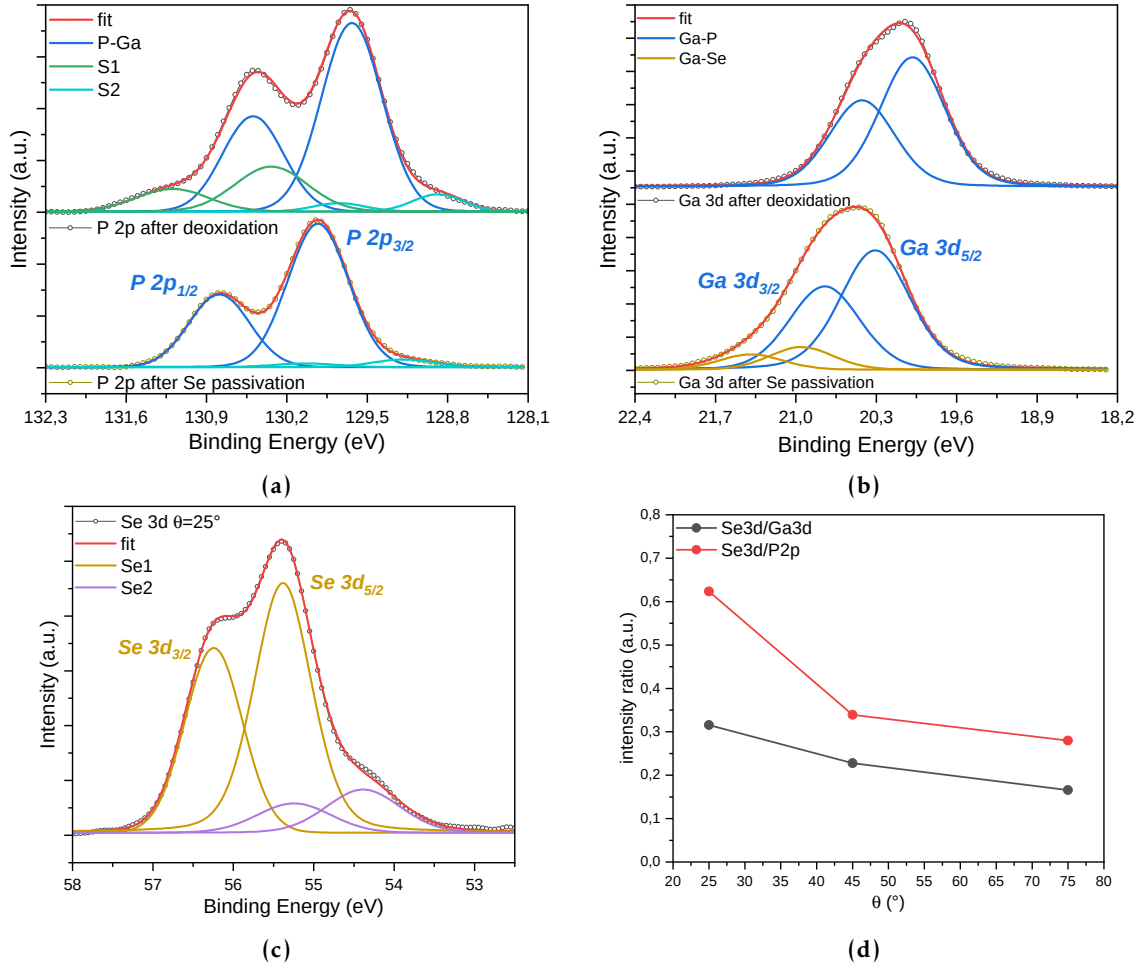


Figure 3.14: Evolution of the (a) P 2p and (b) Ga 3d CLs decomposition of a n-type GaP(111)_B substrate after deoxidation (top) and after a Se-passivation (bottom). (c) Decomposition of Se 3d CLs after a passivation at $T_{\text{Se}}=700^{\circ}\text{C}$ and $F_{\text{Se}}=3.9\times 10^{-6}$ Torr ($V_{\text{Se}}=0.79$ Å/s). The take-off angle is set at $\theta=25^{\circ}$. (d) Evolution of the Se3d/Ga3d and Se3d/P2p intensity ratios with the take-off angle.

In order to confirm that Se atoms are indeed mainly present in the top surface layer, we perform XPD measurements, following the procedure presented in section 2.3.3. Considering that the kinetic energy of the photoelectrons are well above 1 keV, we restrict the analysis to the simplest interpretation of the photodiffraction data, relying on the predominance of the forward scattering at such energies²⁶⁴. It allows us to compare the different CL intensity profiles to a simple calculation of the diffracted photoelectron angles uniquely based on a 2D projection along the two crystallographic directions studied, *i.e.* [11-2] and [1-10].

First, in the case of the projection along [11-2] as represented in Figure 3.15a and 3.15b, we respectively define two values h and y as the vertical and horizontal projection of the spacing between a P and Ga atoms of norm $\sqrt{h^2 + y^2} = \frac{\sqrt{3}}{4}a$. After calculating a slope angle γ of 19.47° , we can estimate the values as $y = 0.408a$ and $h = 0.144a$. From this starting point, we calculate the diffracted angles δ_x and θ_x supposed to induce a modulation in intensity for photoelectrons emitted from P 2p (Table 3.2) and Ga 3d (Table 3.3), respectively.

When confronting these projections to the intensity modulations measured from the P 2p and Ga 3d CLs before Se-passivation (Table 3.2 & Table 3.3), the majority of the observed peaks are in good

agreement with the calculated ones. In the case of the P 2p CL intensity profile, the surface analysis chamber used for this study has a polar angle range between 25° and 155°, which explains why we have not observed the different peaks at δ_1 , δ_2 , δ_{13} and δ_{14} . However, we point out additional peaks at 65° and 137° in the P 2p CL and at 130° in the Ga 3d CL, coupled with the non-occurrence of peaks at $\delta_5=51^\circ$, $\delta_{11}=142^\circ$ and $\theta_{10}=138.5^\circ$, evidencing the limit of this simple model. Besides, the comparison of the profiles recorded before and after the Se-treatment in Figure 3.15c and Figure 3.15d shows great similarities with a decrease of the global intensity of the P 2p CL, which could indicate the replacement of P atoms by Se ones on the surface. Moreover, we clearly observe the suppression of the peaks $\delta_4=47^\circ$ in the P 2p CL profile and the appearance of one slight increase at $\delta_{11}=140^\circ$ and at $\theta_{10}=137^\circ$ in the Ga 3d CL, which highlight a slight change of the surface after Se-passivation.

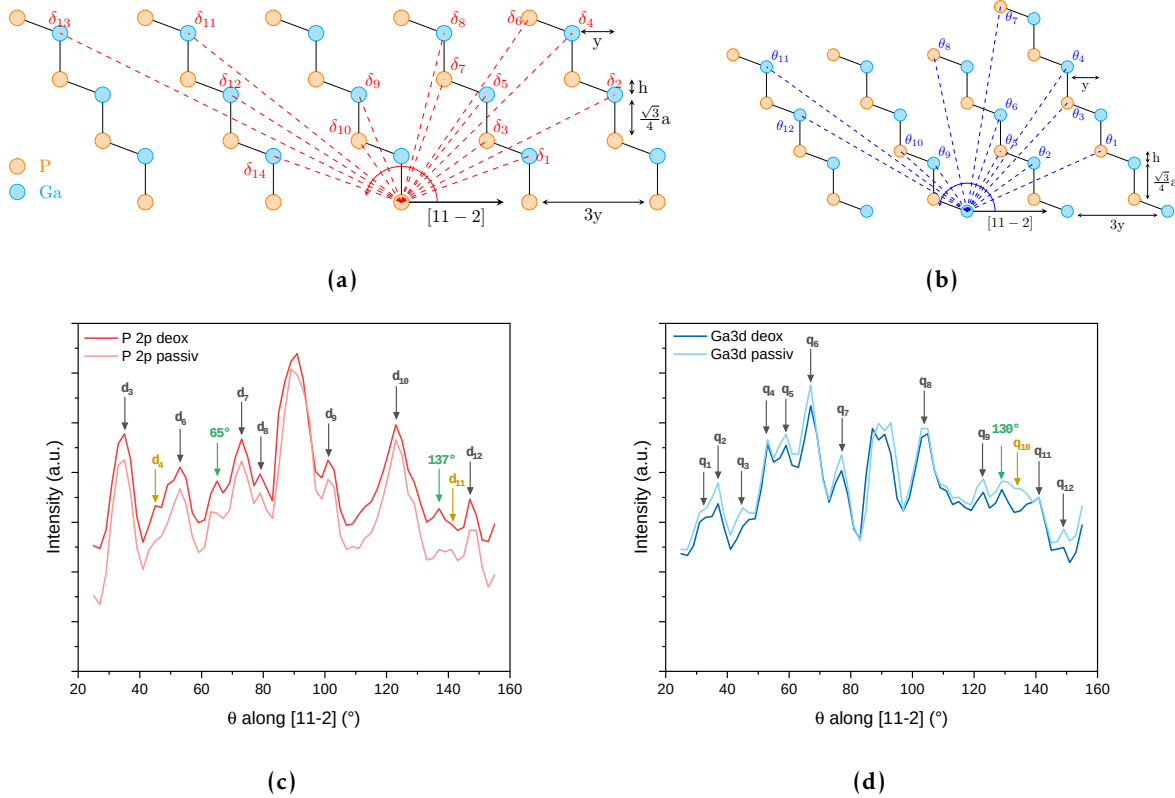


Figure 3.15: GaP schematic along [11-2], diffracted angles representation for a photoelectron emitted from (a) P 2p and (b) Ga 3d. Photodiffraction intensity profiles of (c) P 2p and (d) Ga 3d CLs before and after a Se passivation with $T_{Se}=700^\circ\text{C}$ and $F_{Se}=3.4\times 10^{-6}$ Torr ($V_{Se}=0.47$ Å/s). **Black arrows:** experimental peak in agreement with calculated ones. **Yellow arrows:** apparition or suppression of a peak after Se-passivation, fitting with calculated angles. **Green arrows:** unpredicted additional peak.

	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_8	δ	δ_9	δ_{10}	δ_{11}	δ_{12}	δ_{13}	δ_{14}
P 2p th	19.5	26.3	35.3	44.2	51.1	54.7	70.5	75.6	90	112	125.3	142.1	148.3	154.1	160.5
GaP			35	47	53	65	73	79	91	101	123	137	147		
GaP-Se			35		53	63	73	79	89	103	123	137	141	149	

Table 3.2: Diffracted angles calculation for a photoelectron emitted from P 2p along [11-2].

	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7	θ	θ_8	θ_9	θ_{10}	θ_{11}	θ_{12}
Ga 3d th	23.8	35.3	46.7	54.7	60.5	70.5	80.6	90	102.3	125.3	138.5	144.7	150.5
GaP	31	37	47	53	59	67	77	91	105	123	130	141	149
GaP-Se	31	37	46	53	59	67	77	89	105	123	129	137	141

Table 3.3: Diffracted angles calculation for a photoelectron emitted from Ga 3d along [11-2].

Extending this analysis to a projection along $[1-10]$ as represented in Figure 3.16a and 3.16b, we can directly deduce the diffracted angles α_x and β_x inducing a modulation in intensity for photoelectrons emitted from P 2p and Ga 3d, as referenced in Table 3.4 and 3.5. In Figure 3.16c and 3.16d, the majority of the observed peaks before Se-passivation fit well with the presented model, though no modulations have been identified at $\alpha_3=37.2^\circ$, $\alpha'_9=108.1^\circ$ and $\alpha'_3=142.6^\circ$, while two additional peaks at 55° and 125° in the Ga 3d CL are observed.

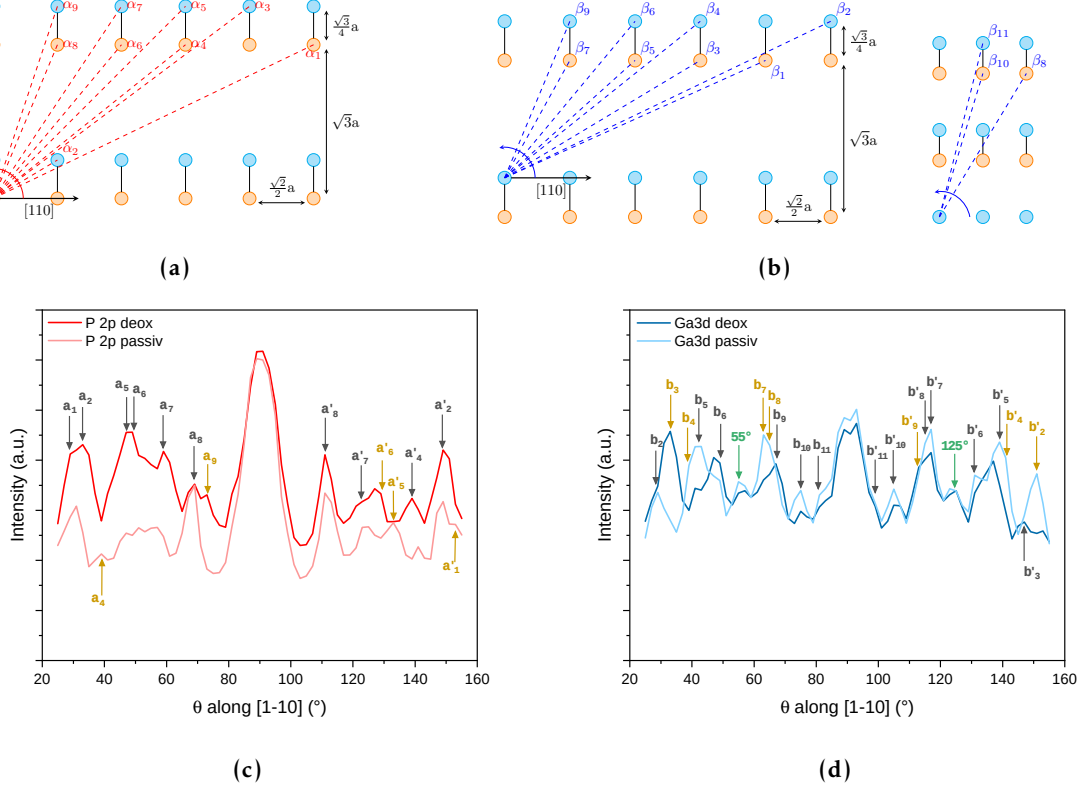


Figure 3.16: GaP schematic along $[1-10]$, diffracted angles representation for a photoelectron emitted from (a) P 2p and (b) Ga 3d. Photodiffraction intensity profiles of (c) P 2p and (d) Ga 3d CLs before and after a Se passivation with $T_{Se}=700^\circ\text{C}$ and $F_{Se}=3.4\times 10^{-6}$ Torr ($V_{Se}=0.47$ Å/s). **Black arrows:** experimental peak in agreement with calculated ones. **Yellow arrows:** apparition or suppression of a peak after Se-passivation, fitting with calculated angles. **Green arrows:** unpredicted additional peak.

In contrast to the $[11-2]$ direction, both Ga 3d and P 2p profiles change after Se passivation. After deoxidation, they are not symmetrical with respect to the normal as expected for a 1×1 surface corresponding to the model used for the calculations. This asymmetry could be ascribed to the 2×2 reconstruction of the deoxidized GaP surface, due to the presence of P-P bonds at the surface. After Se passivation, the reconstruction turns to a 1×1 one, which explains the more symmetrical variations observed in this case. The global intensity of the P 2p CL after Se treatment is strongly reduced, confirming the replacement of P atoms by Se ones on the surface. The evolution of the surface chemistry after passivation is further characterized by the suppression of peaks at $\alpha_9=73^\circ$ and $\alpha'_6=129.2^\circ$, coupled with the appearance of additional peaks at $\alpha_4=39^\circ$, $\alpha'_5=133^\circ$ and $\alpha'_1=153^\circ$ (Table 3.4). In the case of the Ga 3d CL intensity profile, the Se-treatment induces the suppression of the peak at $\beta_3=33^\circ$, while favouring the intensity at $\beta_4=(39^\circ;141^\circ)$, $\beta_7=(63^\circ;117^\circ)$ and $\beta_{10}=(75^\circ;105^\circ)$, and a clear new peak close to $\beta'_2=153^\circ$. This first approach of the photodiffraction evidences the somewhat reliability of the model used and confirms a surface chemistry change after Se-passivation.

	α_1	α_2	α_3	α_4	α_5	α_6	α_7	α_8	α_9	α
P 2p th	26.1	31.5	37.4	39.2	45.6	50.8	56.9	67.8	71.9	90
GaP	29	33			47	49	59	69	73	91
GaP-Se		31		39	47	51	57	69		91

	α'_9	α'_8	α'_7	α'_6	α'_5	α'_4	α'_3	α'_2	α'_1	
P 2p th	108.1	112.2	123.1	129.2	134.4	140.8	142.6	148.5	153.9	
GaP		111	121	129		139		149		
GaP-Se		111	123		133	141		149	153	

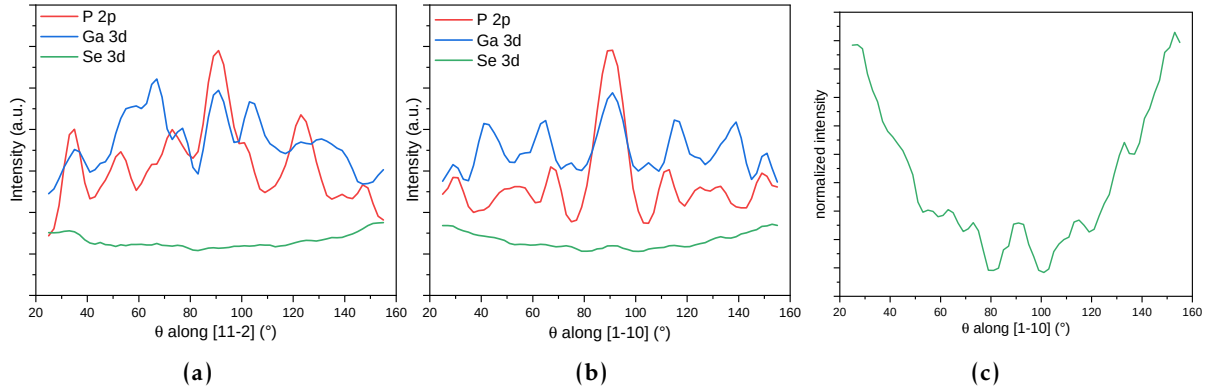
Table 3.4: Diffracted angles calculation for a photoelectron emitted from P 2p along [1-10].

	β_1	β_2	β_3	β_4	β_5	β_6		β_7	β_8	β_9	β_{10}	β_{11}	β
Ga 3d th	24.7	26.1	31.5	39.2	42.6	50.8		61.4	65	67.8	76.9	78.5	90
GaP		29	33		42	49	57			67	75	81	91
GaP-Se		29		39	43	49	55	63	65	67	75	81	93

	β'_{11}	β'_{10}	β'_9	β'_8	β'_7		β'_6	β'_5	β'_4	β'_3	β'_2	β'_1	
Ga 3d th	101.5	103.1	112.2	115	118.6		129.2	137.4	140.8	148.5	153.9	155.3	
GaP	99	105	113	115	117	125	131	137		147			
GaP-Se	99	105		115	117	125	131	139	141	149	151		

Table 3.5: Diffracted angles calculation for a photoelectron emitted from Ga 3d along [1-10].

In addition to these observations, the superposition of the P 2p, Ga 3d and Se 3d CLs intensity profiles for the two selected azimuths (Figure 3.17a & 3.17b) shows a somewhat flat selenium profile, which means that photoelectron emitted by Se atoms do not experience any forward scattering before entering the analyzer. This is a strong evidence that Se atoms mainly lie on the top surface atomic layer. Yet, the normalization of the Se 3d profile along [1-10] (Figure 3.17c) reveals three slight peaks at 75°, 90° and 115°, which might be an indication of the presence of Se atoms in the second atomic plane but to a low extent.

**Figure 3.17:** Photodiffraction intensity profiles of P 2p, Ga 3d and Se 3d CLs, extracted from a GaP(111)_B substrate passivated at 700°C under a $F_{Se}=3.4 \times 10^{-6}$ Torr along the directions (a) [11-2] and (b) [1-10]. Normalized photodiffraction intensity profile of Se 3d CL along [1-10] (c).

As the presence of sub-surface Se could lead to electronic defects once the TMDC grown, it needs to be removed, or at least reduced significantly. In that aim, we consider varying the two parameters T_{Se} and F_{Se} .

3.3.2 Reduction of the sub-surface component and evolution of the band structure

For a high F_{Se} of 4.3×10^{-6} Torr ($V_{\text{Se}}=0.93 \text{ \AA/s}$) and increasing T_{Se} , the Se 3d CL line shape looks rather similar, exhibiting two main components below 700°C (Figure 3.18a). This allows us to choose a passivation temperature based on the TMDC growth temperature as soon as it exceeds 450°C , assuming that this temperature is the lowest one to achieve a well-ordered Se-passivated GaP surface¹⁶⁶. However, increasing T_{Se} up to 815°C favours the formation of the sub-surface Ga-Se component, as the desorption of P atoms is strongly enhanced, inducing a large penetration of the Se species.

On the other hand, the reduction of F_{Se} (Figure 3.18b) down to the 10^{-7} Torr range ($V_{\text{Se}} < 0.1 \text{ \AA/s}$) reduces significantly the presence of the sub-surface component regardless of the temperature, evidencing the need for a low selenium flux during the Se-passivation step for the same exposure time. The decomposition of the Se 3d CL for a high F_{Se} (Figure 3.18c) and a low F_{Se} (Figure 3.18d) shows a clear reduction of the Se2 component linked to sub-surface Ga-Se from 18% of the peak area to 5%.

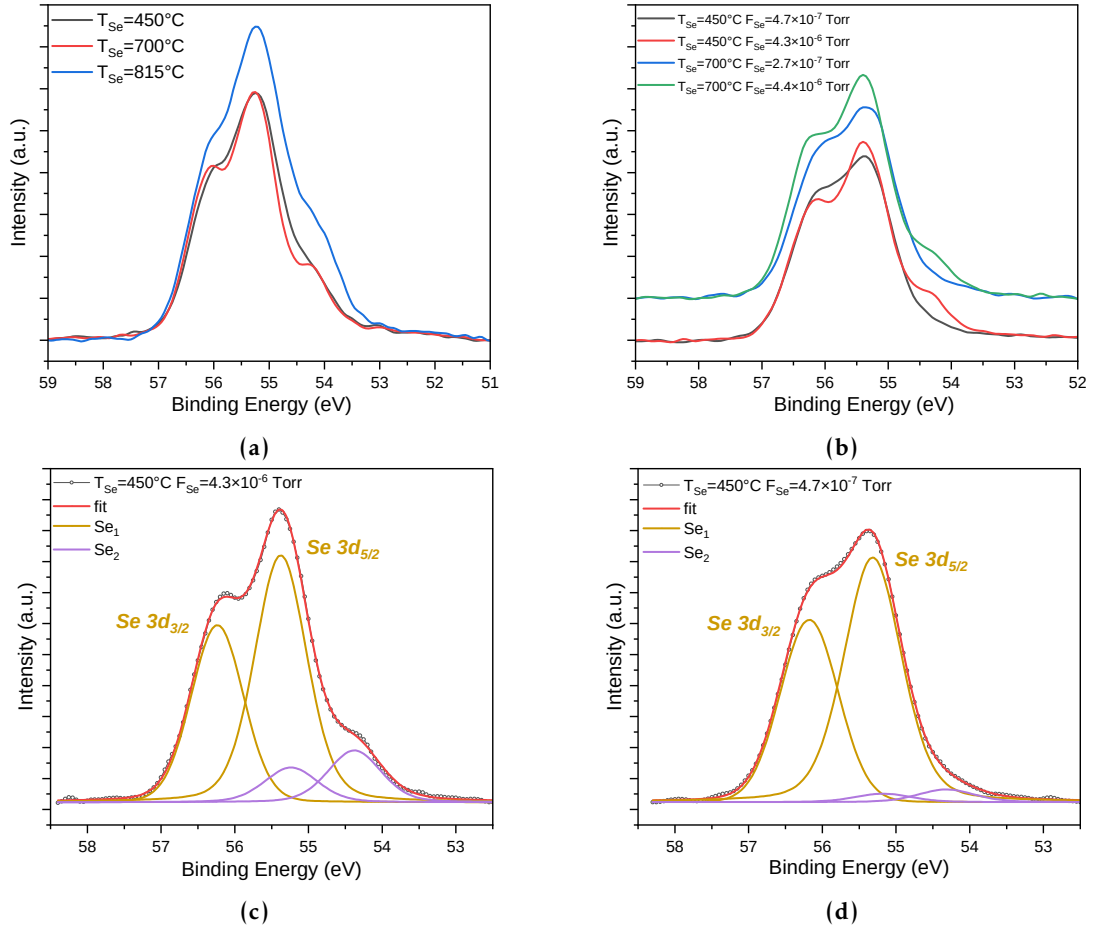


Figure 3.18: Evolution of the Se 3d CL with (a) T_{Se} for a $F_{\text{Se}}=4.3 \times 10^{-6}$ Torr and (b) F_{Se} for temperatures of 450°C or 700°C . Se 3d CL decomposition for (c) a high F_{Se} and (d) a low F_{Se} .

Last, we investigate the variations of the band bending and surface dipole under the different F_{Se} and T_{Se} selected values, focusing on n-type GaP(111)_B substrates. As the Ga 3d CL lineshape may be impacted by the formation of surface GaSe, we evaluate the change in band bending with respect to the bare surface from the evolution of the P 2p binding energy (BE) $\Delta\text{BE}_{\text{P}2\text{p}}$, since it gives directly the variation of the surface band bending $-\Delta\phi_b$. The Figure 3.19a shows a systematic shift in BE, which

reduces the overall band bending and demonstrates an electronic passivation of the surface, although only partial. A 700°C Se-treatment induces a +0.18 eV shift, while a 450°C favours a +0.24 eV shift (Table 3.6), whatever the value of F_{Se} . Therefore, the band bending after Se passivation, defined as $\phi_{bGaP-Se} = \phi_{bGaP} + \Delta\phi_b$, is reduced from 0.63 eV to 0.38 eV for $T_{Se}=450^\circ\text{C}$ and 0.44 eV for $T_{Se}=700^\circ\text{C}$. Considering the measurement uncertainty, we can conclude that the Se passivation of the GaP(111)_B surface reduces the band bending by an amount of ± 0.2 eV, regardless of the T_{Se} and F_{Se} values.

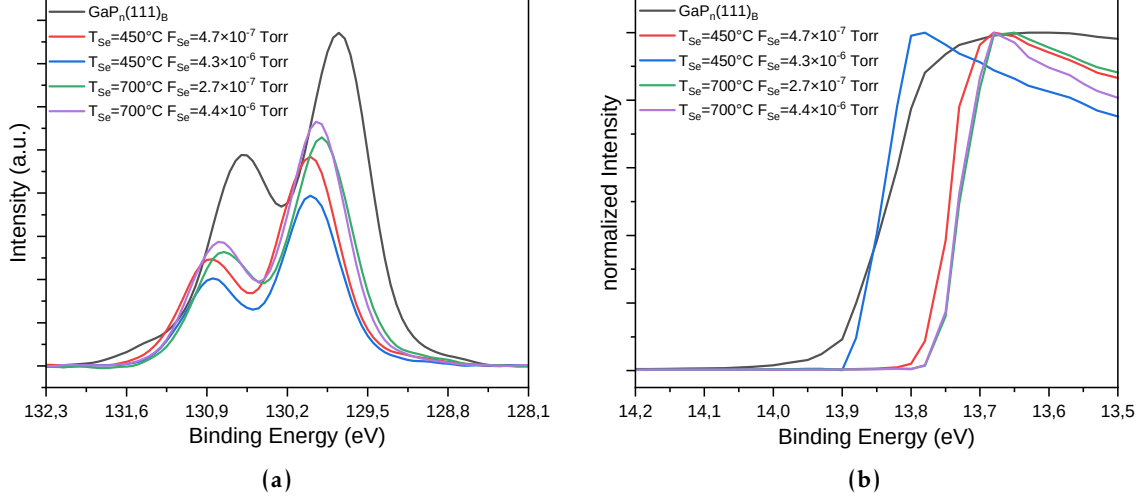


Figure 3.19: Evolution upon Se passivation at different T_{Se} and F_{Se} of (a) the P 2p CL captured with a take-off angle $\theta=75^\circ$, and (b) the threshold energy measured with UPS He I $K\alpha$. The substrate is an n-type GaP(111)_B with $n \sim 2 - 3 \times 10^{18} \text{ cm}^{-3}$.

On the other hand, the variation of the surface dipole $\Delta\phi_s$ is obtained through work function measurement as for the bare surface ($\Delta\phi_s = \Delta\phi - \Delta\phi_b$). Therefore, the surface dipole after a Se-termination is defined as:

$$\phi_{sGaP-Se} = \phi_{sGaP} + \Delta\phi_s$$

For most of the conditions explored, the threshold energy decreases from 13.9 eV to 13.78 eV, yet a passivation at 450°C under strong Se flux doesn't induce any change (Figure 3.19b). Thus, it directly expresses the quasi-suppression of the surface dipole as presented in Table 3.6, while all other conditions favour a ϕ_s of around +0.15 eV. Sketches of the surface electronic structure after Se exposure for the different treatment conditions are presented in Figure 3.20. The positive values of $\Delta\phi_s$ upon Se exposure is indicative of the presence of negative charges on the outer surface, while positive charges are located on the inner one. It is in line with the stronger Se electronegativity than the P one, which is a supplementary evidence of the top surface Se passivation.

		$T_{Se}=450^\circ\text{C}$		$T_{Se}=700^\circ\text{C}$	
	n-type GaP(111) _B	$F_{Se} = 4.7 \times 10^{-7}$ Torr	$F_{Se} = 4.3 \times 10^{-6}$ Torr	$F_{Se} = 2.7 \times 10^{-7}$ Torr	$F_{Se} = 4.4 \times 10^{-6}$ Torr
BE _P 2p	129.75 ± 0.02 eV	129.99 ± 0.01 eV	129.99 ± 0.04 eV	129.94 ± 0.03 eV	129.94 ± 0.02 eV
Φ	4.30 ± 0.05 eV	4.42 ± 0.05 eV	4.31 ± 0.05 eV	4.43 ± 0.05 eV	4.42 ± 0.05 eV
$\Delta_{BE} = -\Delta\Phi_b$		0.24 ± 0.03 eV	0.24 ± 0.06 eV	0.18 ± 0.05 eV	0.19 ± 0.04 eV
$\Delta\Phi$		0.12 ± 0.1 eV	0.01 ± 0.1 eV	0.13 ± 0.1 eV	0.12 ± 0.1 eV
$\Delta\Phi_s$		0.36 ± 0.13 eV	0.25 ± 0.16 eV	0.31 ± 0.15 eV	0.31 ± 0.14 eV
Φ_b	0.63 ± 0.05 eV	0.38 ± 0.08 eV	0.38 ± 0.11 eV	0.44 ± 0.1 eV	0.43 ± 0.09 eV
Φ_s	-0.19 ± 0.1 eV	0.17 ± 0.23 eV	0.07 ± 0.21 eV	0.13 ± 0.18 eV	0.13 ± 0.17 eV

Table 3.6: Determination and evolution of the band bending and the surface dipole before and after the Se-treatment in terms of T_{Se} and F_{Se} for an n-type GaP(111)_B surface.

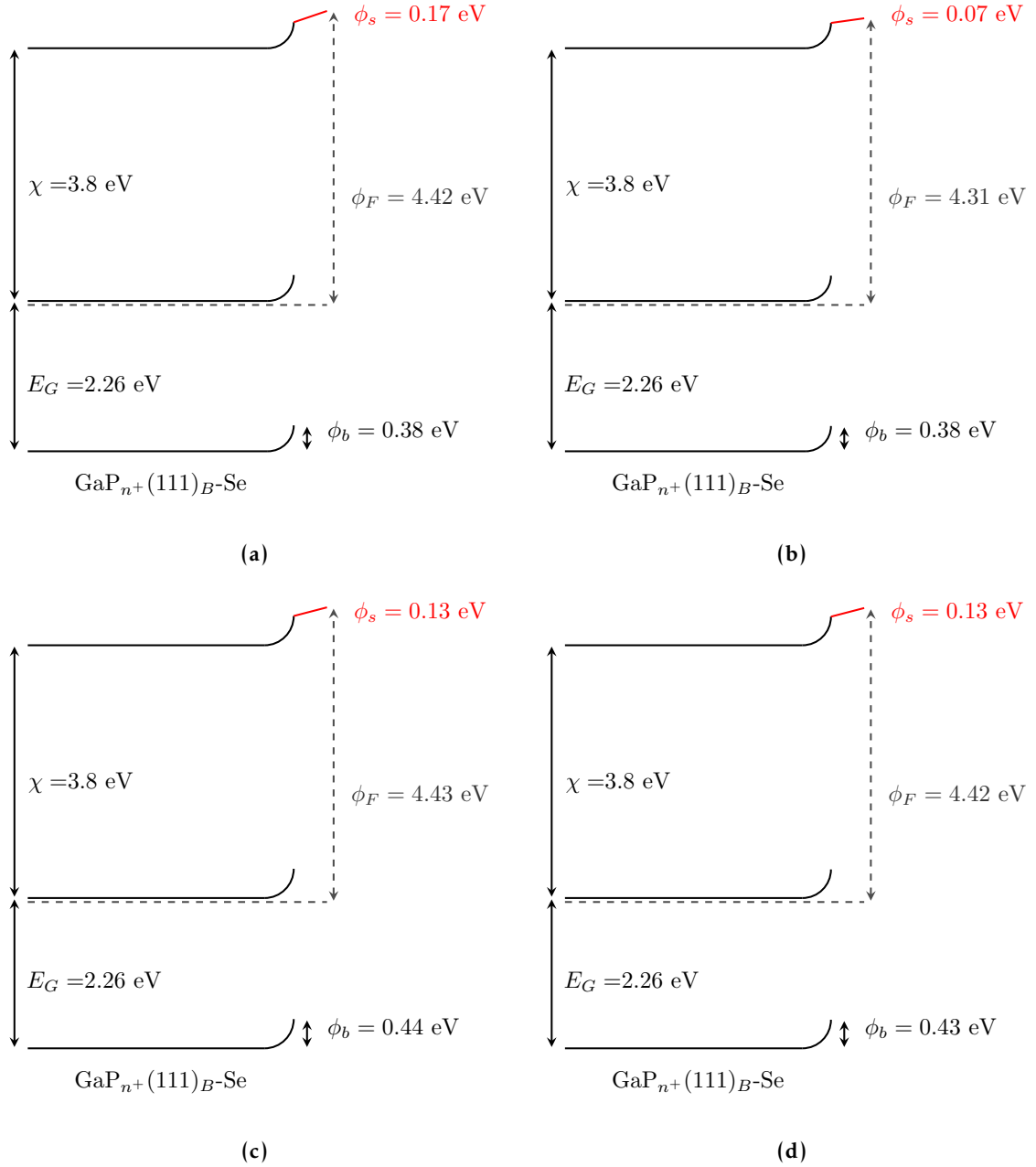


Figure 3.20: Band structure schematic of Se-passivated n-type GaP(111)_B substrate with (a) $T_{\text{Se}}=450^\circ\text{C}$ $F_{\text{Se}}=4.7\times 10^{-7}$ Torr ($V_{\text{Se}}=0.08$ Å/s), (b) $T_{\text{Se}}=450^\circ\text{C}$ $F_{\text{Se}}=4.3\times 10^{-6}$ Torr ($V_{\text{Se}}=0.93$ Å/s), (c) $T_{\text{Se}}=700^\circ\text{C}$ $F_{\text{Se}}=2.7\times 10^{-7}$ Torr ($V_{\text{Se}}=0.03$ Å/s) and (d) $T_{\text{Se}}=700^\circ\text{C}$ $F_{\text{Se}}=4.4\times 10^{-6}$ Torr ($V_{\text{Se}}=0.79$ Å/s).

Conclusion

In this Chapter, we have investigated the surface preparation of the GaP(111)_B surface, from its de-oxidation and the growth of a homoepitaxial buffer, to the Se-termination required for the TMDC growth.

We have demonstrated the need for a combination of H_{at} and cracked phosphine rather than thermal deoxidation using a 3-step sequence. The exposure time of H_{at} has appeared being the key parameter to a successful deoxidation, with an optimal time of 10 minutes. We also point out a maximum substrate temperature of 550°C to prevent the partial desorption of the P atoms, inducing the formation of Ga clusters. The resulting surface exhibits a 2×2 reconstruction and clear atomic steps, with serrated edges, while XPS measurements evidence a phosphorus excess on the surface. In a second time, we tried to improve the morphology - and especially the atomic step edge morphology - by growing a few nanometer-thick GaP(111)_B buffer layer. However, we face the great difficulty in obtaining a rather flat surface, as a too low growth temperature induces the formation of small pyramids, while a too high one favours the appearance of triangular nano-holes originating from gallium droplet formation. Yet, we can conclude on the requirement of a low gallium growth rate, coupled with a large excess of P₂ flux.

Last, the GaP(111)_B deoxidized surface selenium termination prior TMDC growth has been explored, based on earlier results obtained on GaAs(111)_B. We highlight a similar morphology before and after the treatment observed with AFM, while the RHEED indicates a systematic change in reconstruction from a 2×2 pattern to a 1×1 one. Besides, XPS and XPD measurement highlight a change in chemical environment mainly in the outermost P-surface layer. However, the observation of a sub-surface component in the Se 3d CL has required the optimisation of the process. We unveil the predominant effect of the selenium flux on the presence of this sub-surface component, with an optimal value in the 10^{-7} Torr range, whereas the temperature has shown little effect between 450°C and 700°C. Last, we highlight the effect of this passivation to the reduction of the band bending, demonstrating an effective electronic passivation of the surface, although only partial.

Optimization and characterization of the WSe₂/GaP(111)_B-Se growth

In this chapter, we discuss the optimization of the WSe₂ growth on GaP(111)_B-Se, focusing on the impact of the growth and annealing conditions on the structure and the morphology of the epitaxial films. In a second time, we investigate the electronic properties of the optimized layers and the band alignment at the GaP(111)_B-Se/WSe₂ interface, demonstrating a strong p-type character of WSe₂.

The following section describes the growth of few layers WSe₂ on GaP(111)_B substrate after a complete surface preparation, *i.e.* the deoxidation of the substrate and its passivation under selenium flux. We first stress the effect of the growth temperature on the morphology and the phase formed, before considering a subsequent annealing step under selenium flux. In the literature, the formation of the 1T' phase in UHV conditions is reported for a growth temperature (T_G) below 400°C^{148, 191}, which is why we have decided to choose T_G either lower than 400°C (250°C) or higher than 400°C (up to 700°C).

4.1 Impact of the growth temperature

Table 4.1 summarizes the different samples used for the following discussion. No noticeable difference has been observed on the experimental results within the considered Se:W ratio.

4.1.1 WSe₂ nucleation

First, we study the impact of the growth temperature on the WSe₂ nucleation density by comparing the evolution of the surface morphology between 250°C and 550°C for the same nominal deposited thickness around 0.25 ML (samples S_{n-1} , S_{n-2} and S_{n-3}). The growth was performed with a tungsten growth rate $V_W = 0.002 \text{ Å/s} \pm 15\%$ and a strong Se overpressure of 3×10^{-6} Torr. The AFM images presented in Figure 4.1 are treated using the procedure explained in Annex C. They show that raising T_G from 250°C to 450°C reduces the nuclei density from $3000 \mu\text{m}^{-2}$ to $1800 \mu\text{m}^{-2}$, underscoring the increase of the species surface diffusion with T_G . However, this trend seems limited by a critical T_G , as there is no change in density at 550°C. The images also reveal that the nucleation does not occur at preferential sites such as atomic step edges but rather all over the surface. Together with the small grain size (~ 10 nm) reached at 450°C and 550°C, this shows that the surface diffusion remains limited in the explored T_G range, as

n°	substrate	thickness	T_G	P_Se (Torr)	V_W ($\text{\AA}/\text{s}$)	Se:W
S_{n-1}	p GaP	~ 0.25 ML	250°C	3×10^{-6}	0.0018	550:1
S_{n-2}	p GaP		450°C		0.0018	
S_{n-3}	p GaP		550°C		0.0016	
S_{n-4}	p GaP		450°C		0.0018	
S_{4-1}	n^+ GaP	0.6 ML	250°C	1.5×10^{-6}	0.0018	200-1400:1
S_{4-2}	n^+ GaP	2.2 ML	250°C		0.0018	
S_{4-3}	n^- GaP	1.7 ML	250°C		0.0018	
S_{4-4}	n^- GaP	>10 ML	250°C		0.0034	
S_{4-5}	n^+ GaP	3.1 ML	450°C		0.0020	
S_{4-6}	n^- GaP	1.9 ML	500°C		0.0020	
S_{4-7}	semi-insulating	2.2 ML	250°C		0.0016	
S_{4-8}	p GaP	2 ML	450°C		0.0020	
S_{4-9}	p GaP	2.5 ML	550°C		0.0016	
S_{4-10}	n^+ GaP		650°C		0.0022	
S_{4-11}	p GaP		700°C		0.0020	

Table 4.1: samples summary. The calculation of the thickness at 650°C and 700°C is irrelevant due to model limitations.

expected for tungsten-based species. The impact of the $\text{GaP}(111)_\text{B}$ substrate on the WSe_2 nucleation seems limited, suggesting a weak interface interaction.

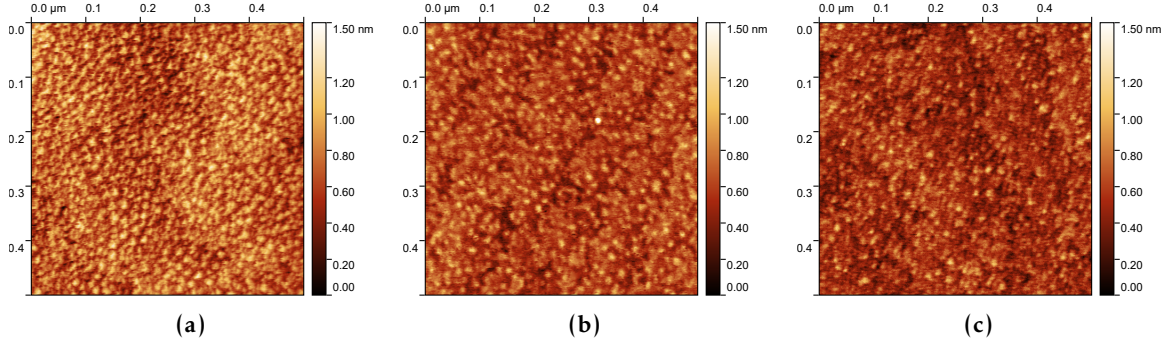


Figure 4.1: Evolution of the nucleation density of WSe_2 after a 0.25 ML growth observed on $0.5 \times 0.5 \mu\text{m}^2$ AFM images. (a) $T_\text{G}=250^\circ\text{C}$ (S_{n-1}). (b) $T_\text{G}=450^\circ\text{C}$ (S_{n-2}). (c) $T_\text{G}=550^\circ\text{C}$ (S_{n-3}).

We then grow 0.25 ML WSe_2 at 450°C with a series of three tungsten exposures (sample S_{n-4}), being spaced from each other by a stabilization under Se of 5 minutes, which artificially reduces the growth rate by a factor of 5. The resulted topography shown in Figure 4.2 exhibits a lower nuclei density of $1600 \mu\text{m}^{-2}$ with slightly bigger grains (~ 13 nm), in good agreement with the KMC study of Nie *et al.*³³. Overall, to favor a reduced density of larger grains, this points out the need for a low tungsten growth rate coupled with a reasonably high growth temperature.

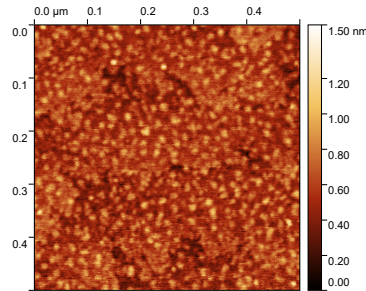


Figure 4.2: $0.5 \times 0.5 \mu\text{m}^2$ AFM image of a 0.25 ML WSe_2 growth at 450°C with a reduced growth rate (S_{n-4}).

4.1.2 Morphology, chemistry and phase identification for growths at 250°C

During the growth of 0.6 ML (sample S_{4-1}) and 2.2 ML (sample S_{4-2}) WSe_2 at $T_G=250^\circ\text{C}$, **RHEED** patterns exhibit a 2D mode characterized by vertical streaks. When reaching half a monolayer thickness, intermediate lines, close to a 2×2 reconstruction appear and remain until the end of the growth (Figure 4.3a & 4.3b). A similar feature is observed on the LEED patterns at 50 eV for both samples (Figure 4.3c & 4.3d), exhibiting intermediate spots. The lattice periodicity between the intermediate streaks/spots seems consistent with the metastable $1T'$ phase coexisting with the more stable $1H$ phase, as already evidenced by Ugeda et al.¹⁴⁸. In addition, the LEED pattern of the sub-monolayer sample S_{4-1} exhibits a Moiré, evidencing the good quality of the substrate to epi-layer interface (Figure 4.3c). The lattice periodicity of both phases can be obtained by using the GaP spots and lattice parameters (3.84 Å) as reference. Therefore, we deduce a lattice periodicity of 6.65 Å and 3.33 Å for the $1T'$ phase and the $1H$ phase, respectively, larger than the theoretical values (5.94 Å and 3.30 Å¹⁴⁷). In addition, the WSe_2 related LEED spots present a circle arc shape of angular spread 2.4° and 2.9° for the sub monolayer (S_{4-1}) and 2.2 ML sample (S_{4-2}), respectively. It clearly evidences a rather large in-plane disorientation. The 2D growth behaviour at low T_G is further confirmed by the AFM images of S_{4-2} (Figure 4.3e), which exhibits a smooth surface of roughness ~ 0.3 nm and small 15 nm wide surface domains.

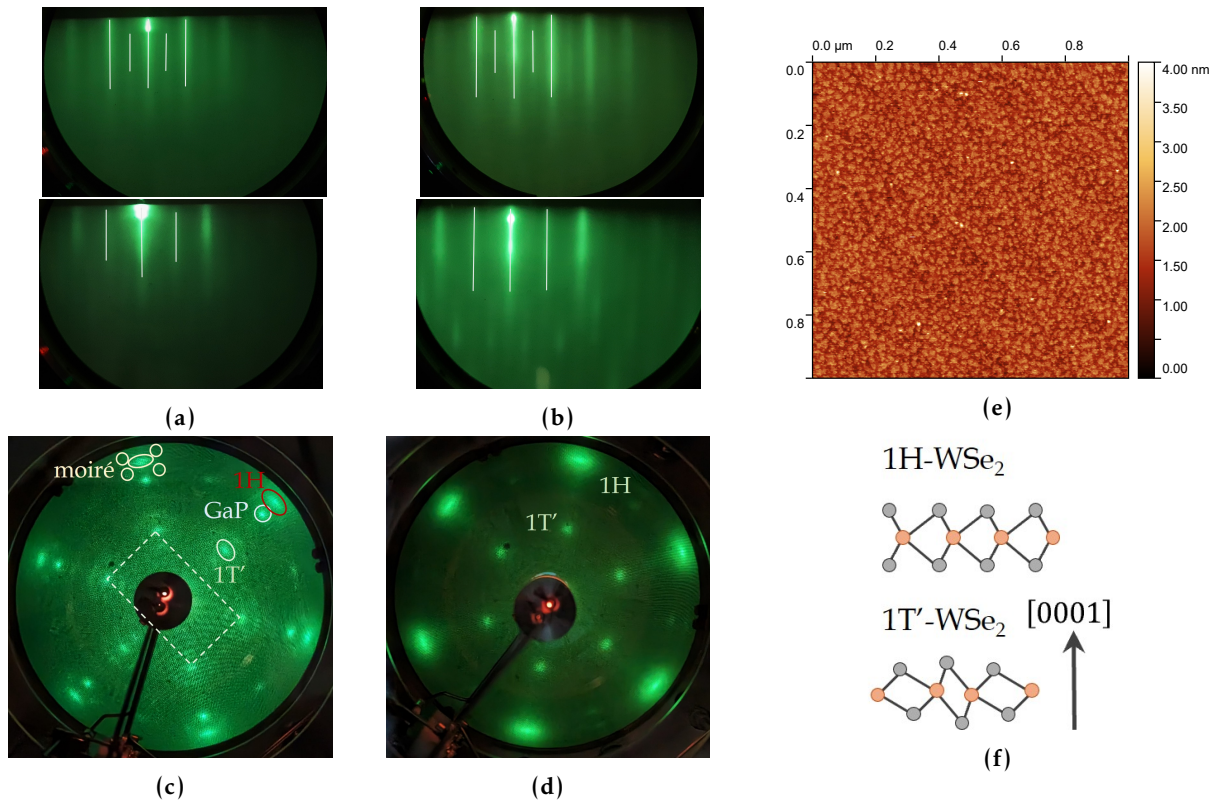


Figure 4.3: WSe_2 grown at 250°C . (a) 0.6 ML (S_{4-1}) and (b) 2.2 ML WSe_2 (S_{4-2}) RHEED patterns along the $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$ azimuths of WSe_2 . 50 eV LEED pattern of S_{4-1} (c) and S_{4-2} (d). (e) $1 \times 1 \mu\text{m}^2$ AFM image of S_{4-2} . (f) Phase schematic adapted from Ugeda et al.¹⁴⁸

As presented in Chapter 1, monolayer TMDCs can be classified in several structural phases, the most common being $1H$) and $1T$. In the case of WSe_2 , the most stable phase is assumed being $1H$, while forming the metastable $1T'$ phase at low temperature. The projection of each unit cell along $\langle 11-20 \rangle$ (Figure 4.4a) allows to easily identify the two phases, with the formation of herringbones in the case of

1H and lines in the case of 1T. Based on the work of Yamamoto *et al.*²⁹ on the heteroepitaxial growth of NbSe_2 on $\text{GaAs}(111)_\text{B}$, the $[11-20]$ direction of the TMDC layer is supposed to align itself with the $[1-10]$ direction of the III-V substrate (Figure 4.4b). Last, the stacking of several 1H-MX₂ layers gives rise to new polytypes, which can be commonly referred as 2H or 3R, digits indicating to the number of layers per repeat unit, and the letter standing for the hexagonal and rhombohedral symmetry, respectively. The formation of the more stable 2H phase is enabled by a 60° in-plane rotation of one monolayer, which can be observed as a herringbones direction switch in the (11-20) plane (Figure 4.4c). On the other hand, the 3R stacking lacks this inversion symmetry, leading to observing herringbones in the same direction.

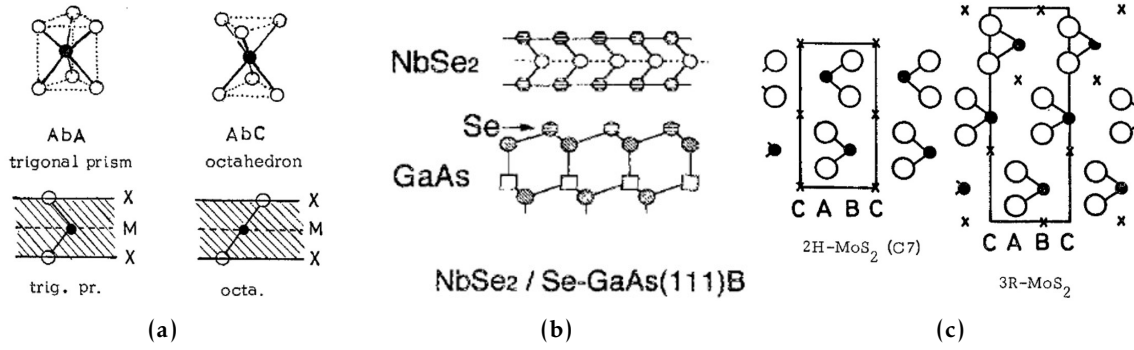


Figure 4.4: Basic form of layer compounds. (a) Coordination units for MX₂ layer structures and the associated (11-20) planes. (b) Schematic diagrams of NbSe₂ films on a van der Waals GaAs surface realized by the Se termination of surface dangling bonds. (c) (11-20) planes of the various stacking polytypes in group VI MX₂ layer dichalcogenides in the trilayer limitation. (a) and (c) are extracted from ⁴, while (b) is extracted from ²⁹.

HAADF-STEM images along the $[-110]$ zones axis from S_{4-1} and a 1.7 ML grown at $T_G=250^\circ\text{C}$ (sample S_{4-3}) (Figure 4.5a & 4.5b) show the chemical contrast between the epi-layer and the GaP substrate. As the brightness contrast in HAADF is roughly proportional to the square of the atomic number ($\sim Z^2$), the interface is easily observed and reveals an extreme GaP surface selenium passivation before growth. This validates the surface treatment used to get a $\text{GaP}(111)_\text{B}$ -Se pseudo van der Waals substrate, inducing the formation of a clear van der Waals gap at the interface between the epi-layer and the substrate. Over larger STEM scans (Figure 4.5c), the WSe_2 thickness is regular, while its continuity is not disturbed by atomic edges as exhibited in Figure 4.5a. Overall, at this temperature, STEM images show a good quality of the substrate to epi-layer interface with no apparent issues during the early selenium passivation, in agreement with the observation of a Moiré on the monolayer LEED pattern (Figure 4.3c). Moreover, the sub-monolayer sample TEM images bring additional proof of the 1T' phase coexisting with a disordered 1H one (Figure 4.5a), respectively represented by lines and herringbones. This latter exhibits a high in-plane disorientation as two different 1H orientations are resolved within the same image, also indicating the presence of MTB. For sub-bilayer, HR-STEM observation mainly points out the formation of a rhombohedral stacking (Figure 4.5b) being related to the 3R-bilayer stacking (AB) by comparing it with its atomic arrangement schematic in Figure 4.4c & Figure 4.5d. The in-plane disorientation appears less important than in the monolayer sample, with a coherence length estimated at 50 nm. We hereby observe a $[11-20]_{\text{WSe}_2} // [-110]_{\text{GaP}}$ and $[1-100]_{\text{WSe}_2} // [11-2]_{\text{GaP}}$ in plane epitaxial relationship, and a $[0001]_{\text{WSe}_2} // [-1-1-1]_{\text{GaP}}$ out of plane relationship, consistent with the observations of Pierucci *et al.* on WSe_2 epitaxy on a $\text{GaAs}(111)_\text{B}$ substrate³⁰. The spacing between two W atoms from different WSe_2 layers is estimated at $6.45 \pm 0.10 \text{ \AA}$ by Mahmoudi *et al.*²⁸⁸, which is consistent with the theoretical value (6.48 Å), while the spacing between the first W and Ga atoms at the quasi-van der Waals interface is estimated at $6.20 \pm 0.20 \text{ \AA}$. The Figure 4.5e also points out a coincidence lattice with 6 units

of GaP matching 7 units of WSe₂, which reduces the average lattice mismatch from 15% to 0.65%.

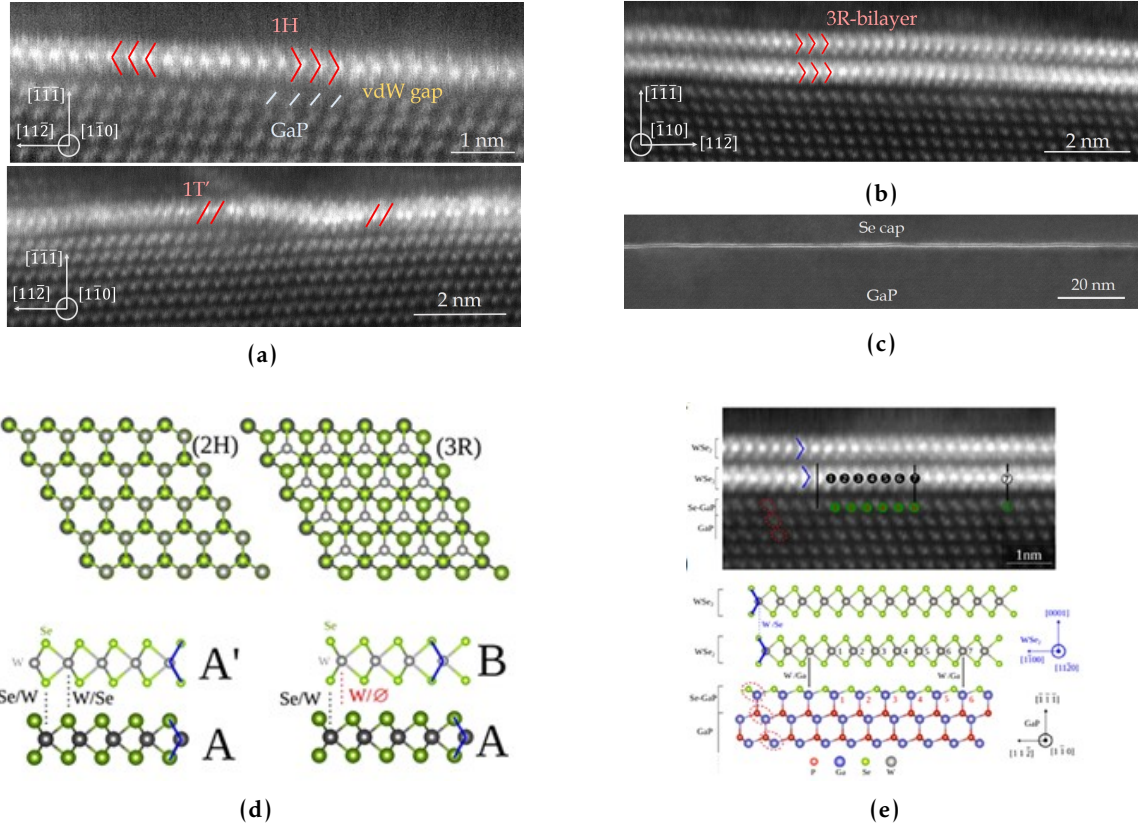


Figure 4.5: HAADF-STEM images of (a) 0.6 ML (S_{4-1}) and (b, c) 1.7 ML (S_{4-3}) WSe₂ grown at $T_G=250^\circ\text{C}$; (d) Schematic representation of bilayer WSe₂: Top view of 2H and 3R stacking sequences of bilayer WSe₂. The coloured layers differentiate the successive position in the in-plane direction where each colour corresponds to an inequivalent layer position, extracted from Mahmoudi et al.²⁸⁸. (e) high-resolution STEM image with the overlaid atomic structure of the sub-bilayer (S_{4-3}) WSe₂ on the GaP(111)_B surface and the associated schematic structure extracted from Mahmoudi et al.²⁸⁸.

Raman spectroscopy measurements on sample S_{4-3} confirm the TEM phases observations (Figure 4.6a), as the Raman spectrum exhibits two distinct contributions at 251.2 cm^{-1} and 247.8 cm^{-1} , attributed to out-of-plane A_{1g} and in-plane E_{2g}^1 vibrations modes, respectively^{188, 289, 290} (Figure 4.6c). The weaker feature at 263.5 cm^{-1} is commonly attributed to the 2LA(M) vibration mode and the strong peak at 237.7 cm^{-1} to the selenium protection cap, which is decreasing during the acquisition due to a local vaporisation. In comparison, the Raman spectrum of a 2H bilayer flake grown with CVD (Figure 4.6d) by Mahmoudi et al.¹⁸⁵ or McCreary et al.¹⁸⁸ shows a clear and strong predominance of the A_{1g} vibration mode over the E_{2g}^1 , while the 3R flake (Figure 4.6e) presents independently resolved peaks with a stronger E_{2g}^1/A_{1g} ratio. By visual analogy, we can infer the presence of a significant amount of 3R stacking in the sub-bilayer WSe₂ S_{4-3} sample. However, the exact percentage of phase purity is not yet accessible since the FWHM of the A_{1g} and E_{2g}^1 peaks (~ 7 and $\sim 4\text{ cm}^{-1}$) is much larger than the ones obtained for CVD grown sample, indicating a larger defect density, and the low signal intensity reduces the accuracy of the fit. Figure 4.6b shows the Raman spectrum of a 15 ML thick WSe₂ sample (sample S_{4-4}) grown on GaP(111)_B at 250°C , exhibiting a thin A_{1g} component (FWHM $\sim 3.5\text{ cm}^{-1}$) and a larger E_{2g}^1 peak ($\sim 5\text{ cm}^{-1}$). The $0.81\text{ }E_{2g}^1/A_{1g}$ ratio still indicates the presence of 3R stacking, pointing out this polytype formation at this temperature even for large thickness. During this work, it has never been possible to observe vibrations modes linked to the 1T' phase, as their intensity is supposed extremely low¹⁹¹.

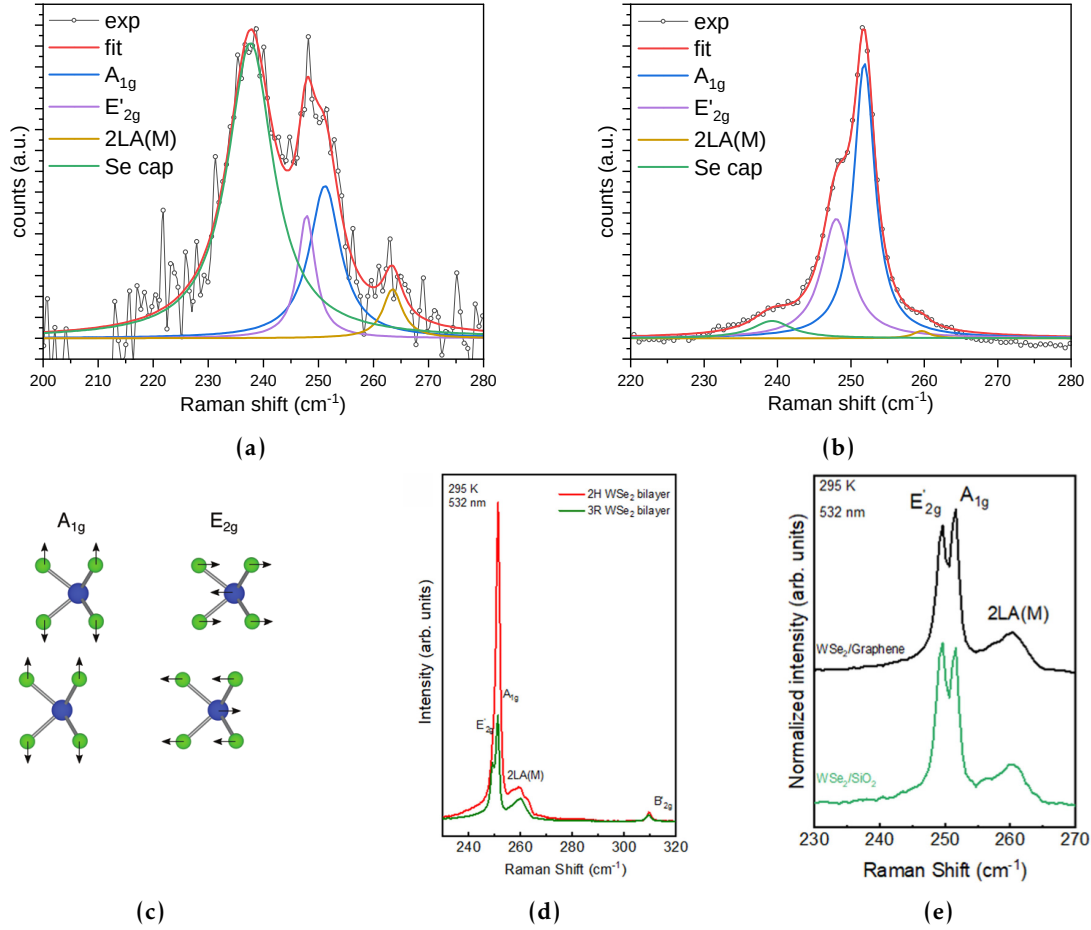


Figure 4.6: Raman spectroscopy measurement on (a) a 1.7 ML WSe_2 (S_{4-3}) and (b) 15 ML thick WSe_2 (S_{4-4}) at low temperature on $\text{GaP}(111)_\text{B}$; (c) Schematic illustration of the side view of the 3R WSe_2 bilayer illustrating the A_{1g} and E_{2g}^1 mode with black arrows, extracted from ¹⁸⁸. The laser wavelength used is 473.1 nm. (d) Comparison of individual Raman spectra acquired in the bilayer regions of 3R and 2H WSe_2 crystals grown by CVD. (e) Room temperature micro-Raman spectra of bilayer before transfer (2 ML $\text{WSe}_2/\text{SiO}_2$: green line), and after transfer (2 ML $\text{WSe}_2/\text{graphene}$: black line). (d) and (e) are extracted from ¹⁸⁵.

The decomposition of the W 4f CL recorded by XPS on S_{4-2} in Figure 4.7a exhibits a first doublet at 32.44 eV linked to the 2H or 3R phase, and a second doublet linked to the 1T' with a binding energy shift of -0.6 eV^{32, 147}. Yet, it is not possible to distinguish the 2H or 3R phases using XPS. Therefore, we only assume the formation of a dominant semiconducting phase that we call 3R according to STEM observations, and a residual 1T' one at low growth temperatures. The Se 3d CL in Figure 4.7b also exhibits two doublets with the main one at 54.61 eV. In this case, the origin of the second low binding energy doublet can be ascribed to both the 1T' phase and to selenium atoms bonded to gallium ones at the top surface of the selenium passivated GaP surface. In comparison, the W 4f and Se 3d CLs of the S_{4-1} sample are presented in Figure 4.7c & 4.7d. The decomposition of the W 4f CL shows a clear dominance of the 1T' phase over the 1H one, while the line shape of the Se 3d CL (Figure 4.7d) makes a valuable decomposition difficult. We hypothesize that the 1T' phase forms mainly on the top surface layer because of the unstable thermodynamically state. The monolayer regime would favour the metastable phase formation, yet a complete 1T' monolayer has never been observed in this work. In the multilayer regime the first layers would be stabilized by the upper ones, resulting in the formation of the 3R or 2H phase with some residual 1T' phase in the top-surface layer.

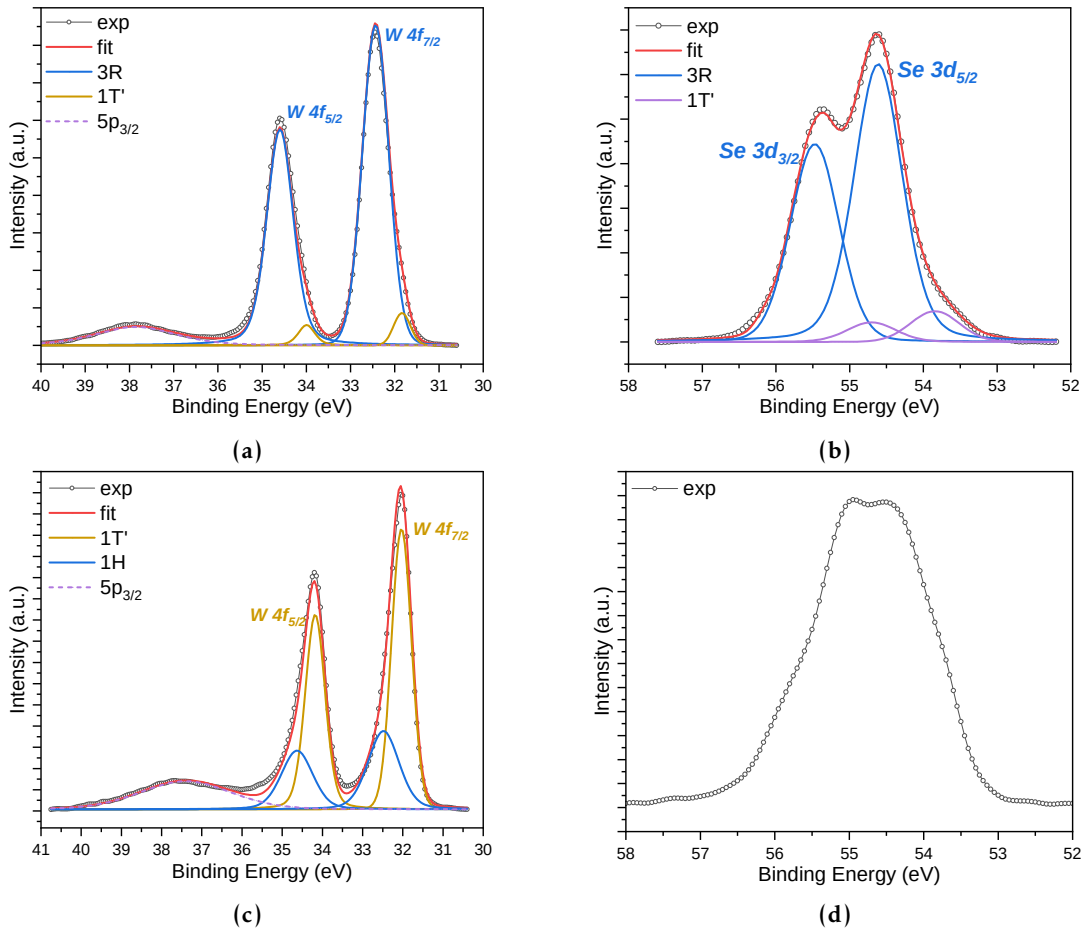


Figure 4.7: Decomposition of W 4f and Se 3d CLs recorded at an electron take-off angle $\theta=25^\circ$ for S_{4-2} (a,b) and S_{4-1} (c,d).

ARPES measurements performed by Mahmoudi *et al.*²⁸⁸ on S_{4-3} confirm the formation of a predominant 3R phase with an energy cutoff at about 0.8 ± 0.1 eV above the **VBM**, indicating the expected semiconducting behaviour of the WSe_2 bilayer. The VBM is located at Γ , simultaneously confirming the indirect band gap character of the sample and a thickness greater than one monolayer over the whole surface. The band splitting in the Q valley of the valence band induced by a lack of symmetry enables the identification of the 3R phase rather than the 2H one²⁸⁸. The measured electronic structure is then compared to a theoretical DFT calculation from a freestanding 3R WSe_2 bilayer, evidencing that the 1.7 ML $WSe_2/GaP(111)_B$ hybrid heterostructure shares the same electronic dispersion as a freestanding 3R WSe_2 bilayer. In addition, the variation of the photon energies from 50 eV to 80 eV along the ΓK high symmetry allowed to resolve two split branches of the valence band at the K point, with an estimated spin orbit coupling of 550 meV.

4.1.3 Morphology and chemistry for growth at temperatures exceeding 400°C

In the literature, the formation of the 1T' phase in **UHV** condition is limited to a maximum growth temperature of 400°C^{148, 191}. In order to favour the growth of the stable 2H WSe_2 phase, T_G is increased up to 450°C (sample S_{4-5}), as a weak 2×2 RHEED pattern is still observable at 400°C. In this case, the RHEED patterns presented in Figure 4.8a shows additional spots along and around the 1×1 vertical streaks, indicating a favoured three-dimensional growth mode. Actually, this 3D behaviour appears at the end of the first half-monolayer with the appearance of two first spots along the $\langle 11-20 \rangle$ direction.

The spots close to but not on the WSe_2 streaks are probably related to the GaP substrate due to the 3D growth. The RHEED diagram then slowly degrades with the formation of numerous spots. As shown in Figure 4.8b, a similar behaviour is observed at 500°C (sample S_{4-6}), resulting in a rough surface (RMS ~ 1.1 nm) with domains 25 nm wide yet less well-defined than at 250°C (Figure 4.8c). The suppression of the $1\text{T}'$ phase in S_{4-5} suggested by the disappearance of the intermediate lines in RHEED is further confirmed by the W 4f and Se 3d CL deconvolutions. Indeed, Figure 4.8d exhibits a single component at 32.41 eV related to stable WSe_2 phase, while the Figure 4.8e displays a component at 54.62 eV linked to WSe_2 ^{182, 291} and a second one at 53.8 eV connected to surface Ga-Se bonds induced by the early Se-treatment³⁰. The rather large FWHM of both W 4f (0.63 eV) and Se 3d (0.68 eV) CLs suggests a poor crystal quality, while the XPS intensity ratio Se/W (calculated from sensitivity factors presented in Annex B) equal to 2.1 indicates a slightly Se-rich layer.

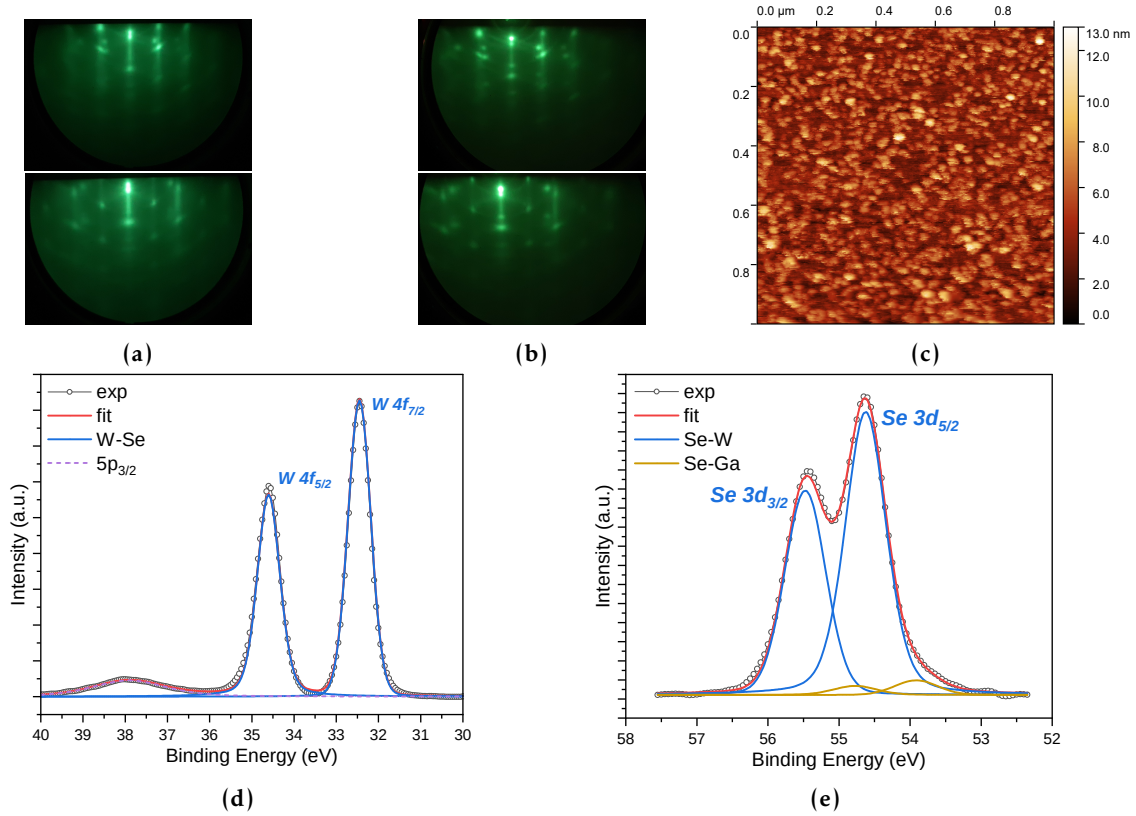


Figure 4.8: RHEED pattern along $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$ of a (a) 3.1 ML WSe_2 layer grown at $T_G=450^\circ\text{C}$ on a n-type substrate (S_{4-5}), (b) 1.9 ML WSe_2 grown at $T_G=500^\circ\text{C}$ (S_{4-6}). (c) $1 \times 1 \mu\text{m}^2$ AFM image of S_{4-5} , with (d) the associated XPS W 4f CL and (e) Se 3d CL recorded with an electron take-off angle of 25° .

We then try to further increase T_G up to 550°C (sample S_{4-9}) in order to confirm the impact of a high growth temperature on the crystal quality above 450°C . However, as presented in Figure 4.9a, the 1×1 RHEED reconstruction is clearly reduced with a stronger 3D growth mode, while the associated W 4f CL decomposition (Figure 4.9b) exhibits a second component at lower binding energy around 31.8 eV that we attribute to metallic tungsten^{245, 292}. When increasing even more T_G up to 650°C (sample S_{4-10}), RHEED patterns exhibit dominant circular rings with blur 1×1 vertical streaks (Figure 4.9c), indicating the formation of randomly oriented crystallites with a strong roughness. At $T_G=700^\circ\text{C}$ (sample S_{4-11}), the diffraction pattern disappears, pointing out the formation of an amorphous layer. The associated W 4f CL in Figure 4.9d shows the disappearance of WSe_2 with the formation of a strong asymmetrical doublet attributed to metallic tungsten. Considering the strong Se overpressure used (Se:W $\sim 400:1$), the formation

of such metallic surface is probably due to excessive selenium desorption at these temperatures.

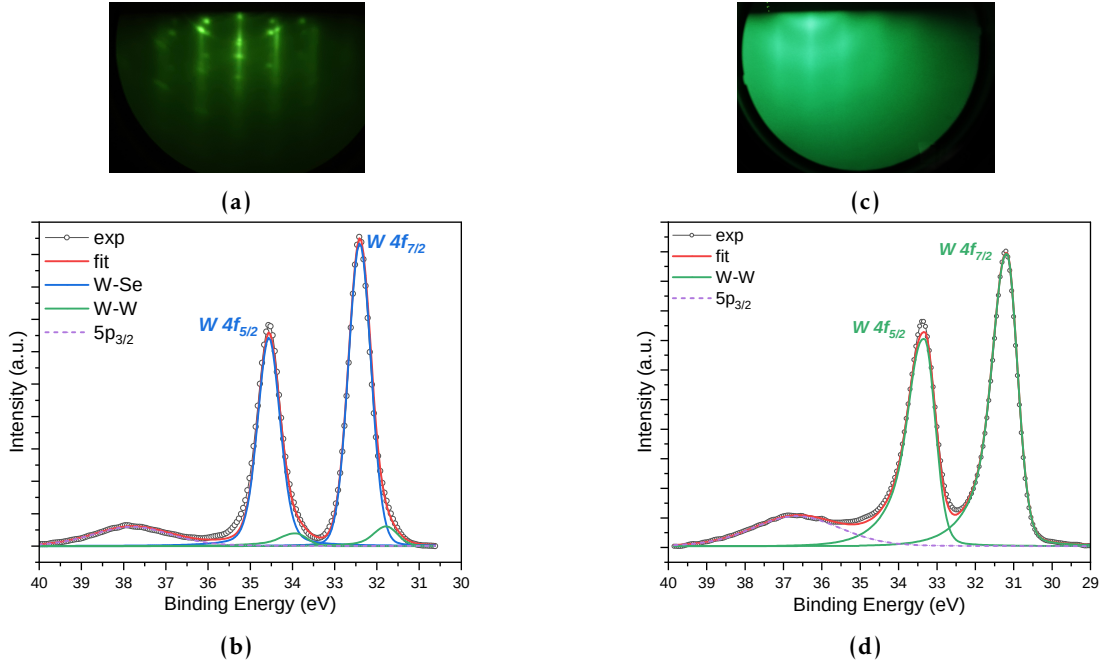


Figure 4.9: (a) RHEED pattern along $\langle 1-100 \rangle$ after a 2.5 ML WSe₂ grown at 550°C and (b) the associated XPS W 4f CL spectrum measured with a take-off angle $\theta=25^\circ$. (c) RHEED pattern along $\langle 1-100 \rangle$ after a growth at 650°C and (d) the XPS W 4f CL spectrum after a growth at 700°C.

4.1.4 Structural information

We measure the alignment of the WSe₂ grains with the GaP symmetry axes from grazing incident XRD global φ scans (Figure 4.10a) and extract the in-plane angular spread from the integral breadth of the most intense (110) ($2\theta_{\chi/\varphi}=55.65^\circ$) φ_{WSe_2} peak. The comparison of the WSe₂/GaP alignment between 2.2 ML grown at 250°C (sample S₄₋₇), 2 ML grown at 450°C (sample S₄₋₈) and 1.9 ML grown at 500°C (S₄₋₆) highlight the relatively good epitaxial relationship of WSe₂ grains with the GaP symmetry axes, though a clear improvement is observable for higher T_G (Table 4.2). As illustrated in Figure 4.10b, the in-plane disorientation tends to be strongly sensitive to T_G as a WSe₂ bilayer grown at 250°C shows a high angular spread of 2.87° , while it decreases to 1.87° when T_G is increased to 450°C and further reduced to 1.51° when T_G reaches 500°C.

As presented in Chapter 2 (section 2.2.1.2), the average grain size of WSe₂ is estimated from a Williamson-Hall (W-H) plot of the integral breadth of the (100), (110), (200) and (300) peaks, respectively at $2\theta_{\chi/\varphi}=[31.4^\circ; 55.6^\circ; 65.3^\circ; 108.1^\circ]$, which are extracted from the global $2\theta_{\chi/\varphi}$ scan presented in Figure 4.10c. The presence of additional peaks at 26.7° and 55.1° in the $2\theta_{\chi/\varphi} \varphi_0+30^\circ$ scan are attributed to (100) and (200) GaSe diffraction peaks, in good agreement with theoretical calculations presented in Annex A and earlier results obtained on GaAs(111)_B³⁰. Increasing T_G up to 450°C or 500°C reduces the integral breadth of the different peaks, yet doesn't change the average grain size, which remains in the 20-25 nm range (Figure 4.10d & Table 4.2). However, it clearly leads to a reduction of the slope (Figure 4.10e), which indicates a reduction of micro-strains and defects. We argue that the increase of the temperature does not have an impact on the average grain but clearly improves the quality of the layer.

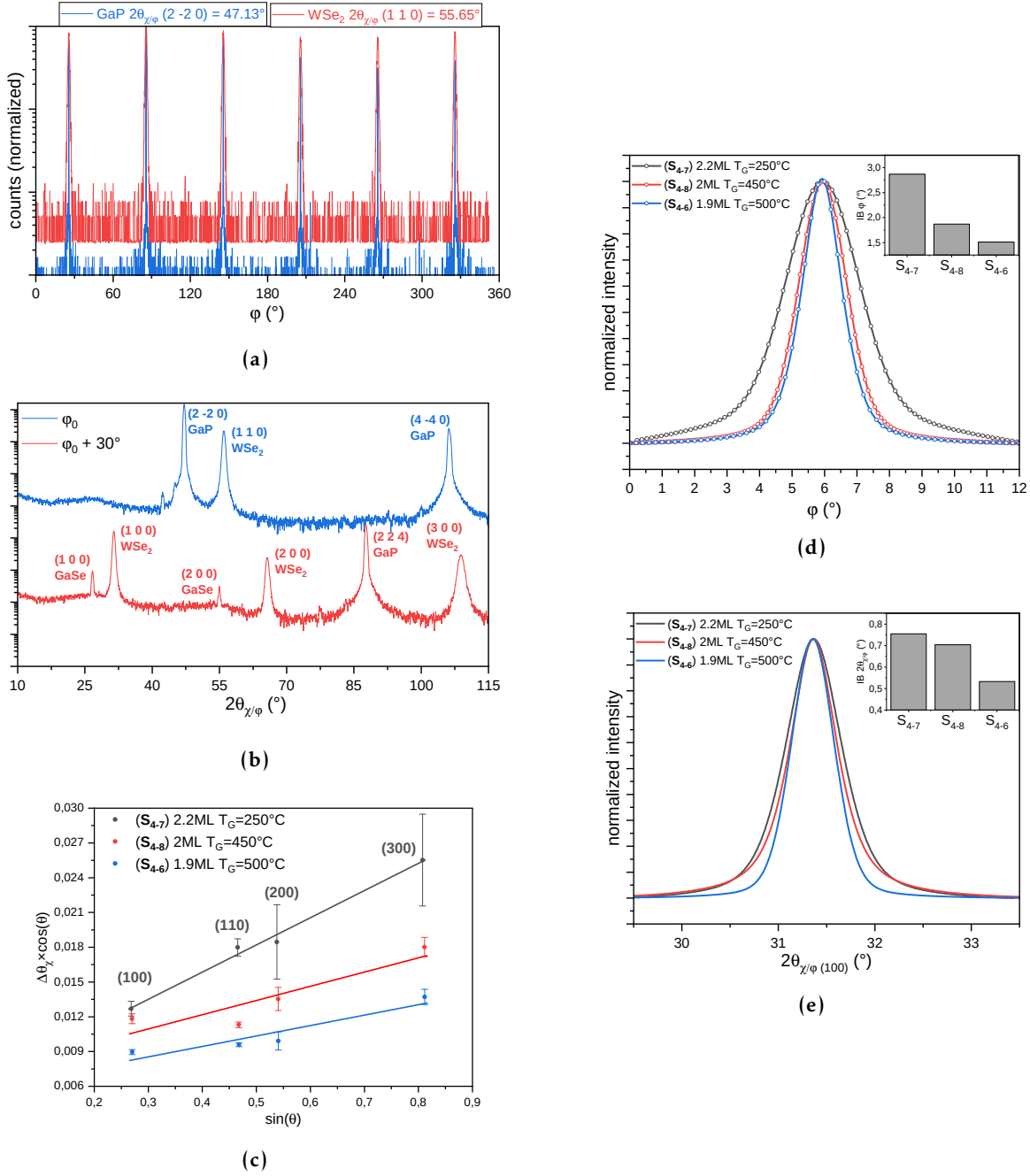


Figure 4.10: (a) 360° GaP (2-20) ($2\theta_{\chi/\phi}=47.13^\circ$) and WSe_2 (110) ($2\theta_{\chi/\phi}=55.65^\circ$) azimuthal spectrum for a WSe_2 bilayer grown at 450°C (S_{4-8}). (b) Evolution of normalized WSe_2 (110) ϕ scan with T_G . (c) XRD $2\theta_{\chi/\phi}$ spectrum along two azimuthal directions for the same sample. (d) Evolution of normalized $2\theta_{\chi/\phi(100)}$ scans with T_G . (e) Graphic plot of the (110), (100), (200) and (300) $2\theta_{\chi/\phi}$ integral breadth using the Williamson-Hall method.

sample	WSe ₂ /GaP alignment	$\varphi_{(110)}$ IB (°)	(100) IB	Grain size Scherrer (nm)	Grain size W-H (nm)	strain (Cε)
2.2 ML 250°C (S ₄₋₇)	0.73°	2.87 ± 0.11	0.755°	11.3 ± 0.1	23.9 ± 3.3	0.0235 ± 0.0016
2 ML 450°C (S ₄₋₈)	0.19°	1.87 ± 0.03	0.704°	12.1 ± 0.1	21.2 ± 6.8	0.0123 ± 0.0042
1.9 ML 500°C (S ₄₋₆)	0.07°	1.51 ± 0.03	0.533°	16.0 ± 0.1	26.4 ± 5.9	0.0090 ± 0.0023

Table 4.2: WSe₂/GaP alignment, in-plane angular spread and integral breadth of the (100) $2\theta_{\chi/\varphi}$ scan for WSe₂ multilayers grown at different T_G. The grain size obtained with the Scherrer relation is calculated from the (100) integral breadth.

To summarize, we have presented in the above section the evolution of the WSe₂ layer morphology and structure with the growth temperature, highlighting the partial formation of the metastable phase 1T' at 250°C and its suppression above 400°C. STEM images and XPS measurements have shown the coexistence of this metastable phase and a disordered yet more stable 1H phase in the monolayer regime at 250°C. The growth of a sub-bilayer at this temperature exhibits a lower fraction of 1T' in the top surface layer and a favoured 3R stacking, as confirmed by STEM images, Raman spectroscopy and ARPES measurements. When increasing the growth temperature up to 450°C and 500°C, we have observed a radical change in growth mode, as the RHEED pattern suggests a partially 3D growth rather than 2D, resulting in a strongly textured surface. Yet, this increase in T_G induces a significant improvement in in-plane disorientation (1.51°), while the average grain size remains stable (~24 nm). Increasing T_G above 500°C has exposed several issues, notably with the progressive formation of metallic tungsten clusters even at high Se:W ratios. The suppression of the different drawbacks induced by increasing T_G and the maximization of the grain size and in-plane orientation have yet to be explored.

4.2 Impact of an annealing under selenium flux at 650°C

In the following section, we investigate the impact of an annealing step under selenium flux on the phase formation as well as on the film morphology and structure within the explored T_G range. The temperature ramp after the growth is set at 20°C/min and the sample is maintained at T_A=650°C for 5 to 10 minutes before decreasing the temperature. We close the selenium shutter only once the substrate temperature has decreased below 450°C, in order to limit any desorption or accumulation of Se on the surface. The different samples used in this discussion are presented in Table 4.3.

n°	substrate	thickness	T_G/T_A	P_{Se} (Torr)	V_W ($\text{\AA}/\text{s}$)	Se:W
S ₄₋₁₂	p GaP	0.7 ML	250°C/650°C		0.0017	
S ₄₋₁₃	p GaP	1.6 ML	250°C/650°C		0.0019	
S ₄₋₁₄	p GaP	1.9 ML	250°C/650°C		0.0011	
S ₄₋₁₅	n ⁻ GaP	2.9 ML	250°C/650°C		0.0016	
S ₄₋₁₆	n ⁻ GaP	1.2 ML	450°C/650°C		0.0020	
S ₄₋₁₇	n ⁺ GaP	2 ML	450°C/650°C		0.0016	
S ₄₋₁₈	n ⁻ GaP	2.8 ML	450°C/650°C		0.0023	
S ₄₋₁₉	p GaP	4 ML	450°C/650°C		0.0021	
S ₄₋₂₀	n ⁻ GaP	>10 ML	450°C/650°C		0.0035	
S ₄₋₂₁	p GaP	2.5 ML	450°C/650°C	1-5×10 ⁻⁶	0.0019	200-1500:1
S ₄₋₂₂	n ⁻ GaP	2 ML	500°C/650°C		0.0016	
S ₄₋₂₃	n ⁺ GaP	2.2 ML	550°C/650°C		0.0018	
S ₄₋₂₄	p GaP	2.7 ML	550°C/650°C		0.0016	
S ₄₋₂₅	n ⁺ GaP		600°C/700°C		0.0017	
S ₄₋₂₆	n ⁻ GaP	1.9 ML	500°C/650°C IA		0.0017	
S _{4-27a}	n ⁺ GaP	2 ML	450°C/650°C IA		0.0023	
S _{4-27b}	semi-insulating					
S ₄₋₂₈	n ⁻ GaP	2.4 ML	500°C/650°C IA		0.0023	
S ₄₋₂₉	semi-insulating	3.9 ML	500°C/650°C IA		0.0021	
S ₄₋₃₀	p GaP	2.5 ML	250°C/650°C		0.018	66:1
S ₄₋₃₁	n ⁺ GaP	2.1 ML	450°C/650°C		0.019	83:1

Table 4.3: sample summary. *IA* stands for *Intermediate Annealing*.

4.2.1 Evolution of thin layers grown at 250°C

We consider different growth thickness of 0.7 ML (sample S₄₋₁₂), 1.6 ML (sample S₄₋₁₃), 1.9 ML (sample S₄₋₁₄) and 2.9 ML (sample S₄₋₁₅) for WSe_2 layers grown at $T_G=250^\circ\text{C}$ and then annealed at 650°C . As evidenced by both 1×1 LEED and RHEED patterns in Figure 4.11a & 4.11b, the Se annealing treatment totally suppresses the additional 1T' phase previously observed at low T_G . The 2D morphology is preserved under the post-growth treatment as demonstrated by the AFM image of sample S₄₋₁₄ (Figure 4.11c) with a slight decrease of the roughness (RMS~0.2 nm), coinciding with the reduction of the surface domain size and density. The appearance of 125 nm wide GaP atomic steps in the image background indicates a good interface formation, whereas the small dots are associated with the nucleation of the third layer. The main evolution of the RHEED pattern, *i.e.* the total suppression of the 2×2 diagram, occurs when T_A reaches 550°C . Thereafter, the vertical streaks are thinned with the temperature until reaching 650°C , evidencing a crystal quality improvement. Apart from the GaP spots, the LEED pattern of the sub-monolayer sample (S₄₋₁₂) no more exhibits intermediate spots as in Figure 4.3c but only one set of characteristic ones with an estimated lattice periodicity of $3.23 \text{ \AA}$, consistent with the 1H WSe_2 phase.

The observation of a Moiré on this sample also indicates the good quality of the van der Waals interface, further confirmed by the associated HAADF-STEM image (Figure 4.11d), in which the suppression of the 1T' phase is supported by the formation of a single 1H phase. Besides, we observe a clear reduction of the in-plane disorientation after annealing, as a sole orientation of the 1H herringbones within the same image can be observed. In the case of the 2.9 ML sample (S₄₋₁₅), both 2H (AA') and 3R-bilayer (AB) stacking are detected on the same STEM image (Figure 4.11e), with a preferential 3R-bilayer formation on the top surface layer. The epitaxial relationship expressed earlier as well as the coincidence lattice previously defined with 6 units of GaP matching 7 units of WSe_2 remain, with a constant coherence

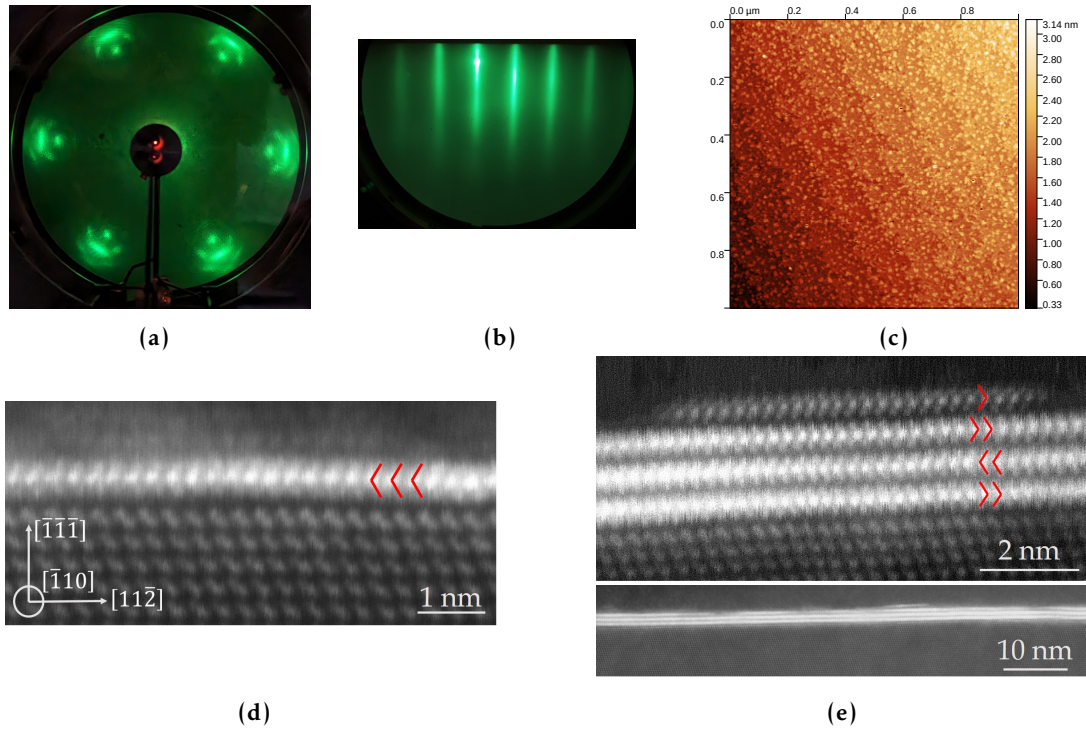


Figure 4.11: Impact of the Se-annealing treatment on the morphology of WSe₂ layer grown at 250°C. (a) LEED pattern of a 0.7 ML WSe₂ (S₄₋₁₂) recorded at 52 eV. (b) RHEED pattern along the <1-100> direction of a 1.6 ML WSe₂ (S₄₋₁₃). (c) $1 \times 1 \mu\text{m}^2$ AFM image of a 1.9 ML WSe₂ (S₄₋₁₄) after Se-annealing. HAADF STEM images of (d) S₄₋₁₂ and (e) the 2.9 ML WSe₂ (S₄₋₁₅).

length of 50 nm and a continuous film over the whole scanned area.

Before annealing, both CLs for the sub-monolayer sample S₄₋₁₂ present line shapes close to those recorded on S₄₋₁ (Figure 4.7c & 4.7d), considering a -0.6 eV shift due to substrate doping change. After the Se-annealing, the decomposition of the W 4f and Se 3d CLs (Figure 4.12a & 4.12b) confirms the suppression of the 1T' phase, with only one remaining doublet at 31.76 eV for the W 4f CL. The Se 3d CL decomposition exhibits three doublets, a first one at 53.92 eV linked to 2H-WSe₂ and a second at 53.22 eV linked to surface GaSe. The third doublet at 54.52 eV is attributed to some excess selenium accumulated at the surface during the cooling down following the annealing process. The reduction of the W 4f (0.76 to 0.57 eV) FWHM after annealing can also be linked to crystal quality improvement. The XPS decomposition of the W 4f and Se 3d CLs (Figure 4.12c & 4.12d) for the 2.9 ML sample (S₄₋₁₅) exhibits similar features with a binding energy shift of 0.63 ± 0.2 eV induced by the substrate doping. Both samples S₄₋₁₂ and S₄₋₁₅ exhibit a Se/W ratio amounts to 1.95 ± 0.02 .

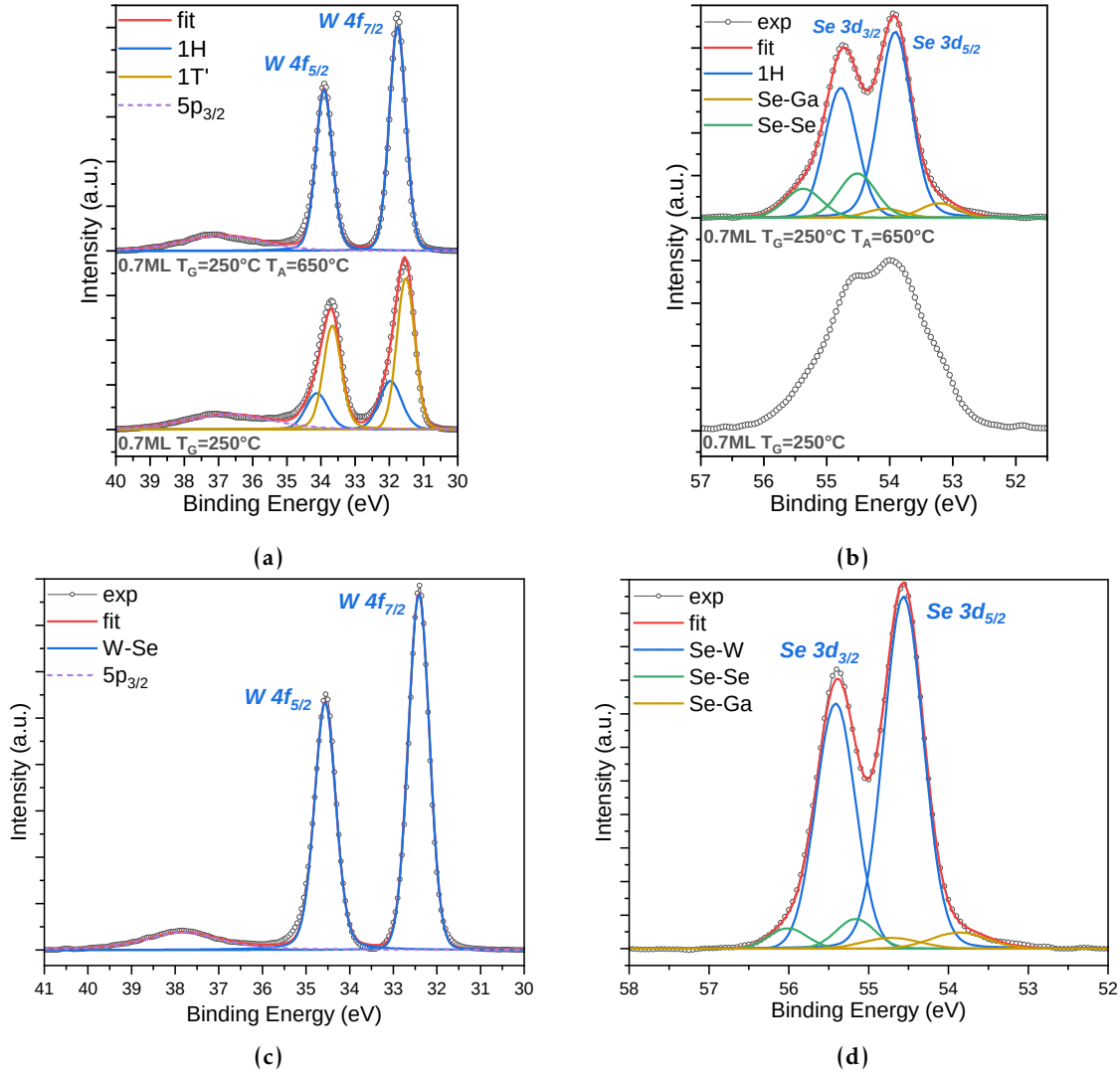


Figure 4.12: Impact of the Se-annealing treatment on W 4f CLs (a) and Se 3d CLs (b) decompositions for a sub-monolayer sample (S_{4-12}) grown on a p-type GaP substrate. Decomposition of (c) W 4f CL and (d) Se 3d CL for a 2.9 ML WSe_2 (S_{4-15}) grown on an n-type GaP substrate after a Se-annealing treatment. The different spectra are recorded with a take-off angle $\theta=25^\circ$.

In addition, UPS measurements performed around the K point before and after annealing on the sub-monolayer sample S_{4-12} (Figure 4.13a) show the suppression of a component near E_F that we link to the $1T'$ phase. The threshold energy measurement in Figure 4.13b indicates a decrease in work function after annealing from 5.32 eV to 5.25 eV, consistent with the VBM energy evolution as the ionization energy E_i remains constant at 5.37 ± 0.05 eV, in good agreement with theoretical estimations ($4.87 \text{ eV} < E_i < 5.61 \text{ eV}$ ^{43, 49, 72}). The UPS analysis of the 2.2 ML WSe_2 grown without Se-annealing treatment (S_{4-2}) and the 2.9 ML WSe_2 annealed (S_{4-15}) show similar trends (Figure 4.13b & 4.13c), with the clear suppression of a component inducing a transition of the $E_F - E_{\text{VBM}}$ value from 0.21 eV to 0.74 eV. In this case, the multilayer stacking is assumed to induce a direct-to-indirect bandgap transition with a VBM migrating from K to Γ , which implies performing UPS at this point.

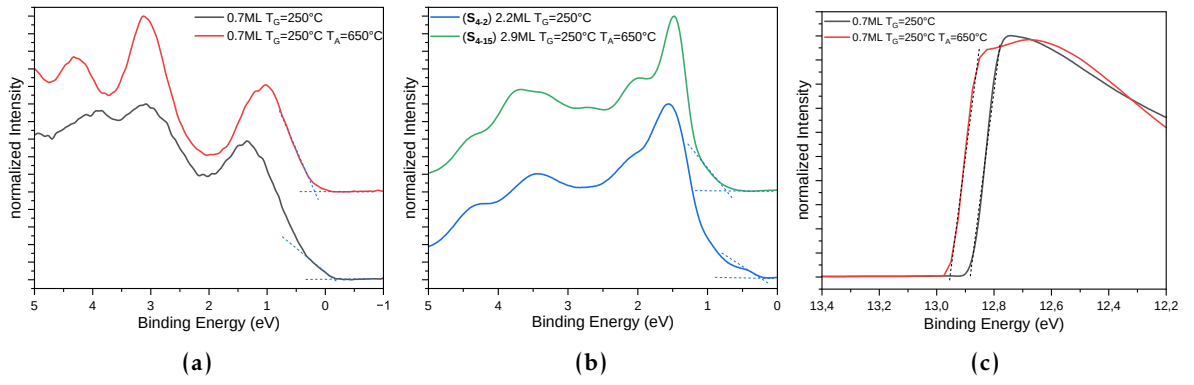


Figure 4.13: UPS measurements, evolution of the VBM energy with the Se-annealing treatment, the thickness and the substrate doping. The spectrum is recorded using a He II radiation (a) on a sub-monolayer grown on p-type GaP (S_{4-12}) around the K point and (b) the associated threshold energy measurement in Γ using a He I radiation and applying a -3 V polarization. (c) UPS measurement using a He I radiation on a 2.2 ML (S_{4-2}) and 2.9 ML (S_{4-15}) grown on n-type GaP in Γ .

Besides, the Raman shift measurements on the annealed 2.9 ML sample (S_{4-15}) presented in Figure 4.14a highlight a 3R/2H mix phase with a strong E_{2g}^1/A_{1g} ratio of 0.87, similar to the one estimated on a 15 ML thick sample grown at 250°C without Se-annealing treatment (S_{4-4}), which stands in good agreement with the STEM images observations of Figure 4.11e. The reduction of the FWHM of both A_{1g} (FWHM $\sim 3 \text{ cm}^{-1}$) and E_{2g}^1 ($\sim 5 \text{ cm}^{-1}$) peaks after annealing suggests once more a crystalline quality improvement.

This is further confirmed by the reduction of the integral breadth of the most intense (110) ($2\theta_{\chi/\varphi}=55.65^\circ$) φ_{WSe_2} peak extracted from grazing incident XRD measurement before (S_{4-7}) and after annealing (S_{4-13}) (Figure 4.14b). Thus, the in-plane angular spread is slightly reduced from $2.87 \pm 0.11^\circ$ to $2.73 \pm 0.06^\circ$. In addition, the Se-annealing treatment have only a slight impact at this temperature on the integral breadth of the $2\theta_{\chi/\varphi(100)}$ peak (Figure 4.11c), while the Williamson-Hall plot in Figure 4.14d shows a clear improvement of the (110), (200) and (300) peak integral breadths. It results in a significant reduction of the slope after annealing from 0.0235 to 0.0152. Since this slope characterizes local micro-strains, we can deduce that the Se-annealing treatment reduces the number of defects or relaxes the WSe_2 layer grown at low temperature. On the other hand, the resulting calculated average grain size amounts to $19 \pm 4 \text{ nm}$ smaller than the $24 \pm 3 \text{ nm}$ value obtained before annealing on S_{4-7} . Therefore, the post-growth treatment has a lower impact on the in-plane disorientation and the average grain size than the increase of T_G up to 450°C or 500°C (Figure 4.10 & Table 4.4).

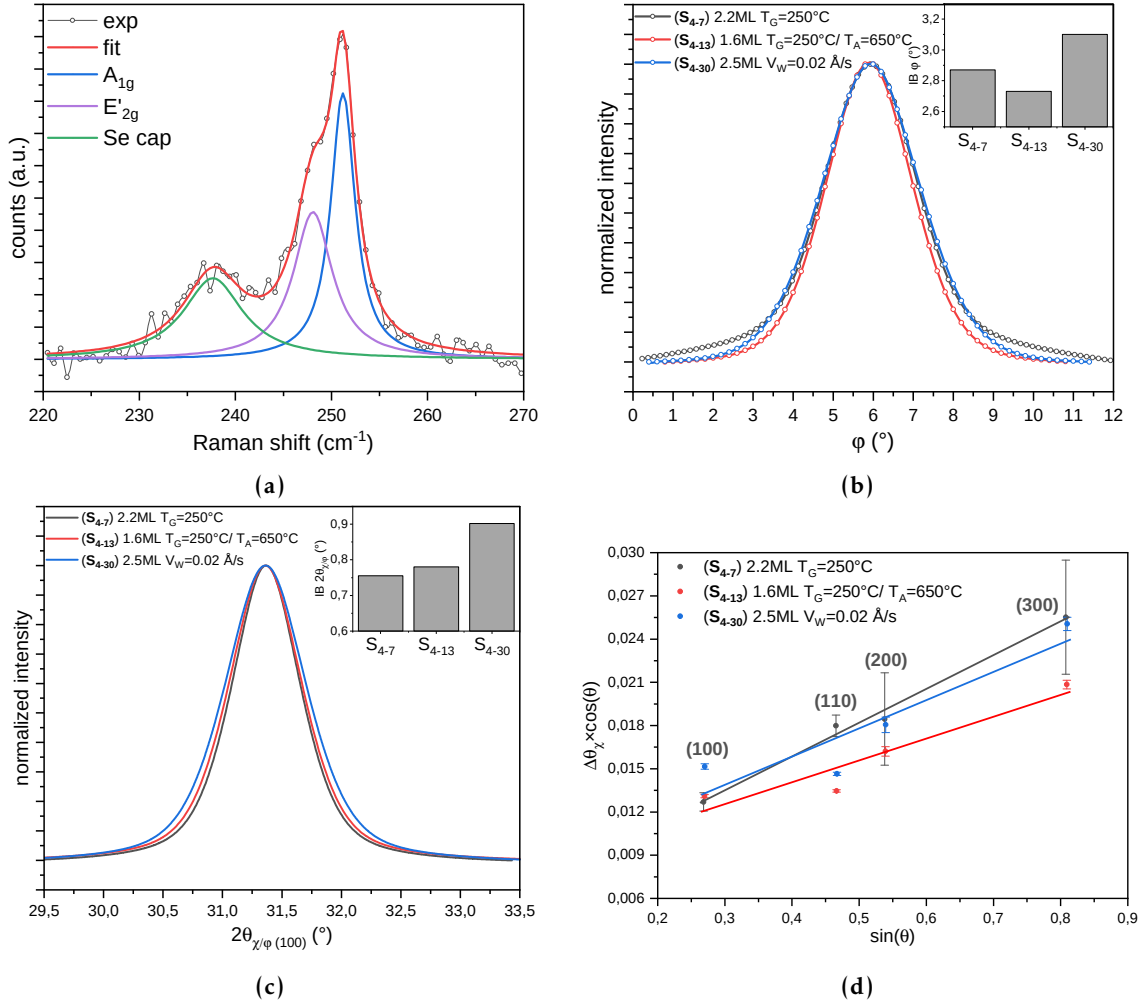


Figure 4.14: (a) Raman shift after Se-annealing treatment of a trilayer grown at $T_G=250^\circ\text{C}$ (S_{4-15}). Influence of the Se-annealing treatment on grain size and in-plane spread angle at low T_G , measured with grazing incident XRD on S_{4-7} and S_{4-13} . Evolution of normalized (b) WSe_2 (110) ϕ and (c) $2\theta_{\chi/\phi(100)}$ with T_A . (d) Graphic plot of the (100), (110), (200) and (300) $2\theta_{\chi/\phi}$ integral breadth using the Williamson-Hall method.

In order to hasten the growth process, the tungsten growth rate was increased up to $0.02 \text{ \AA/s} \pm 15\%$, while maintaining a strong Se overpressure (sample S_{4-30}). The resulted RHEED pattern expresses a degradation of the 2D behaviour with the appearance of spots along the vertical streaks, further suppressed during the annealing step. The XPS and UPS measurements both exhibits the same features at high V_W and low V_W , with a p-type semiconducting behaviour. However, the comparison of the XRD measurements between S_{4-30} and S_{4-13} show an increase of the in-plane disorientation, along with a degradation of the $2\theta_{\chi/\phi(100)}$ integral breadth. It results in a spread angle of 3.10° , a stable 19 nm average grain size and an increased slope from 0.015 to 0.020, which evidences a degradation of the layer quality. In fact, increasing the transition metal growth rate tends to increase the nuclei density and reduce their size during the nucleation step. The use of the lowest possible V_W appears necessary, in good agreement with the Nie *et al.* observations and calculations on graphene substrates³³.

4.2.2 Evolution of WSe₂ thin layers grown at 450°C and 500°C

As presented in section 4.1.3, increasing the growth temperature above 400°C to prevent the 1T' phase formation favours a 3D growth mode characterized by the appearance of spots along the 1×1 RHEED pattern (Figure 4.15a). This results in a rough surface morphology at $T_G=450^\circ\text{C}$ or 500°C , which needs to be improved. Therefore, we propose to apply the same annealing treatment as for $T_G=250^\circ\text{C}$ on 1.2 ML (sample S₄₋₁₆), 2 ML (sample S₄₋₁₇) and 2.8 ML (sample S₄₋₁₈) WSe₂ grown at 450°C .

In this case, the main evolution of the RHEED pattern occurs once the substrate temperature reaches a minimum of 630°C . This sudden improvement might be induced by the cracking of the selenium molecules at the surface, leading to more active species allowing an improvement of the film morphology. Indeed, the selenium cracking temperature has been reported to be in the 350°C - 750°C range, with a dominance of Se₂ species above 600°C ²⁹³. Therefore, the majority of the dots associated to the 3D mode are suppressed, with the exception of the first two ones along the $\langle 11-20 \rangle$ direction (Figure 4.15b), leading to a rather thin 1×1 pattern. The improvement of the RHEED pattern is totally independent of the film thickness, as Figure 4.15b & 4.15c exhibit a similar behaviour for a 1.2 ML (S₄₋₁₆) and a 2.8 ML (S₄₋₁₈) WSe₂ grown at 450°C . The $1 \times 1 \mu\text{m}^2$ AFM image (Figure 4.15d) of an annealed bilayer (S₄₋₁₇) reveals a great improvement of the morphology. The roughness decreases down to 0.3 nm (vs RMS~1.1 nm prior annealing on S₄₋₅), and the appearance of clear GaP atomic steps with a mean height of 0.32 nm and a mean terrace width of 175 nm indicates a rather well defined interface. In view of the phase image which does not exhibits variations, the surface grains are assumed being WSe₂ nuclei.

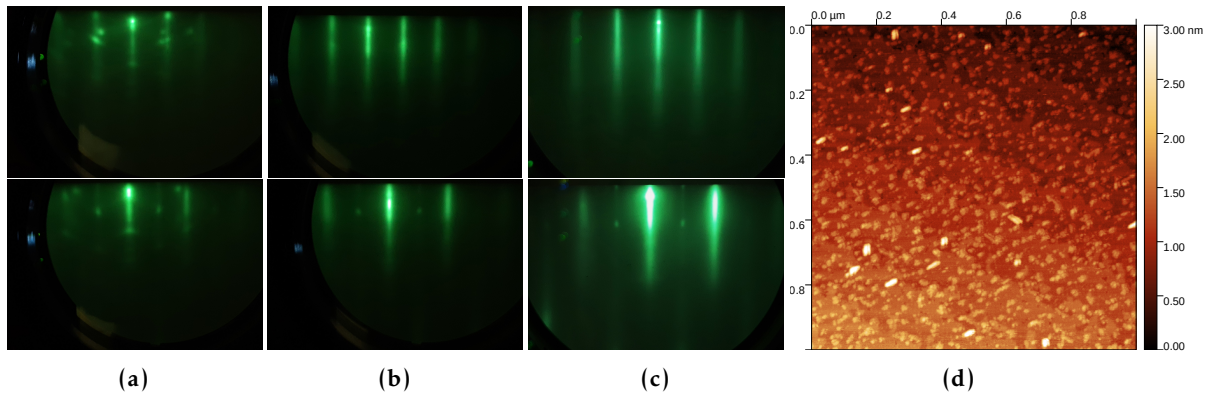


Figure 4.15: 1.2 ML WSe₂ (S₄₋₁₆) RHEED pattern along $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$ (a) before annealing (b) after annealing. (c) 2.8 ML WSe₂ (S₄₋₁₈) RHEED pattern after annealing. (d) $1 \times 1 \mu\text{m}^2$ AFM image of an annealed WSe₂ bilayer (S₄₋₁₇) grown at 450°C .

The quality of the epitaxial layer is further demonstrated by the large STEM HAADF image in Figure 4.16a, highlighting the WSe₂ continuity over the whole surface with a coherence length exceeding 50 nm for sample S₄₋₁₈. It underscores the formation of at least two monolayers with a partial third one. In the same way as for the 1.7 ML layer grown at $T_G=250^\circ\text{C}$ (S₄₋₃), the WSe₂ continuity is not disturbed by the GaP atomic step edges, with a clean van der Waals interface. The upper part of the image reveals that the selenium cap is partly crystallized near the TMDC layer, explaining the presence of a vibration mode peak at 237.7 cm^{-1} in Raman spectroscopy. The zoom-in STEM image in Figure 4.16b demonstrates the local formation of a bi-dimensional 2H phase layer with the alternating herringbones directions over three WSe₂ monolayers. The van der Waals interface shows no evidence of selenium penetration into the substrate and no peculiar degradation due to the annealing step. Combining the RHEED and STEM observations, the epitaxial relationships are $[11-20]_{\text{WSe}_2} // [-110]_{\text{GaP}}$, $[1-100]_{\text{WSe}_2} // [11-2]_{\text{GaP}}$ in-plane

and $[0001]_{\text{WSe}_2} // [-1-1-1]_{\text{GaP}}$ out of plane, with a coincidence lattice with 6 units of GaP matching 7 units of WSe_2 . On the other hand, the associated Raman shift (Figure 4.16c) shows a reduction of the E'_{2g} peak intensity compared to $T_G=250^\circ\text{C}$, with a E'_{2g}/A_{1g} ratio equal to 0.59. If not confirming the total suppression of the 3R phase, it implies an increase of the 2H one after a growth at 450°C followed by a Se-annealing step. For thicker samples (4 ML sample S_{4-19} and 15 ML sample S_{4-20}), the Raman signal looks similar (Figure 4.16d), with a vibration mode ratio remaining at 0.53 ± 0.05 and the FWHM of the A_{1g} and E'_{2g} peaks at $3.2 \pm 0.1 \text{ cm}^{-1}$ and $4.9 \pm 0.1 \text{ cm}^{-1}$, indicating the good crystallinity and stability with thickness. We observe though a slight wavelength shift of the A_{1g} peak of about 0.4 cm^{-1} for thickness exceeding 10 monolayers, in good agreement with previous report on exfoliated samples. In fact, the succession of layers is assumed to induce a lattice stiffening effect, which lead to a slight blue shift of the A_{1g} mode^{294, 295}. The Raman peak FWHMs after annealing a sample grown at 250°C and 450°C are very close, clearly pointing out a similar effect of the Se-treatment on the layer quality.

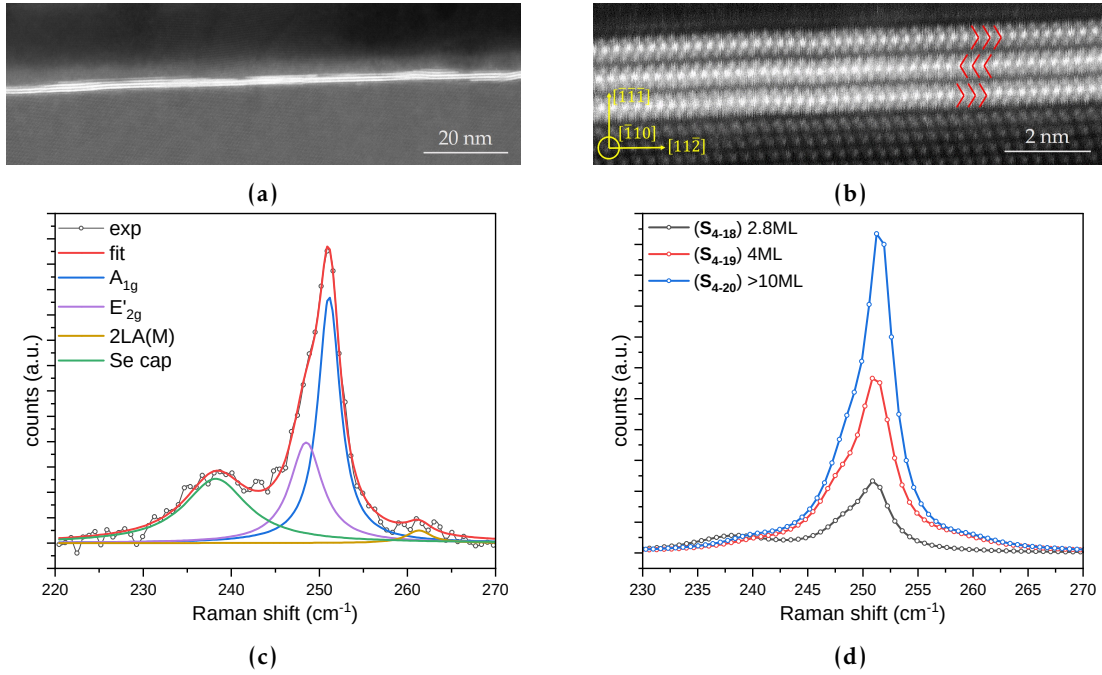


Figure 4.16: (a) large and (b) zoomed HAADF STEM images of 2.8 MLs WSe_2 grown at $T_G=450^\circ\text{C}$ (S_{4-18}) after Se-annealing treatment, (c) the associated Raman shift with its decomposition. (d) Raman shift signal evolution with the thickness of the WSe_2 layer (S_{4-18} , S_{4-19} and S_{4-20}).

This crystal quality improvement is also attested by the clear reduction of the FWHM of the W 4f (0.63 eV before annealing to 0.54 eV after annealing) and Se 3d (0.68 eV to 0.57 eV) CLs (Figure 4.17a & 4.17b), even lower than the ones obtained on an annealed bilayer grown at 250°C . The decomposition of both spectra recorded on an n-type GaP substrate only requires one single doublet at 32.41 eV for W 4f CL and three doublets at 53.86 eV, 54.56 eV and 55.16 eV for Se 3d CL linked to surface GaSe, 2H- WSe_2 and excess Se, respectively. It results in a stoichiometric ratio Se/W equal to 1.91 ± 0.05 , a proportion of surface GaSe and of excess selenium in the Se 3d spectrum of 5% and 6%, respectively, identical to what was obtained on the annealed 2.9 ML grown at 250°C (S_{4-15}). In addition, the UPS spectra of samples S_{4-15} and S_{4-18} (Figure 4.17c & 4.17d) reveal a very similar valence band spectrum and a close work function after the annealing process.

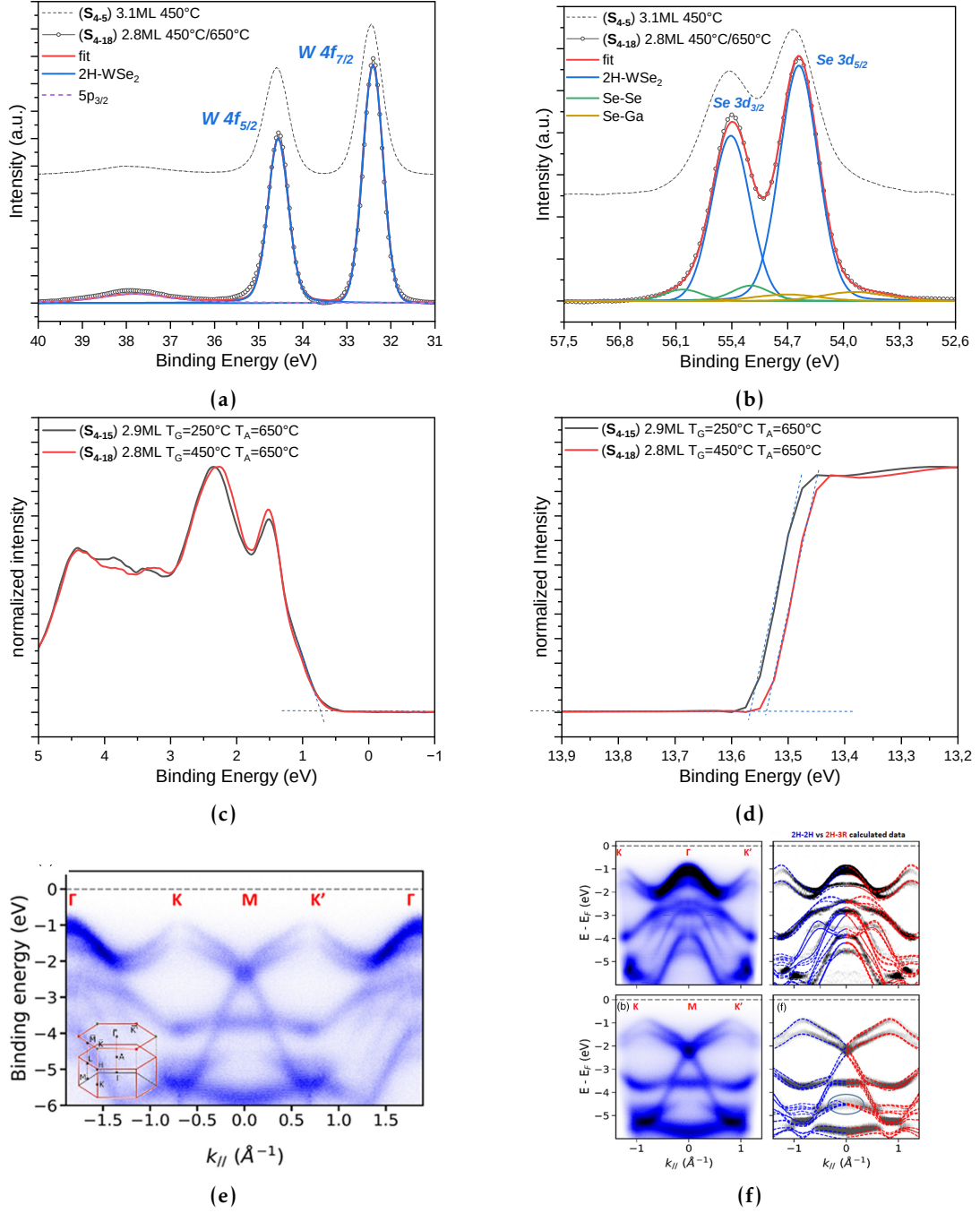


Figure 4.17: (a) W 4f and (b) Se 3d CLs decomposition of a 2.8 ML thick WSe₂ grown at 450°C and Se-annealed on an n-type GaP substrate (S₄₋₁₈). Dashed lines are the W 4f and Se 3d CLs of sample S₄₋₅. The take-off angle is set at $\theta=25^\circ$. (c) UPS measurement comparison around the Γ point for sample S₄₋₁₅ and S₄₋₁₈, recorded using He II radiation. (d) The associated threshold energy measurement using He I. (e) Nano-ARPES measurements with $h\nu=96$ eV and $T=70$ K of the electronic structure of S₄₋₁₈ along the Γ KMK' high-symmetry directions. The Fermi level position is located at the zero of the binding energy, marked by a grey dotted line. (f) Comparison of the band structure with the DFT data from 2H-2H and 2H-3R stacking. On the left, ARPES measurement of the sample S₄₋₁₈ structure along K Γ K' and KMK'. On the right, the calculated band structure overlaid on the second derivative of the raw scans. The simulation is performed using a trilayer relaxed structure with a lattice parameter of 3.26 Å and an interlayer vacuum of 15 Å. Extracted from ²⁹⁶.

More precisely, ARPES measurements performed by Mahmoudi et *al.*²⁹⁶ on the annealed 2.8 ML grown at 450°C (S₄₋₁₈) highlight a VBM located at 0.8 eV below the Fermi level (Figure 4.17e) in good agreement with the UPS measurements, which exhibit an $E_F - E_{VBM}$ value of 0.72 eV and a work function of 4.65 ± 0.01 eV. By superposing the experimental data with the k - E maps of the calculated electronic band structure using **Heyd Scuseria Ernzerhof (HSE)** functionals for the KΓK' and KMK' high-symmetry direction of the Brillouin zone, Mahmoudi et *al.* have successfully identified the stacking order of the sample. Indeed, they evidenced a slight difference between the two more stable configurations 2H-2H and 2H-3R at the M point (around -4.5 eV), where the experimental data match better with the calculated 2H-2H stacking (Figure 4.17f). Last, the large band splitting in the uppermost WSe₂ valence band at the K point is quantified using an energy distribution curve, resulting in a spin orbit coupling of 520 ± 10 meV, close to the values extracted from exfoliated WSe₂ monolayers²⁹⁷.

Besides, the application of the Se annealing treatment on 2.5 ML samples grown at 450°C (S₄₋₂₁) shows promising results in improving the in-plane orientation of the layer, as the in-plane angular spread measured by XRD (Figure 4.18a) is reduced from 1.87° down to 1.53°, while the alignment of the φ_{WSe_2} peaks with the substrate ones is improved down to 0.13°. This trend is reinforced for a 2 ML growth at $T_G=500^\circ\text{C}$ (sample S₄₋₂₂), with a reduction of the in-plane spread angle from 1.51° down to 1.34° while the evolution of the RHEED pattern, the W 4f and Se 3d CLs and UPS spectrum after the annealing treatment are identical for $T_G=450^\circ\text{C}$ and $T_G=500^\circ\text{C}$. On the other hand, the annealing leads to a clear reduction of the $2\theta_{\chi/\varphi(100)}$ for $T_G=450^\circ\text{C}$ (Figure 4.18b), but appears to have a rather limited effect for $T_G=500^\circ\text{C}$ (Figure 4.18c). The comparison of the Williamson-Hall plots for samples S₄₋₈, S₄₋₆, S₄₋₂₁ and S₄₋₂₂ in Figure 4.18d evidences the improvement of the crystal quality after annealing. At 450°C and 500°C, we notice a decrease of the slope and hence of the microstrain, the reduction being larger at 500°C. Regarding the average grain size, it is clearly enlarged at 450°C, but remains nearly constant at 500°C. In a similar way to low T_G , a larger tungsten growth rate up to 0.02 Å/s (sample S₄₋₃₁) induces a rather strong degradation of the spread angle up to 2.26° (Figure 4.18a), as well as the broadening of the $2\theta_{\chi/\varphi(100)}$ peak (Figure 4.18b), which leads to an increase of the Williamson-Hall slope up to 0.022 (Figure 4.18d).

sample	$\varphi_{(110)} \text{ IB } (^\circ)$	(100) IB	Grain size Scherrer (nm)	Grain size W-H (nm)	strain (Cε)
2.2 ML 250°C (S ₄₋₇)	2.87 ± 0.11	0.755°	11.3 ± 0.1	23.9 ± 3.3	0.0235 ± 0.0016
1.6 ML 250°C/650°C (S ₄₋₁₃)	2.73 ± 0.06	0.780°	10.9 ± 0.1	19.3 ± 4.9	0.0152 ± 0.0036
2.5 ML 0.02 Å/s (S ₄₋₃₀)	3.10 ± 0.04	0.902°	9.4 ± 0.2	19.3 ± 8.3	0.0196 ± 0.0062
2 ML 450°C (S ₄₋₈)	1.87 ± 0.03	0.704°	12.1 ± 0.1	21.2 ± 6.8	0.0123 ± 0.0042
2.5 ML 450°C/650°C (S ₄₋₂₁)	1.53 ± 0.02	0.459°	18.6 ± 0.1	35.7 ± 15.3	0.0095 ± 0.0033
2.1 ML 0.02 Å/s (S ₄₋₃₁)	2.26 ± 0.06	0.785°	10.8 ± 0.2	28.2 ± 19.2	0.0224 ± 0.0067
1.9 ML 500°C (S ₄₋₆)	1.51 ± 0.03	0.533°	16.0 ± 0.1	26.4 ± 5.9	0.0098 ± 0.0023
2 ML 500°C/650°C (S ₄₋₂₂)	1.34 ± 0.02	0.444°	19.2 ± 0.2	24.6 ± 0.9	0.0040 ± 0.0004

Table 4.4: In-plane spread angle, average grain size and local strain evolution with T_G and T_A based on XRD measurements.

Table 4.4 summarizes the effect of the post-growth treatment over the explored temperature range, evidencing the systematic improvement of both in-plane spread angle and relaxation. We point out the rather strong uncertainty induced by the linear fit through only four experimental points within the Williamson-Hall method, which explains the large error bars for the average grain size.

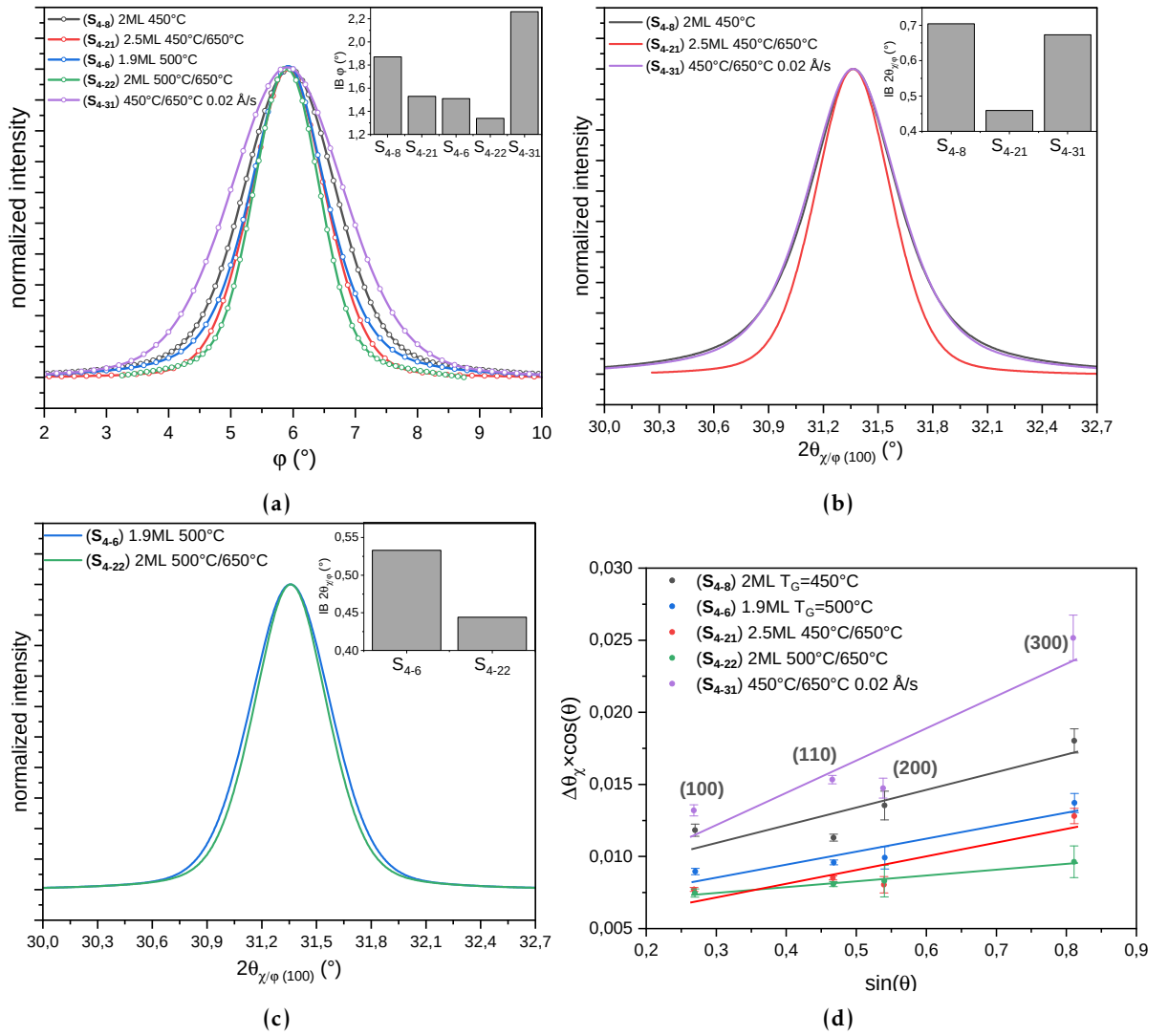


Figure 4.18: Influence of the Se-annealing treatment on grain size and in-plane spread angle at $T_G=450^\circ\text{C}$ and 500°C , measured with grazing incident XRD. **(a)** Evolution of normalized WSe_2 ϕ with T_A . Evolution of the $2\theta_{\chi/\phi(100)}$ peak with T_A for a growth at **(b)** $T_G=450^\circ\text{C}$ and **(c)** at $T_G=500^\circ\text{C}$. **(d)** Graphic plot of the (110), (100), (200) and (300) $2\theta_{\chi/\phi}$ integral breadth using the Williamson-Hall method. In purple the XRD measurements on sample S₄₋₃₁ grown with a $V_W=0.02 \text{ Å/s}$.

4.2.3 Evolution of WSe_2 thin layers grown above 500°C

As the metallic tungsten content revealed by XPS was rather low at $T_G=550^\circ\text{C}$ (S₄₋₉), we have tried to anneal such sample under selenium (2.2 ML sample S₄₋₂₃, 2.7 ML sample S₄₋₂₄). As expected, the RHEED pattern (Figure 4.19a) is strongly improved with a thin 1×1 reconstruction, combined with a reduction of the in-plane spread angle to 1.20° . However, the 3D morphology is not totally suppressed with well-defined spots along the vertical streaks. In fact, the AFM image of sample S₄₋₂₃ (Figure 4.19b) shows a slightly rougher surface than at lower T_G (RMS~0.4 nm) due to an increase of the surface domain density. The atomic steps of GaP are impossible to observe, while Raman spectroscopy on sample S₄₋₂₄ indicates an increase in crystal quality with a reduction in A_{1g} and E_{2g}^1 peaks FWHM (Figure 4.19c, 2.5 cm^{-1} and 4.1 cm^{-1} , respectively). The ratio between the two vibration mode intensities remains identical to the one observed at $T_G=450^\circ\text{C}$. Therefore, we assume that the simple combination of a growth step followed by a Se-annealing treatment provides a stable 2H/3R mix phase with the dominance of 2H

when T_G exceeds 450°C . However, the decomposition of W 4f CL (Figure 4.19d) points out a remaining small amount of metallic tungsten ($\sim 2\%$), resulting in a selenium poor layer with an intensity ratio Se/W equal to 1.83. Moreover, a new component in the P 2p CL appears at 128.9 eV (Figure 4.19e), that we associate to P-W bonds. This implies that the van der Waals interface might be degraded due to the interaction of the transition metal with the substrate. A similar feature has also been observed during the growth of TaSe_2 on GaP when T_G exceeds 550°C , yet with a stronger relative intensity.

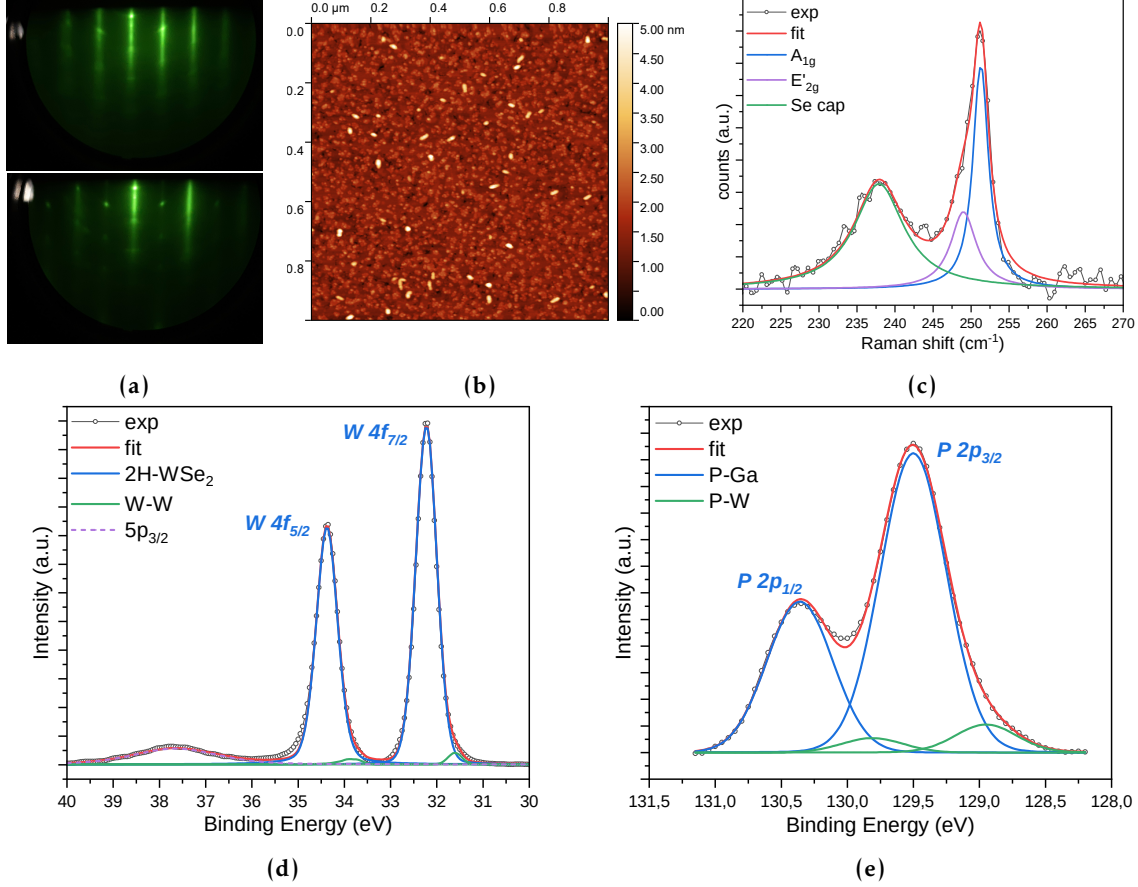


Figure 4.19: Evolution of the morphology and the structure of an annealed WSe_2 (S_{4-23} and S_{4-24}) grown at 550°C . (a) RHEED pattern along $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$, (b) the associated $1 \times 1\ \mu\text{m}^2$ AFM image and (c) the Raman shift signal with its decomposition. XPS W 4f (d) and P 2p (e) CLs decompositions for a 2.2 ML WSe_2 grown on an n-type GaP substrate, with a take-off angle $\theta=25^\circ$.

At higher temperature, we observe a limitation in spread angle reduction with a sudden increase up to 1.61° of the integral breadth when reaching 600°C , combined with a strong increase in metallic tungsten in W 4f (Figure 4.20a & 4.20b). In addition, we observe a non-negligible increase of the P-W bond intensity at high T_G (Figure 4.20c), especially characterized by a reduction of the depression between the $2p_{3/2}$ and $2p_{1/2}$ components. Thus, increasing T_G up to 650°C (S_{4-10}) evidences the dominance of the metal formation on the TMDC, resulting in a clear metallic behaviour in UPS (Figure 4.20d) with $E_\text{F}-E_\text{VBM}=0\text{ eV}$, even after a Se-annealing. The progressive formation of tungsten and the degradation of the interface induce a deformation of the band structure in Γ in addition of a $E_\text{F}-E_\text{VBM}$ value decrease for a n-type GaP substrate, from 0.5 eV at 500°C , to 0.45 eV at 550°C and 0.17 eV at 600°C (sample S_{4-25}). This behaviour clearly evidences the inefficiency of the Se-annealing treatment to sufficiently improve the film quality when T_G exceeds 500°C , confirming an optimum growth temperature at $T_\text{G}=450^\circ\text{C}$ or 500°C .

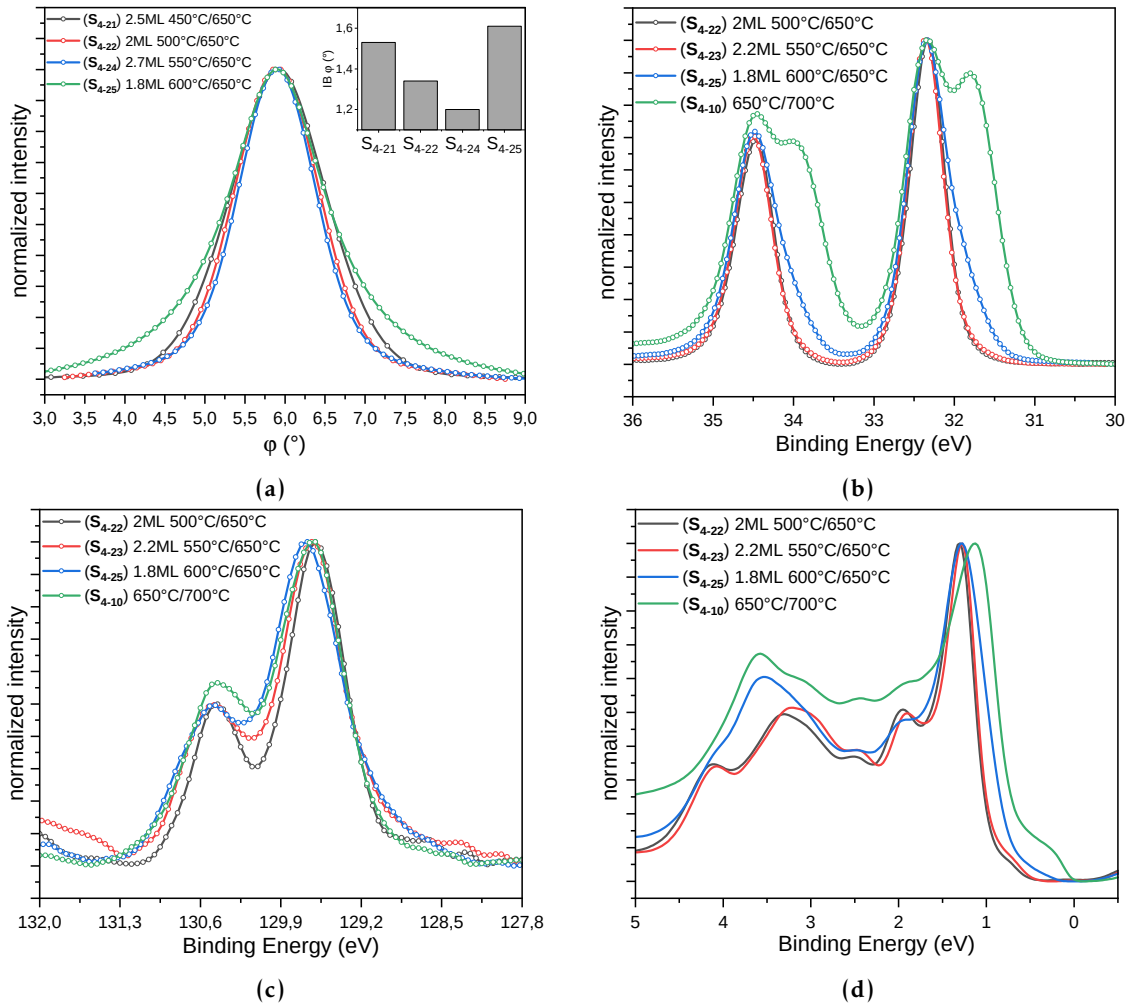


Figure 4.20: (a) evolution of the in-plane spread angle at high T_G after annealing. Normalized W 4f (b) and P 2p (c) CLs evolution with T_G . (d) The associated UPS spectrum captured with He I. Each sample has been annealed under Se flux. The different spectrum associated to the growth at 600°C are manually shifted by +0.2 eV due to clear issues in calibration.

4.2.4 Improvement of the annealing sequence at 450°C and 500°C

Yet, the duration of the Se-annealing step has not been questioned in this work, with a temperature ramp set at 20°C/min and a common stabilization at 650°C for a few minutes. As the results in average grain size and spread angle obtained by Vergnaud *et al.* on mica²² remain better than those obtained on S₄₋₂₁ and S₄₋₂₂, we extend the annealing time at 650°C, looking for a significant improvement. On sample S₄₋₁₆, a 1.2 ML WSe₂ grown at 450°C, a standard stabilization of 3 minutes at 650°C leads to the now well-known stable WSe₂ 1 × 1 RHEED pattern with the addition of two spots along the <11-20> direction (Figure 4.21a). By increasing the stabilization time up to 60 minutes, we observe a clear reduction of the spot intensity along <11-20> and a sharpening of the different vertical streaks (Figure 4.21b & 4.21c), pointing out a clear enhancement of the morphology. On the opposite, the XPS and UPS measurements are similar for the two durations, while XRD in Figure 4.21d and 4.21e points out a slight increase in spread angle from 1.53° to 1.66° and an average grain size of 25 nm, calculated with the Williamson-Hall method. Considering the small thickness of the analysed sample, we assume that the Se-annealing stabilization time does not play a significant role in the WSe₂ phase formation nor in the in-plane orientation and the average grain size.

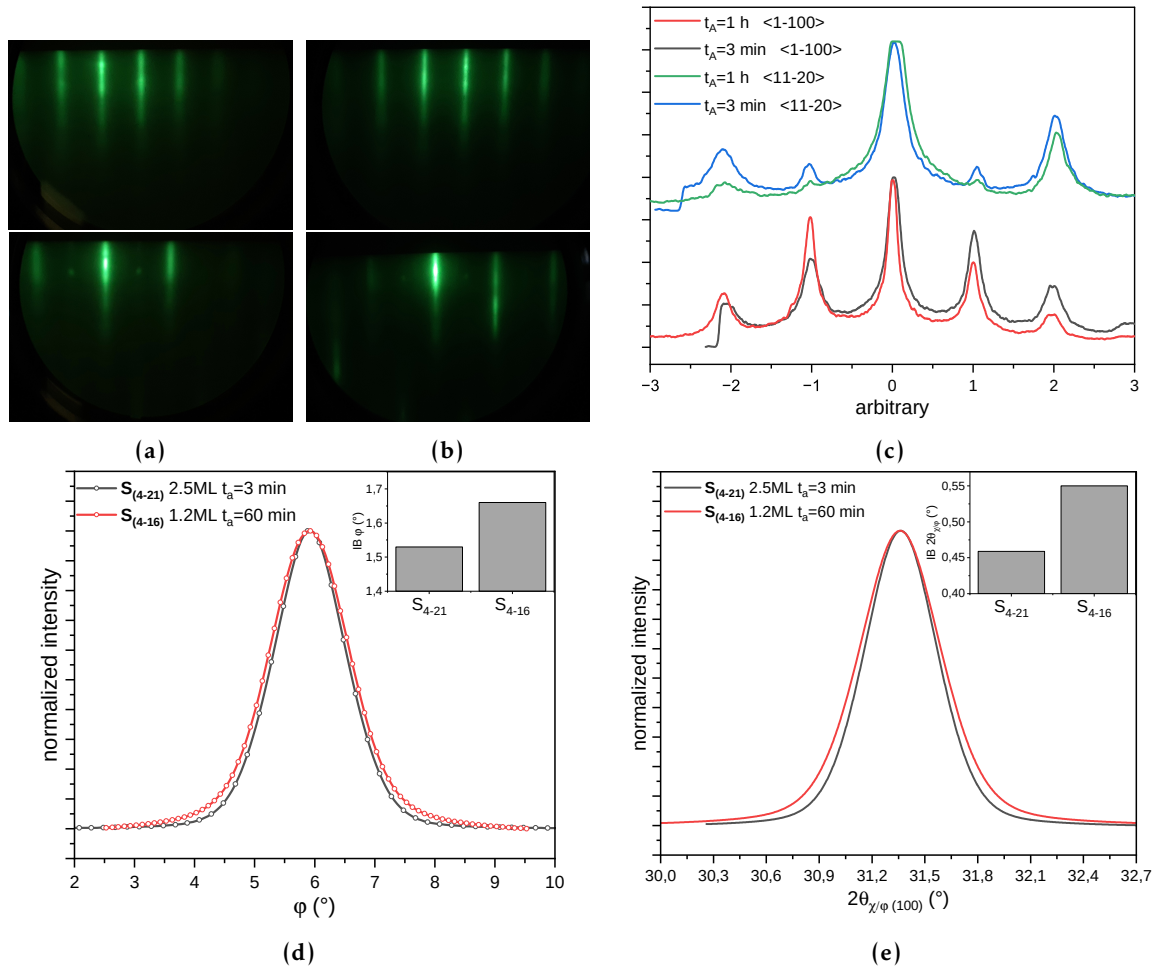


Figure 4.21: Impact of the Se annealing step time on a 1.2 ML grown at 450°C (S_{4-16}). RHEED pattern along $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$ (a) after 3 minutes and (b) after 1 hour of annealing, with (c) the associated and normalized RHEED intensity profiles. Evolution of normalized (d) WSe_2 $\varphi(110)$ and (e) $2\theta_{\chi/\varphi(100)}$ with the annealing time.

Moreover, even if the 60 minutes long annealing step reduces considerably the intensity of the additional spots in RHEED, it appears quite difficult to totally suppress them after a long growth step. As the 3D behaviour at 450°C or 500°C appears at the beginning of the second layer (Figure 4.22a), we propose to interrupt the growth at the completion of the first layer and apply an intermediate annealing step at 650°C with a temperature ramp of 20°C/min and a stabilization of 3 minutes. The sample temperature is then decreased under Se down to T_G and the growth is resumed before applying a final Se-annealing. As expected, the 3D behaviour is considerably decreased under the action of the intermediate annealing step (Figure 4.22b). However, the two spots along $\langle 11-20 \rangle$ are not suppressed and will remain during the whole process. When resuming the growth, we observe a clear improvement of the morphology during the second monolayer with a weaker 3D behaviour (Figure 4.22c). This peculiar evolution could be induced by the formation of a van der Waals interface instead of a quasi-van der Waals one, reducing the potential effect of surface defects. The final annealing of the bilayer with a 3 minutes stabilization at 650°C under selenium (Figure 4.22d) suppresses the majority of the visible spots with the exception of the two first ones. Their relative intensity is close to what was previously observed on S_{4-16} after a 1 hour annealing, which should indicate a very good surface morphology.

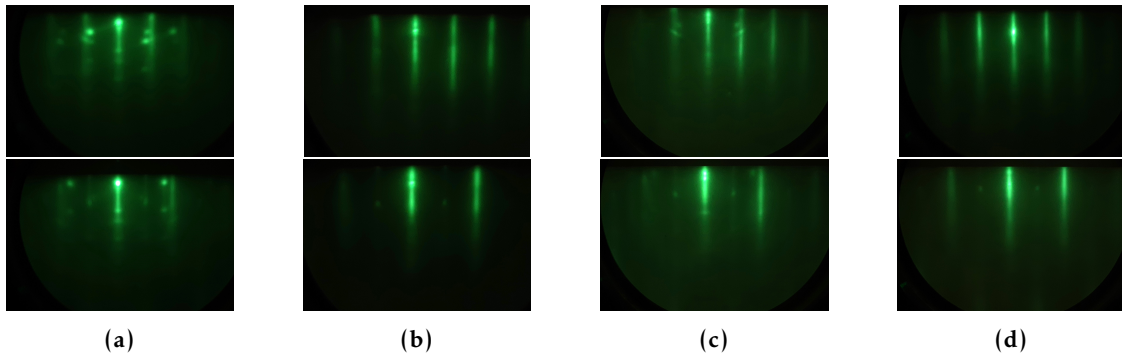


Figure 4.22: Evolution of a bilayer RHEED pattern along $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$ during a growth at 500°C. The different images are captured (a) after the growth of a nominal bilayer, (b) after an intermediate annealing step with a 3 minutes stabilization, (c) at the end of the nominal 4 ML growth and (d) at the end of the final Se-annealing treatment.

When comparing the XRD measurements after this new growth sequence, we directly observe a strong decrease of the spread angle for 1.9 ML grown at 500°C (sample S_{4-26}) from 1.34° to 1.14° when applying a 2-step annealing (Figure 4.23a), which is so far one of the best reported values for a TMDC layer grown on monocrystalline 3D substrate. As presented in Table 4.5 and Figure 4.23b, the new growth sequence also induces a reduction of the $2\theta_{\chi/\varphi(100)}$ peak integral breadth, which leads to an increase in average grain size up to 42 nm coupled to a slight increase of the local strain, close to the value obtained before annealing. In addition, the integral breadth of the peak $2\theta_{\chi/\varphi(100)}$ is rather close to the values obtained on mica with an optimum $\beta_{(100)2\theta_{\chi/\varphi}}$ equal to 0.37° against 0.33°, making this S_{4-26} sample one of the best results in crystal quality for TMDCs grown on 3D substrates. In addition, STM images (Figure 4.23c) captured on a 2 ML grown at 450°C with the new annealing sequence (sample S_{4-27}) evidence the clear formation of ~50 nm wide grains with a somewhat circular shape, confirming our previous XRD measurements, while not breaking at the GaP atomic edges.

sample	$\varphi_{(110)}$ IB (°)	(100) IB	Grain size Scherrer (nm)	Grain size W-H (nm)	strain (Cε)
2 ML 450°C (S_{4-8})	1.87 ± 0.03	0.704°	12.1 ± 0.1	21.2 ± 6.8	0.0123 ± 0.0042
2.5 ML 450°C/650°C (S_{4-21})	1.53 ± 0.02	0.459°	18.6 ± 0.1	35.7 ± 15.3	0.0095 ± 0.0033
1.9 ML 500°C (S_{4-6})	1.51 ± 0.03	0.533°	16.0 ± 0.1	26.4 ± 5.9	0.0098 ± 0.0023
2 ML 500°C/650°C (S_{4-22})	1.34 ± 0.02	0.444°	19.2 ± 0.2	24.6 ± 0.9	0.0040 ± 0.0004
1.9 ML 500°C/650°C IA* (S_{4-26})	1.14 ± 0.01	0.374°	22.8 ± 0.3	42.3 ± 13.3	0.0078 ± 0.0002

Table 4.5: Integral breadth (IB) of different $2\theta_{\chi/\varphi}$ scans, the calculated grain size and the in-plane spread angle measured for WSe₂ layers grown at 450°C and 500°C with different annealing sequences. *IA: Intermediate Annealing.

Beyond the grain size and disorientation improvement, this new annealing sequence also provides some benefits in structural features. Indeed, the Raman shift measurement (Figure 4.23d) of a 2.4 ML thick sample grown at 500°C (S_{4-28}) shows a stronger dominance of the A_{1g} vibration mode over E_{2g}^1 , with a E_{2g}^1/A_{1g} intensity ratio reduced down to 0.38. This leads us to assume the formation of a 100% pure 2H phase sample with a rather high crystal quality, as XPS measurements exhibit single and thin doublets in W 4f and Se 3d CLs and a Se/W intensity ratio of 1.93. In addition, there is no presence of additional P-W bonds in P 2p, confirming the good quality of the van der Waals interface. UPS measurements indicate a rather strong p-type behaviour of the sample, with the VBM located at 0.5 eV below the Fermi level and a work function of 4.8 eV (Figure 4.23e).

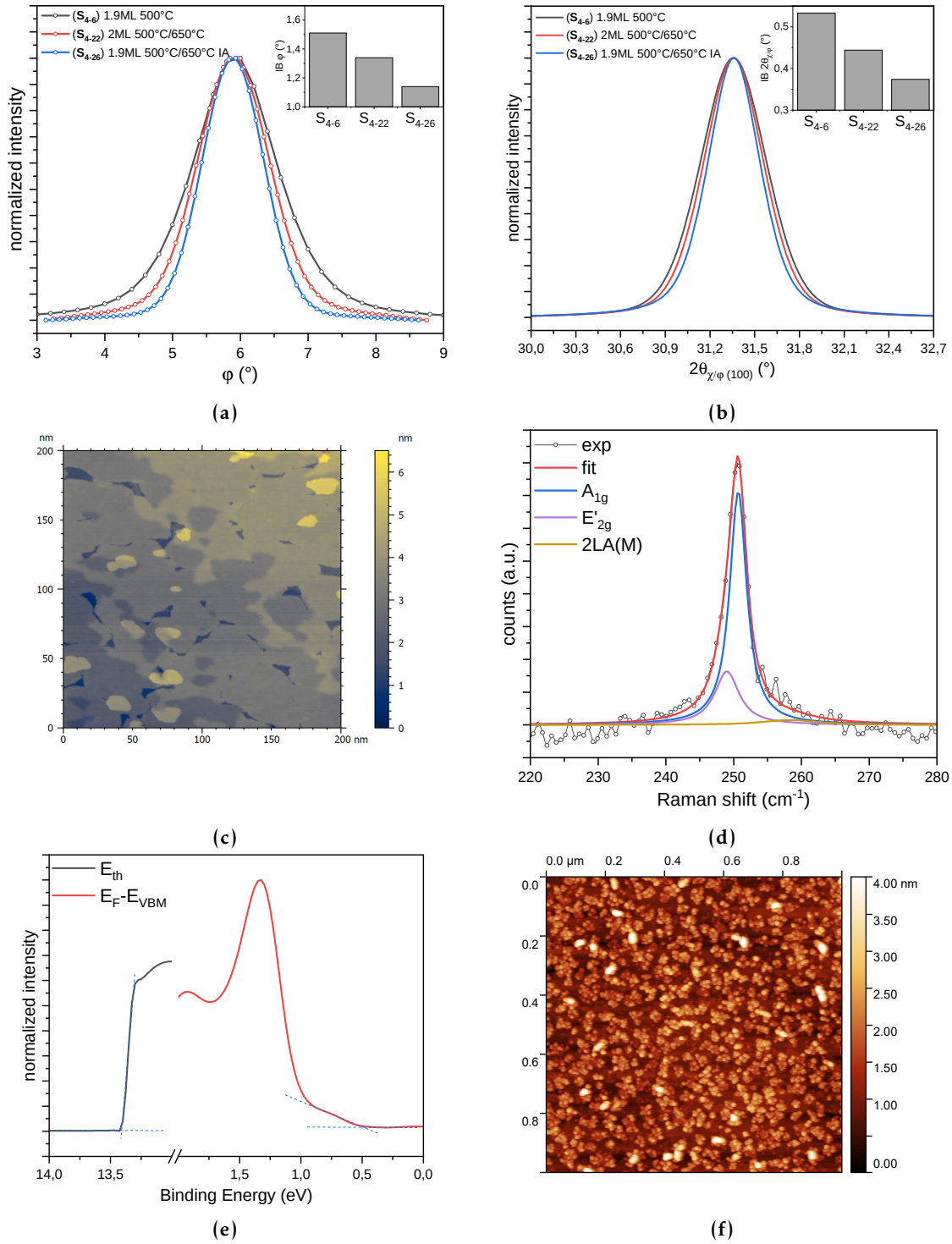


Figure 4.23: impact of an intermediate annealing step on (a) the in-plane angular spread and (b) the average grain size for layers grown at 500°C. (c) STM image of sample S_{4-27a} . (d) The Raman shift measurement on a sample S_{4-28} , (e) the associated UPS measurements and (f) the associated $1 \times 1 \mu\text{m}^2$ AFM image.

On the other hand, this new growth sequence has a rather strong effect on the surface morphology. Considering the sample S_{4-28} , the AFM image in Figure 4.23f shows 50 to 60 nm large surface domains defined as an agglomeration of smaller domains (~ 10 nm), which induces an increase of the roughness up to 0.6 nm. The AFM analysis indicates only a small change in phase between the background and the domains, implying a close chemical nature of the two environments, which leads us to confirm the WSe_2 nature of the surface grains. However, this surface roughness is not suitable for heterostructure development. Therefore, we will rather select a growth sequence with T_G equal to 450°C for the band structure analysis and the $HfSe_2/WSe_2/GaP$ heterostructure growth.

4.2.5 Discussion on the effect of the WSe_2 layer thickness

n°	substrate	thickness	T_G/T_A
S_{4-22}	$n^- GaP$	2 ML	500°C/650°C
S_{4-26}	$n^- GaP$	1.9 ML	500°C/650°C IA
S_{4-27a}	$n^+ GaP$	2 ML	450°C/650°C IA
S_{4-27b}	semi-insulating	2 ML	450°C/650°C IA
S_{4-28}	$n^- GaP$	2.4 ML	500°C/650°C IA
S_{4-29}	semi-insulating	3.9 ML	500°C/650°C IA

Table 4.6: sample summary. *IA stands for Intermediate Annealing.*

Up to now, the presented results have shown a somewhat monotonous behaviour in phase formation: the metastable 1T' is mixed with 3R at 250°C, suppressed with the annealing sequence, which also favours the formation of a mix between the 3R and 2H phases. Increasing T_G also tends to reduce the amount of 3R in the layer with the purest 2H sample obtained at 500°C when applying a two-step annealing sequence (Figure 4.23d). However, it seems that the film thickness also plays a role in the resulting phase formed and therefore complicate this simple picture of the evolution with the temperature. Indeed, we observed a strong 2H-3R mix phase in 2 ML thick samples S_{4-22} and S_{4-27a} , as exhibited by STEM images in Figure 4.24a and 4.24b. As those two samples have been grown at 500°C with a unique annealing step and at 450°C with an intermediate annealing sequence, respectively, this unexpected 2H-3R mix phase is not linked to the temperature. In addition, the Raman shift decomposition of sample S_{4-26} (1.9 ML, $T_G=500^\circ C$, 2-step annealing sequence) shows a rather strong E_{2g}^1 component (Figure 4.24c), also indicating a strong 2H-3R mix phase. Moreover, the comparison of Raman signals for samples grown at 500°C with a two-step annealing sequence for different thicknesses (Figure 4.24d) highlights an increase in 2H dominance as soon as exceeding the bilayer regime, with E_{2g}^1/A_{1g} ratios decreasing from 0.73 to 0.38. At 250°C, the annealed WSe_2 layer exhibits a strong 2H/3R mix phase regardless of the thickness (S_{4-15}), while tending to form pure 2H at 450°C and 500°C when exceeding 2 monolayers. Based on these observations, we assume that the formation of a pure 2H layer would be influenced by both temperature and thickness, with a minimum thickness of 3 monolayers.

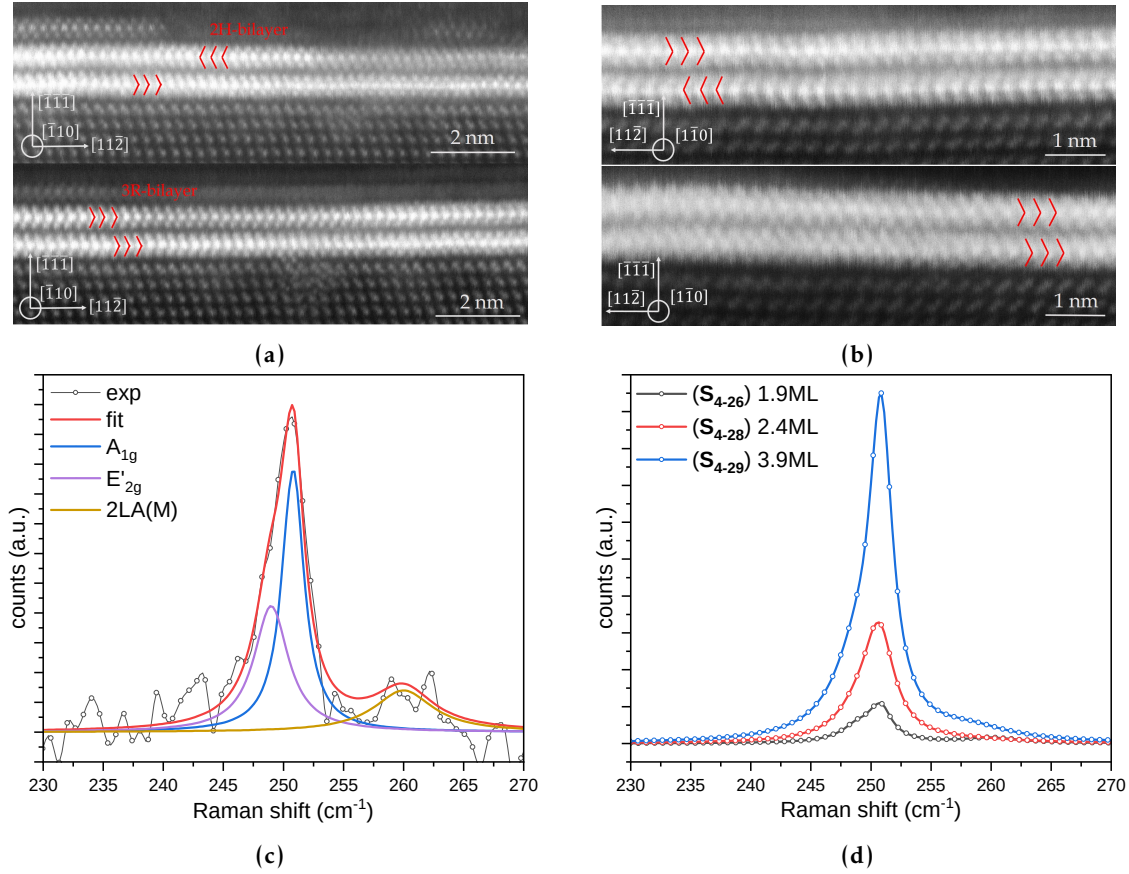


Figure 4.24: impact of the film thickness. HAADF STEM images of (a) an annealed 2 ML grown at $T_G=500^\circ\text{C}$ (S_{4-22}) and (b) a 2 ML grown at $T_G=450^\circ\text{C}$ with a two-step annealing treatment (S_{4-27a}). (c) The Raman shift decomposition for a 1.9 ML grown at $T_G=500^\circ\text{C}$ with a two-step annealing sequence (S_{4-26}). (d) The evolution of the Raman shift signal with the thickness (1.9 ML S_{4-26} , 2.4 ML S_{4-28} and 3.9 ML S_{4-29}) of the sample grown at 500°C with a two-step annealing sequence.

To summarize, we have presented the evolution of the WSe_2 layer morphology and structure with the growth temperature and the followed annealing treatment. We show that a low growth temperature promotes the formation of the $1\text{T}'$ phase coexisting with a more stable phase. In the bilayer regime, we emphasize the simultaneous formation of the $1\text{T}'$ within a dominant 3R stacking. Higher growth temperature induces the suppression of the metastable phase, yet exhibiting a 3D growth mode, which ultimately would lead to the formation of tungsten clusters when exceeding 500°C . We demonstrate the efficiency of the application of a subsequent annealing under selenium flux at 650°C , highlighting the suppression of the $1\text{T}'$ phase at low growth temperature and with the significant reduction of the roughness and the suppression of the 3D morphology at 450°C and 500°C . STEM images and Raman spectroscopy have revealed the formation of a $2\text{H}/3\text{R}$ mix phase at 250°C and at $450^\circ\text{C}/500^\circ\text{C}$ in the sub-bilayer regime, while promoting a pure 2H phase formation at 450°C and 500°C when the thickness exceeds 2 monolayers, as confirmed by ARPES measurements. We highlight the strong impact of the annealing step on the in-plane disorientation and/or the average grain size measured with XRD. The application of a two-step annealing sequence induces a significant increase in grain size up to 42 nm and a stronger decrease of the disorientation down to 1.14° , evidenced by XRD and STM measurements. XPS measurements show that Se-annealing does not prevent the formation of metallic tungsten clusters when increasing T_G above 500°C , nor the appearance of a P-W bond in P 2p CLs.

4.3 Band structure for an optimized layer

In the following section, we are investigating the band structure of WSe₂ grown on GaP(111)_B after considering all the various improvements of the growth and annealing sequence demonstrated in the previous section. We are focusing on two main measurements: STS, which allows us to estimate a bandgap energy value, and XPS/UPS measurements performed in order to define the valence band discontinuity, the work function and the energy of the VBM.

We discuss the evolution of the band structure of WSe₂ grown on GaP(111)_B with the temperature conditions, the thickness and the substrate doping type. We exclude growth conditions exhibiting the 1T' phase, metallic clusters and high roughness. Therefore, we focus on studying samples grown at 250°C, 450°C and 500°C and further annealed. We calculate the valence band discontinuity (ΔE_V), measure the work function (Φ) and the energy of the VBM, and finally draw the band alignment assuming a GaP bandgap and an electron affinity of 2.26 eV and 3.8 eV, respectively²⁹⁸.

The valence band discontinuity ΔE_V is extracted using the Waldrop method^{299, 300} which stands from the following equation:

$$\Delta E_V = \Delta E_{CL} + (E_{P\ 2p}^{GaP} - E_V^{GaP}) - (E_{W\ 4f}^{WSe_2/GaP} - E_V^{WSe_2/GaP})$$

On a deoxidized GaP(111)_B substrate, we measure the binding energy of the P 2p CL $E_{P\ 2p}^{GaP}$ and the energy of the top of the valence band E_V^{GaP} by XPS at $\theta=75^\circ$ in such a way that $(E_{P\ 2p}^{GaP} - E_V^{GaP})=128.00\pm0.05$ eV (Figure 4.25a). In the same way, we get $(E_{W\ 4f}^{WSe_2/GaP} - E_V^{WSe_2/GaP})=31.71\pm0.05$ eV recorded on a thick WSe₂ (~15 ML) grown at 450°C and Se-annealed on a GaP(111)_B-Se substrate (Figure 4.25b). In complement, the ΔE_{CL} value is extracted by measuring the binding energy difference between W 4f and P 2p CLs on the analysed heterostructure with a take-off angle $\theta=25^\circ$ (Figure 4.25c).

In the case of a WSe₂ growth on a p-type GaP(111)_B substrate, we estimate an extracted ΔE_{CL} value of -97.02 ± 0.05 eV, inducing a band offset of $\Delta E_V=-0.73 \pm 0.1$ eV. In comparison, the ΔE_{CL} value of a n-type GaP(111)_B/WSe₂ heterostructure is slightly increased up to -97.23 ± 0.05 eV, resulting in a larger band offset of $\Delta E_V=-0.94 \pm 0.1$ eV (Table 4.7). This difference between n-type and p-type GaP(111)_B/WSe₂ heterojunction is supposed to come from the van der Waals nature of the substrate/epi-layer interface. Indeed, a difference in the surface dipole between n and p-type GaP(111)_B surfaces after the Se-passivation treatment prior growth could explain the band offset difference. This observation is in good agreement with previous ones, showing that the band offset of GaAs/MoS₂³⁰¹ and GaAs/WSe₂³⁰ heterojunctions changes depending on the doping type of GaAs. In addition, the band-offset value is independent to growth conditions or epi-layer thicknesses.

To get a bandgap measurement on a multilayer WSe₂ sample, we have performed STS measurements on sample S_{4-27b}, grown on semi-insulating (SI) GaP(111)_B substrate to avoid any parasitic conduction from the substrate. We used a T_G=450°C and the intermediate annealing sequence to favour large grains and small in-plane disorientation. It resulted in a 2 ML with 50 nm large WSe₂ domains, as observed with STM in Figure 4.23c.

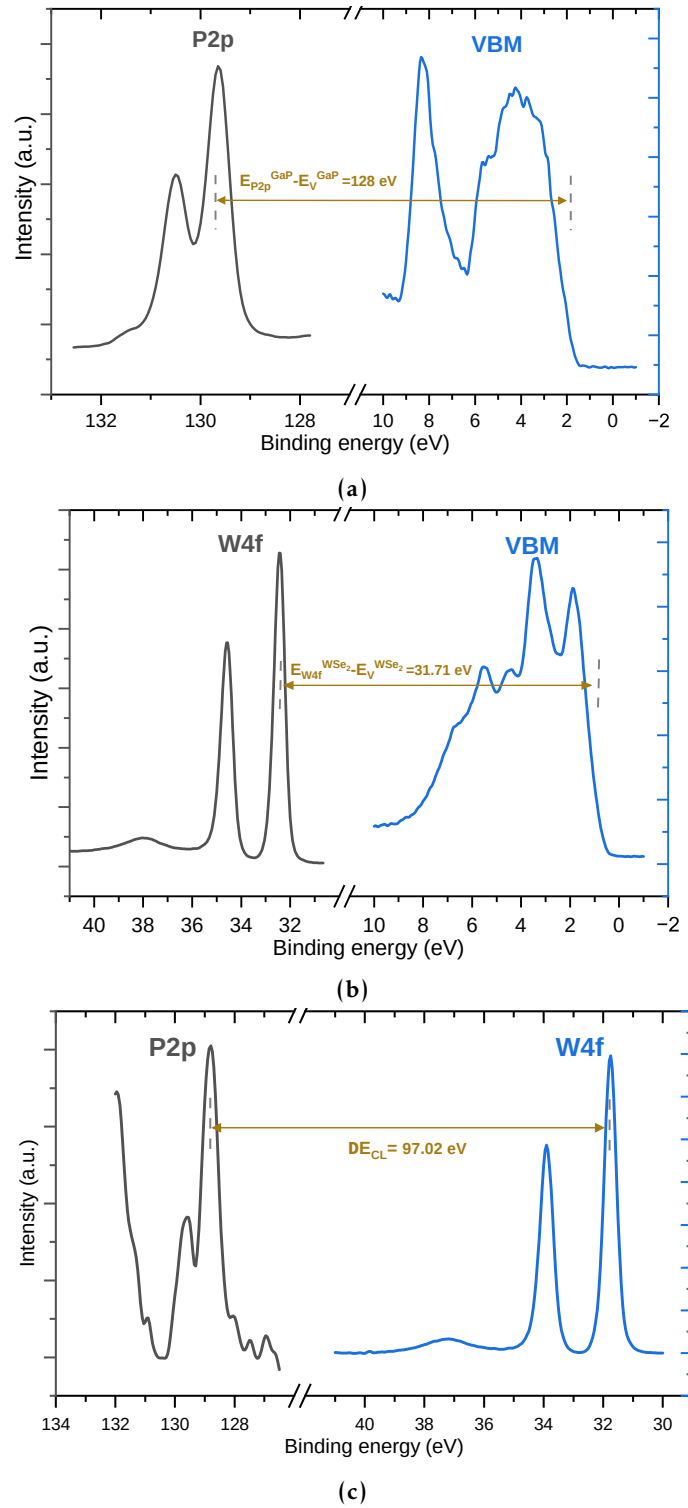


Figure 4.25: (a) $E_{\text{P2p}}^{\text{GaP}} - E_{\text{V}}^{\text{GaP}}$ measured on a deoxidized $\text{GaP}(111)_\text{B}$ substrate with XPS at an incident angle $\theta=75^\circ$. (b) $E_{\text{W4f}}^{\text{WSe}_2} - E_{\text{V}}^{\text{WSe}_2}$ measured in a 15 ML WSe_2 sample grown on $\text{GaP}(111)_\text{B}$ at 450°C and Se-annealed. (c) ΔE_{CL} measurement with XPS at $\theta=25^\circ$ on a 1.8 ML WSe_2 grown on a p-type $\text{GaP}(111)_\text{B}$ substrate at $T_{\text{G}}=450^\circ\text{C}$ and Se-annealed.

In Figure 4.26 is presented the differential conductance (dI/dV) measurements as a function of the bias modulation with a tunnel current set at 500 pA over three different zones on the sample surface. As presented in section 2.4.3, (dI/dV) is proportional to the local density of electronic states. The bandgap can be visualized as a depletion zone with no differential conductance, while the CBM and VBM are expressed by a strong increase of (dI/dV). The logarithmic representation allows to easily identify the depletion zone. For the three different zones, the estimated bandgap energy lies between 1.8 and 1.6 eV, *i.e.* close to the expected values for a bilayer^{138, 288} WSe₂. Therefore, these measurements seem to indicate a slight heterogeneity of the semiconducting behaviour over the surface. As the second bilayer is supposed incomplete, it is not excluded that the different spectra have been recorded on isolated grains with various thicknesses.

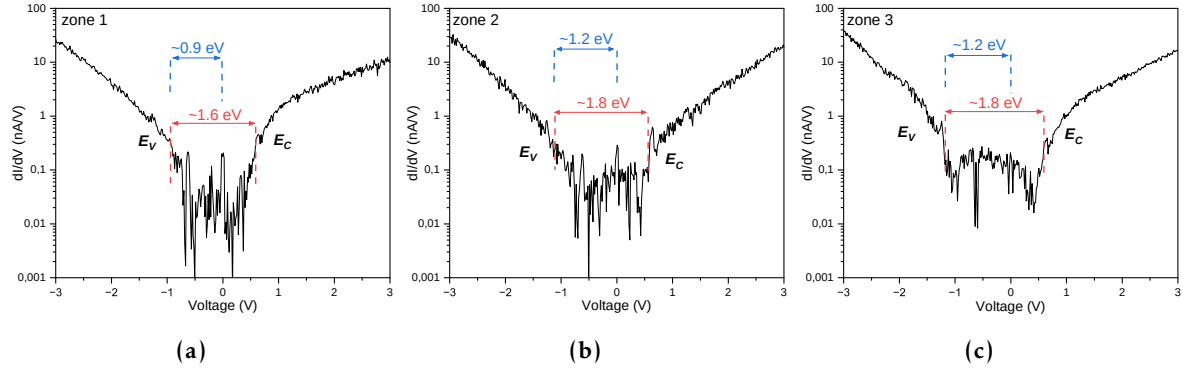


Figure 4.26: differential conductance in function of a bias modulation measured with STS over 3 different zones of a 2 ML WSe₂ grown at 450°C using a two-step annealing sequence (S₄–27b). Each spectrum has been recorded with a 500 pA current. The log values are normalized and absolute.

Besides, considering a Fermi level at 0 V, the three spectrum tend to highlight an n-type behaviour, with $E_F - E_{VBM}$ between to 0.9 eV and 1.2 eV. The UPS measurements around the Γ point of WSe₂ bilayer and trilayer on p-type GaP substrate both indicate the energy of the VBM at 0.29 ± 0.05 eV and a work function of 5.05 ± 0.05 eV. Thus, considering the measured electronic bandgap between 1.6 eV and 1.8 eV for a WSe₂ bilayer, and around 1.5 eV for a trilayer²⁹⁶, it expresses a rather strong p-type doping of the epi-layer with a VBM energy independent to the thickness.

On the other hand, UPS measurements on n-type GaP/WSe₂ heterostructures show a thickness dependence in VBM energy (Table 4.7) induced by the charge transfer. While a p-type doping of the epi-layer in the bilayer regime is observed ($E_F - E_{VBM} = 0.39 \pm 0.05$ eV), it evolves into an ambipolar behaviour in the trilayer regime when considering the reduction of the electronic bandgap down to 1.5 eV. This thickness dependence of the carrier type has been already observed on WSe₂-based FETs with metallic contacts, yet with a transition from p-type to ambipolar in the 5 ML thick regime instead of trilayer^{302, 303}.

Therefore, UPS never reveals an n-type character of the WSe₂ layer, whatever the doping type of the substrate. The strong difference between STS and UPS measurements can be induced by the use of SEM before the observation of the surface with STM. Indeed, the SEM electrons can create surface defects, pinning the Fermi level. For thin nanocrystals films, transport measurement generally evidence an n-type character, while ambient or controlled atmosphere measurement usually lead to a p-type character. Therefore, we assume that the electronic bandgap measurement by STS is rather reliable, but that the Fermi level positions is disturbed by experimental artefacts and do not trust in the apparent n-type character of the WSe₂ layer.

substrate	sample	ΔE_{CL}	ΔE_V	$E_F - E_{VBM}$	Φ
p GaP ($p \sim 6 - 7 \times 10^{17} \text{ cm}^{-3}$)	1.5 ML 250°C/650°C	-97.08	-0.79		
	1.6 ML 250°C/650°C	-97.07	-0.78		
	1.8 ML 450°C/650°C	-97.02	-0.73	0.29	5.05
	2 ML 450°C/650°C	-97.04	-0.75		
	3.3 ML 450°C/650°C	-97.06	-0.77	0.28	5.04
n ⁻ GaP ($n \sim 2 - 4.7 \times 10^{16} \text{ cm}^{-3}$)	2.4 ML 250°C/650°C	-97.21	-0.92	0.72	4.63
	2.3 ML 450°C/650°C	-97.23	-0.94	0.72	4.66
	1 ML 450°C/650°C	-97.19	-0.90	0.35	4.91
n ⁺ GaP ($n \sim 2 - 3 \times 10^{18} \text{ cm}^{-3}$)	1.7 ML 450°C/650°C	-97.23	-0.94	0.39	4.95
	2 ML 500°C/650°C	-97.24	-0.95	0.5	4.79

Table 4.7: Evolution of the band offset, the VBM energy and the work function with the substrate doping type, the epi-layer thickness and the growth conditions.

The final arrangement of the p-type GaP(111)_B/WSe₂ bilayer heterojunction exhibits a staggered gap type-II band alignment with nearly no charge transfer at the interface (Figure 4.27a), while the reduction of the electronic bandgap down to 1.5 eV in the trilayer regime induces a type-I band alignment for the p-GaP/WSe₂ heterojunction. On the other hand, the final arrangement of the n-type GaP(111)_B/WSe₂ bilayer heterojunction also exhibits a type-II band alignment with an electron charge transfer at the interface of potential step $\Delta V = 0.22$ eV (Figure 4.27b). As the band offset remains stable with the thickness and the growth conditions, the heterojunction will still exhibit a type-II alignment less staggered in the trilayer regime, though with a slight increase of the charge transfer at the interface ($\Delta V = 0.26$ eV).

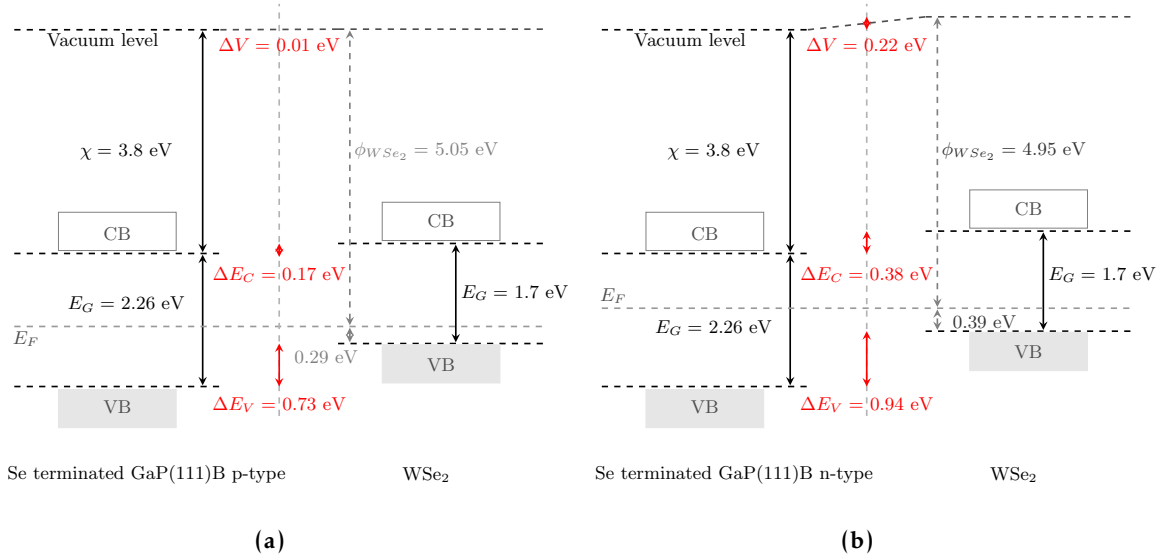


Figure 4.27: Band structure schematic (a) 1.8 ML WSe₂/p-GaP(111)_B heterojunction. (b) 1.7 ML WSe₂/n-GaP(111)_B heterojunction.

Overall, we point out the systematic formation of a staggered type-II band alignment between monolayer and bilayer WSe₂ and GaP(111)_B substrate with a highly p-doping character regardless of the substrate doping type. The increase of the film thicknesses up to 3 ML has a double effect on the band structure, with a decrease in electronic bandgap altering the band alignment, and an evolution of the WSe₂ doping into ambipolar on n-type GaP substrate. We highlight the band offset difference induced by the substrate doping type with a preferential use of n-type GaP for a more staggered band alignment.

Conclusion

In this Chapter, we have demonstrate the epitaxial growth of few layers WSe₂ on top of a deoxidized and Se-terminated GaP(111)_B substrate, pointing out the effect the growth temperature and the subsequent Se-annealing treatment on the polytype formation, the structural and morphological properties.

We have found that a low growth temperature promotes the partial formation of the metastable 1T' phase, coexisting with the dominant 3R stacking in the bilayer regime. The increase of T_G up to 450°C or 500°C induces a radical change in growth mode from 2D to 3D, resulting in a degradation of the surface roughness, while suppressing the presence of 1T'. We have demonstrated the impact of such increase on improving the in-plane disorientation down to 1.48° and the average grain size around 24 nm. On the other hand, increasing the temperature above 500°C has appeared irrelevant, with the progressive formation of metallic tungsten clusters regardless of the selenium flux. The suppression of the different drawbacks induced by T_G have been then explored by means of a subsequent annealing under selenium flux of the grown layer at 650°C. We have demonstrated the clear improvement of the morphological and structural properties of WSe₂ layers, highlighting the suppression of the 1T' phase at low T_G and the significant reduction of the roughness at 450°C or 500°C with the strong reduction of the 3D surface morphology. STEM images and Raman spectroscopy have expressed the formation of a 2H/3R mix phase at 250°C and at 450°C/500°C in the bilayer regime, while promoting a pure 2H phase formation at 450°C and 500°C when the thickness exceeds 2.5 monolayers. We highlight the strong impact of the annealing step on the in-plane disorientation measured with XRD, and its inefficiency in improving the average grain size. Moreover, the application of a two-step annealing sequence induces a significant increase in grain size up to 42 nm and a stronger decrease of the in-plan disorientation down to 1.1°. XPS measurements show that the annealing treatment is not preventing the formation of metallic tungsten clusters when T_G exceeds 500°C, nor the appearance of an additional P-W bond in P 2p CL. We also emphasize the need of a rather low transition metal growth rate set at 0.002 Å/s in order to prevent the formation of metallic clusters at 450°C, limit the in-plane disorientation and favour the formation of larger grains.

The resulting layers exhibit clear epitaxial relationships with the GaP(111)_B substrate with well-defined van der Waals interface. We point out the systematic formation of a staggered type-II band alignment between monolayer and bilayer WSe₂ and GaP(111)_B substrate with a highly p-doping character regardless of the substrate doping type. The increase of the film thicknesses up to 3 ML has a double effect on the band structure, with a decrease in electronic bandgap altering the band alignment, and an evolution of the WSe₂ doping into ambipolar on n-type GaP substrate. We highlight the band offset difference induced by the substrate doping type with a preferential use of n-type GaP for a more staggered band alignment.

HfSe₂ and WSe₂/HfSe₂ heterostructure growth

With the aim of fabricating p-n junction, once the growth of p-type WSe₂ has been optimized, that of HfSe₂, assumed being naturally n-type, has been studied. In this chapter, we first discuss the epitaxy of multilayer 1T-HfSe₂ on the GaP(111)_B-Se surface, focusing on the impact of the growth and annealing conditions. We then turn to the epitaxy of the GaP(111)_B/HfSe₂/WSe₂ and GaP(111)_B/WSe₂/HfSe₂ heterostructures.

5.1 HfSe₂ Growth on GaP(111)_B substrate

We first present the effect of the growth temperature, before considering a subsequent annealing step under selenium flux. We will then shortly investigate the effect of the transition metal growth rate and the impact of a reduced selenium overpressure on the layer structure and morphology.

sample	substrate	thickness	T _G /T _A	P _{Se} (Torr)	V _{Hf} (Å/s)	Se:Hf
S ₅₋₁	n ⁻ GaP	2.8 ML	250°C/680°C	4-5×10 ⁻⁶	0.0013	500:1
S ₅₋₂		2.4 ML	350°C/650°C		0.0017	-
S ₅₋₃		2.4 ML	450°C/680°C		0.0013	1500:1
S ₅₋₄	n~6.8-7.4×10 ¹⁷ cm ⁻³	2.6 ML	250°C/670°C	5.2×10 ⁻⁸	0.013	100:1
S ₅₋₅		2.9 ML	250°C/650°C		0.0018	8:1

Table 5.1: sample summary

5.1.1 Impact of the growth temperature

In this section, the growth of multilayer HfSe₂ was performed with a growth rate of 0.0013 Å/s±15% and a strong Se overpressure of 4 – 5 × 10⁻⁶ Torr. The **RHEED** patterns along <1-100> and <11-20> at the end of the growth for three different T_G are presented in Figure 5.1. At 250°C (sample S₅₋₁), it exhibits a rather blur 1 × 1 2D diagram, whose intensity is progressively decreasing. When increasing T_G up to 350°C (sample S₅₋₂), additional spots appear in a similar way to the growth of WSe₂ (Figure 4.8a), highlighting a favoured three-dimensional growth mode and indicating a rough surface morphology. This 3D behaviour emerges at the end of the first half-monolayer with a slow degradation of the morphology evidenced by the appearance of numerous spots. Furthermore, a T_G of 450°C (sample S₅₋₃) induces a

total 3D growth mode with the suppression of the 1×1 vertical streaks. Considering this strong 3D behaviour, the growth temperature has not been further increased.

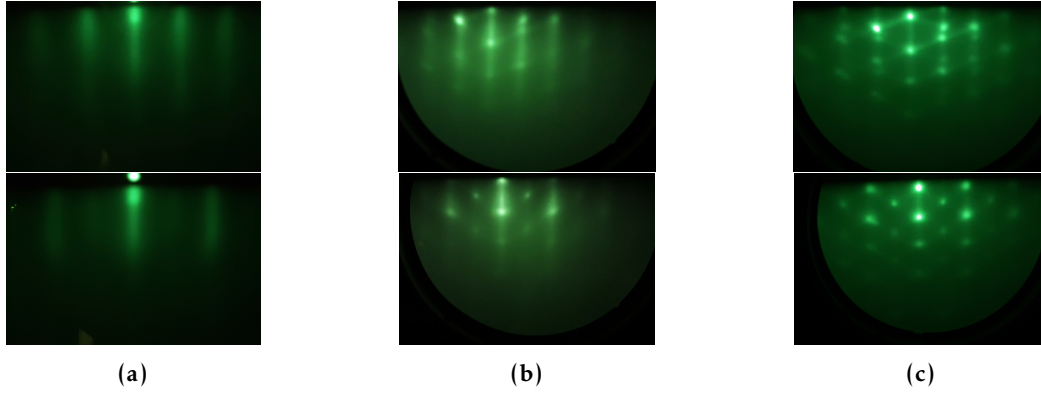


Figure 5.1: Evolution of the RHEED pattern along the $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$ directions at the end of an HfSe₂ growth at (a) $T_G=250^\circ\text{C}$ (S_{5-1}), (b) $T_G=350^\circ\text{C}$ (S_{5-2}) and (c) $T_G=450^\circ\text{C}$ (S_{5-3}).

For the three growth temperatures considered, the decomposition of the Hf 4f CL (Figure 5.2a) evidences a single doublet at 16.90 eV linked to 1T-HfSe₂ while the Se 3d CL decomposition at 250°C and 350°C (Figure 5.2b) displays a main component at 54.22 eV linked to HfSe₂. We assign the second component at 53.67 eV to surface Ga-Se bonds and the third one at 54.97 eV to excess selenium accumulated on the surface. All three samples exhibit a strong selenium excess, as the Se/Hf ratios calculated from the Se-Hf bonds in the Se 3d and Hf 4f CLs, and corrected for the sensitivity factors (Annex B), equal to 2.33 at 250°C, and 2.55 at 350°C and 450°C. In addition, the FWHM of the Hf 4f CL is progressively reduced with the temperature from 0.72 eV at 250°C to 0.65 eV at 450°C, suggesting an improvement of the crystal quality. The proportion of surface GaSe in the Se 3d spectrum remains at $6 \pm 1\%$, indicating the stability of the van der Waals interface in this T_G range.

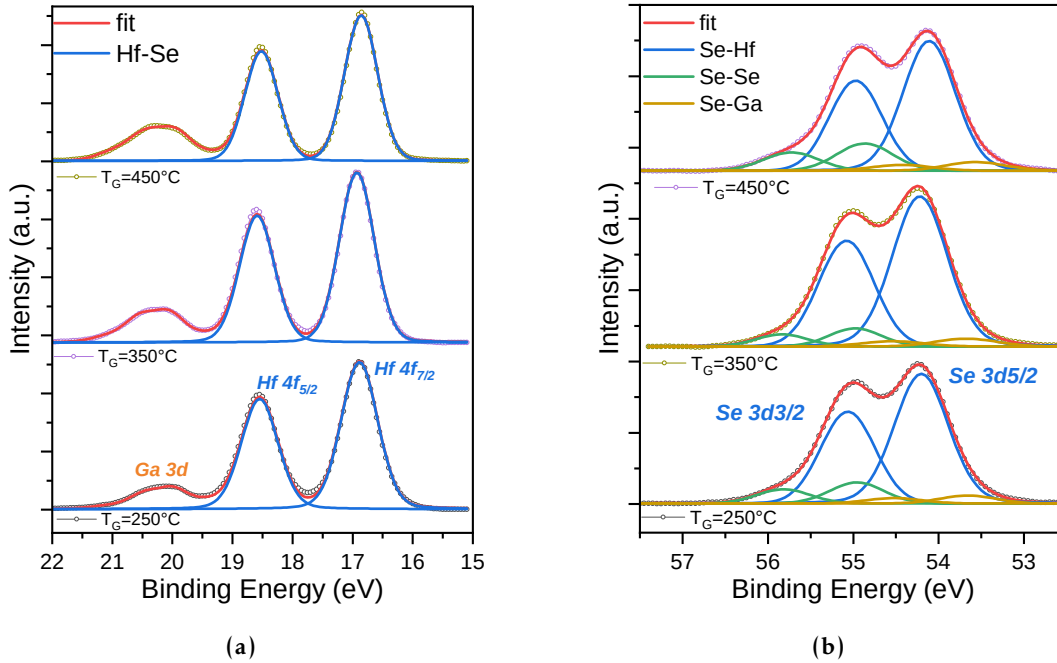


Figure 5.2: Evolution of the Hf 4f (a) and Se 3d (b) CL decompositions with the growth temperature. The take-off angle is 25° and the substrate is a n-type GaP(111)_B.

5.1.2 Impact of annealing under selenium flux above 650°C

We investigate the effect of a subsequent Se-annealing treatment to improve the layer crystallography, composition and morphology of the previous samples, *i.e.* S₅₋₁, S₅₋₂ and S₅₋₃ in the following section. The temperature ramp after the HfSe₂ growth is set at 20°C/min and the sample is maintained above 650°C for 3 minutes before decreasing the temperature. We close the selenium shutter only once the substrate temperature has decreased below 450°C.

5.1.2.1 Morphology and structure

As evidenced by the three 1×1 RHEED patterns in Figure 5.3, the Se annealing treatment suppresses the 3D morphology at $T_G=350^\circ\text{C}$ and 450°C (samples S₅₋₂ and S₅₋₃, respectively), while thinning the vertical streaks of the sample S₅₋₁ grown at 250°C , which evidences a clear improvement of the crystal quality. The main evolution of the RHEED pattern for S₅₋₂ occurs once the substrate temperature reaches a minimum of 600°C , while the RHEED pattern of sample S₅₋₃ changes at 650°C due to the strong 3D behaviour previously presented. However, two spots along the $\langle 1-100 \rangle$ direction still remain after annealing (Figure 5.3c), which should lead to a slightly rougher surface. In addition, the AFM image of the annealed 2.8 ML thick HfSe₂ grown at 250°C (Figure 5.3d) reveals a surface composed of numerous ~ 20 nm large domains, inducing a roughness of 0.5 nm, with the appearance of 50 nm large circular pustules that we attribute to air oxidation.

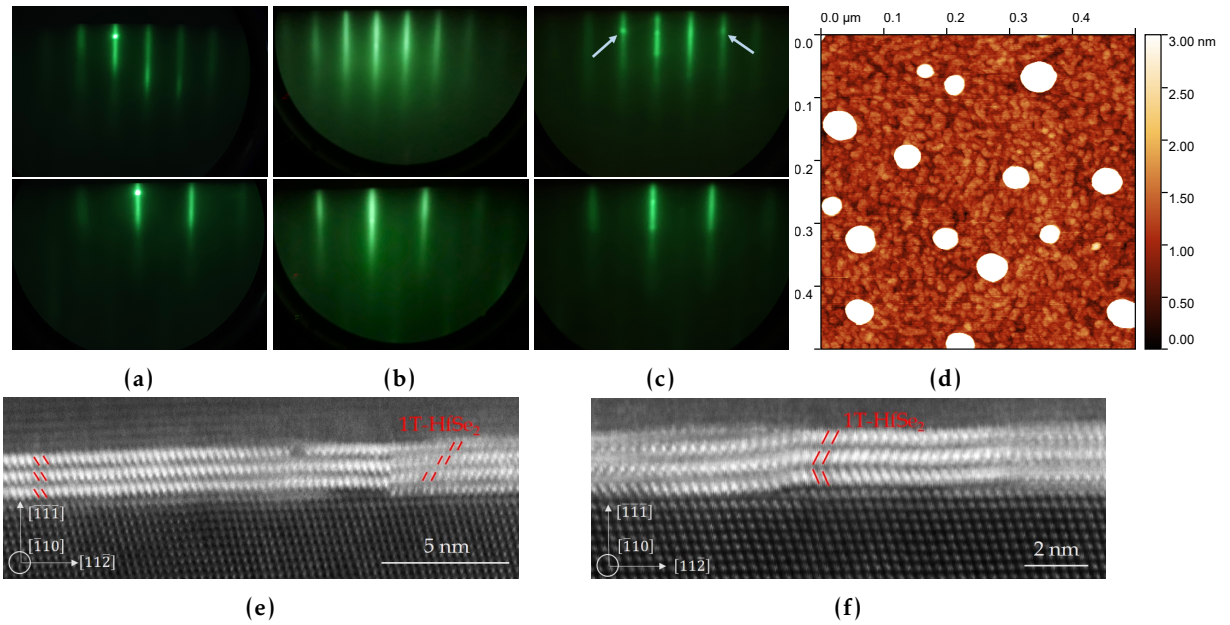


Figure 5.3: Evolution of the RHEED pattern along the $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$ directions after a Se-annealing step above 650°C for growth at (a) $T_G=250^\circ\text{C}$ (S₅₋₁), (b) $T_G=350^\circ\text{C}$ (S₅₋₂) and (c) $T_G=450^\circ\text{C}$ (S₅₋₃). (d) $0.5 \times 0.5 \mu\text{m}^2$ AFM image of a 2.8 ML HfSe₂ growth at $T_G=250^\circ\text{C}$ further annealed at 680°C under selenium flux (S₅₋₁). (e, f) HAADF-STEM images of a 2.4 ML HfSe₂ growth at 450°C , further annealed at 680°C (S₅₋₃).

The HAADF-STEM images along the $[-110]$ zone axis from a 2.4 ML HfSe₂ grown at 450°C (S₅₋₃) and further annealed (Figure 5.3e & 5.3f) confirm the formation of a single 1T-phase, as evidenced by the red lines, with numerous changes in the grain orientation within a layer or between two subsequent layers. The van der Waals interface in Figure 5.3e is slightly degraded compared to the WSe₂ growth. In both images, we observe an atomic step, which in the case of Figure 5.3f does not disturb the continuity of the layer. However, in Figure 5.3e, it clearly appears that the atomic step induces a change in the 1T-HfSe₂

orientation, coupled to the apparition of a fourth layer. Thus, we determine a $[11-20]_{\text{HfSe}_2} // [-110]_{\text{GaP}}$ and $[1-100]_{\text{HfSe}_2} // [11-2]_{\text{GaP}}$ in plane epitaxial relationship, and a $[0001]_{\text{HfSe}_2} // [-1-1-1]_{\text{GaP}}$ out of plane relationship, although considering two possible grain orientations with a 180° rotation.

We performed grazing incident **XRD** measurements with the same procedure as for the WSe₂ layers. As presented in Figure 5.4a, the global $2\theta_{\chi/\varphi}$ scans along two azimuthal directions exhibit the (2-20), (4-2-2) and (4-40) GaP diffraction peaks at $2\theta_{\chi/\varphi} = [47.13^\circ; 87.5^\circ; 106.1^\circ]$, as well as the (110), (220), (100), (200) and (300) HfSe₂ ones at $2\theta_{\chi/\varphi} = [48.3^\circ; 110.1^\circ; 27.3^\circ; 56.5^\circ; 90.4^\circ]$, respectively. As the majority of the HfSe₂ peaks are located close to a more intense GaP one, the determination of each peak integral breadth has appeared challenging, inducing serious issues in estimating the average grain size using the Williamson-Hall method and leading to a meaningless negative value of the y-intercept at the origin (Figure 5.4b). Therefore, we have restricted ourselves to the use of the Scherrer relation (section 2.2.1.2) considering the integral breadth of the (100) HfSe₂ peak to estimate a minimal value of the grain size. The integral breadth as well as the FWHM of the (100) peak are only slightly changed with the growth temperature after annealing, which results in a stable average grain size around 19 nm (Figure 5.4c & Table 5.2). In comparison, for the WSe₂ growth at 500°C with a two-step annealing sequence (S₄₋₂₆), the integral breadth of the (100) WSe₂ peak was 0.374°, leading to a grain size calculated with the Scherrer equation around 23 nm. Therefore, we conclude that the HfSe₂ grains are slightly smaller than the largest one measured on WSe₂ although in the same range.

In a second time, we extract the in-plane angular spread from the integral breadth of the most intense (110) ($2\theta_{\chi/\varphi} = 48.3^\circ$) φ_{HfSe_2} peak. The in-plane disorientation tends to be rather low ($\sim 1.16^\circ$) compared to WSe₂, with a slight increase at 350°C up to 1.33° (Figure 5.4d & Table 5.2), that we associate to the lower annealing temperature used for this sample.

T _G	φ (110) IB	(100) FWHM	(100) IB	Grain size (nm)
(S ₄₋₂₆) WSe ₂ 500°C/650°C IA	$1.14 \pm 0.01^\circ$	0.415°	0.374°	22.8 ± 0.2
(S ₅₋₁) 2.8 ML 250°C/680°C	$1.18 \pm 0.01^\circ$	0.456°	0.411°	19.7 ± 0.5
(S ₅₋₂) 2.4 ML 350°C/650°C	$1.33 \pm 0.01^\circ$	0.458°	0.446°	18.1 ± 0.3
(S ₅₋₃) 2.4 ML 450°C/650°C	$1.14 \pm 0.01^\circ$	0.459°	0.394°	20.5 ± 0.1

Table 5.2: In plane spread angle, FWHM and integral breadth of the (100) HfSe₂ peak and the deducted average grain size at different growth conditions.

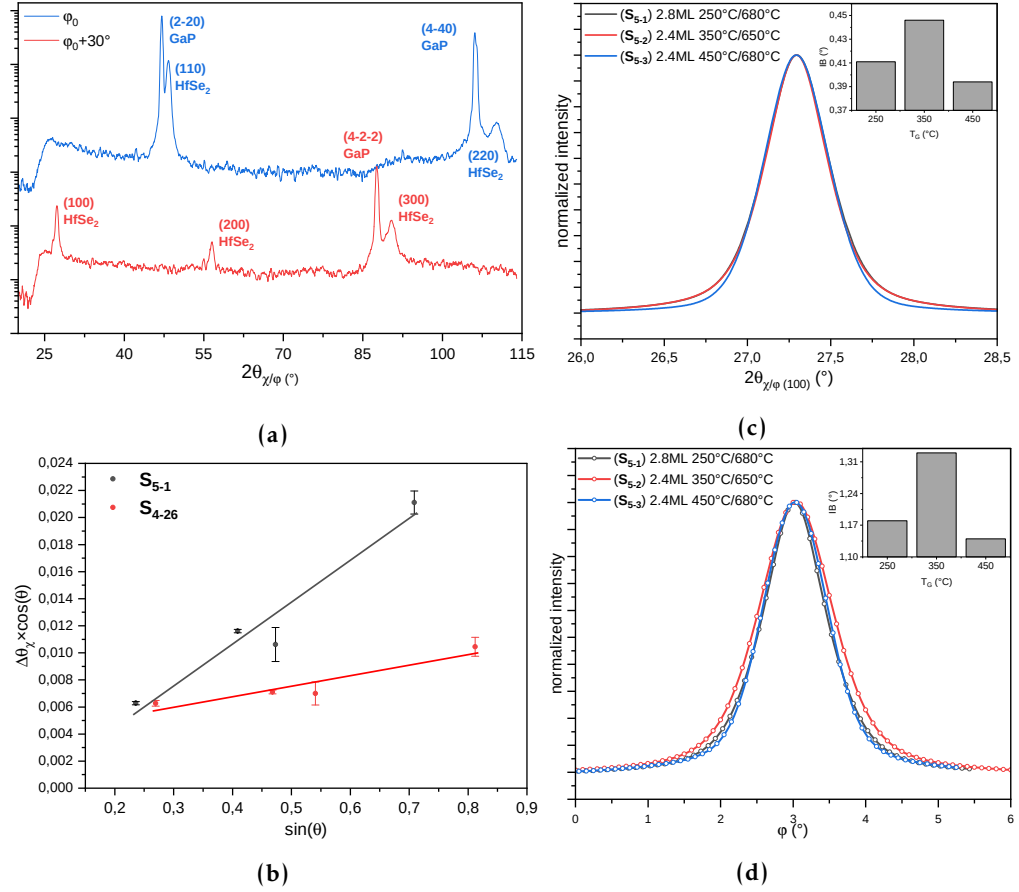


Figure 5.4: (a) XRD $2\theta_{\chi/\phi}$ spectrum along two azimuthal directions for a 2.8 ML thick HfSe₂ layer grown at 250°C and Se-annealed. (b) The Williamson-Hall plot for sample S₅₋₁ compared to the WSe₂ sample S₄₋₂₆ used as reference. (c) Evolution of normalized $2\theta_{\chi/\phi(100)}$ scans with T_G and (d) the evolution of normalized HfSe₂ ϕ scan with T_G .

5.1.2.2 Physical-chemistry and electronic properties

The crystal quality improvement after annealing is further confirmed by XPS measurements, as Figure 5.5a and Figure 5.5b show a clear reduction of the FWHM of the Hf 4f (from 0.67 eV to 0.59 eV) and Se 3d (from 0.74 eV to 0.68 eV) CLs for the three samples, coupled to a reduction of the Se-Se component intensity. It globally results in a slight reduction of the Se/Hf intensity ratio down to 2.3 for all three samples, highlighting a Se-rich growth. In addition, we point out a -0.1 ± 0.02 eV shift of all the spectra after annealing already observed after the annealing step of WSe₂, probably related to a change in Fermi level position at the surface.

Before annealing, for a 250°C growth, UPS measurements (Figure 5.5c) show the presence of a small component between 0.5 and 1 eV, leading to a VBM energy of 0.22 eV, further suppressed after annealing. At higher T_G , the measured VBM energy (0.96 eV and 1.02 eV at 350°C and 450°C, respectively) denotes a strong n-type character of the layer, assuming an electronic bandgap of 1.1 eV. After annealing, the UPS spectra look very similar regardless of the growth temperature with a VBM energy at 1.05 ± 0.03 eV and the emergence of a peak around 2.9 eV. The threshold energy measurement (Figure 5.5d) indicates a work function value between 5.06 and 5.23 eV, which is lower than the value obtained by Tsoutsou *et al.*^{157, 195} on AlN(0001)/Si(111) (5.5 eV), yet significantly stronger than the value obtained by Yue *et al.*³⁵ on HOPG (4.4 eV).

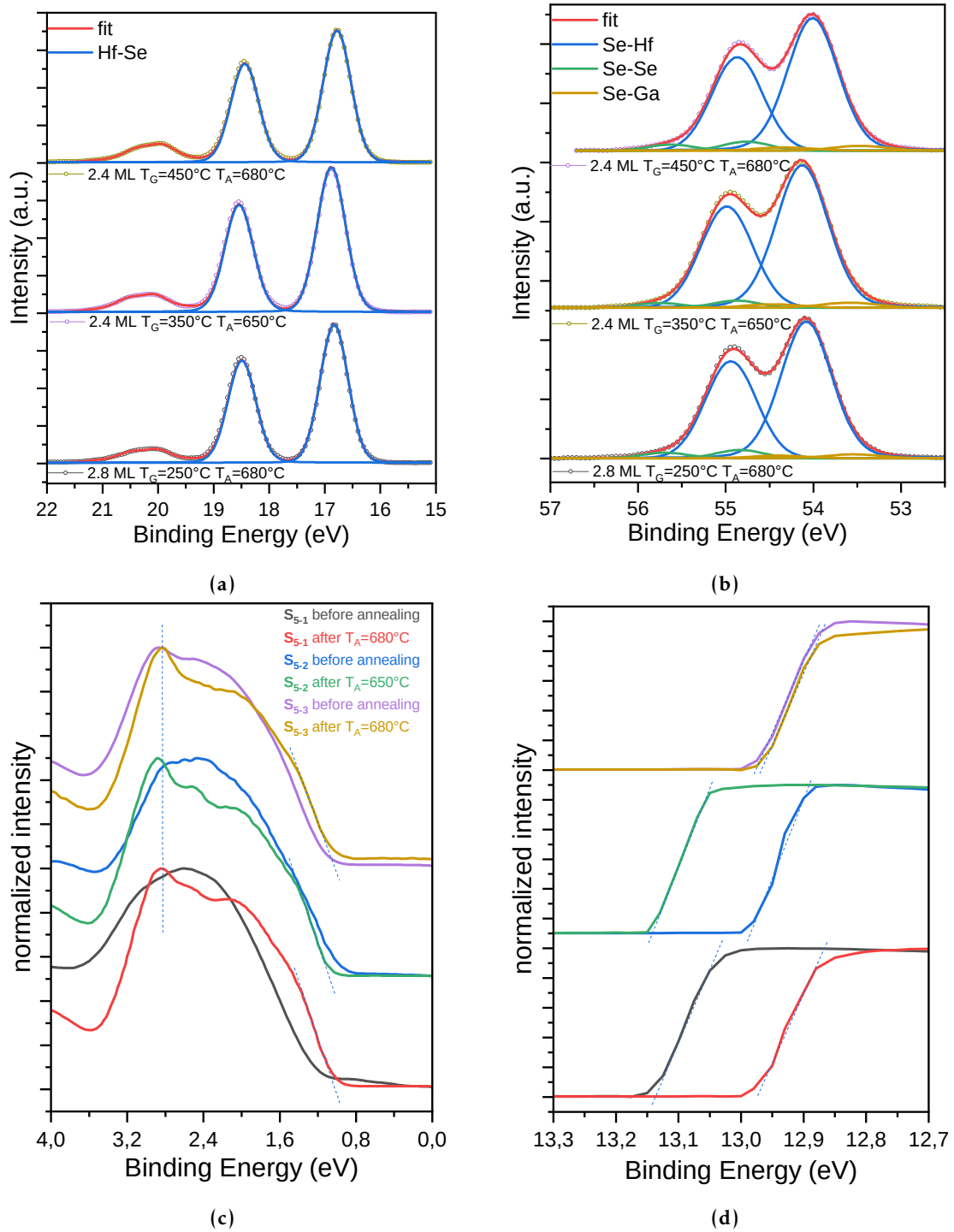


Figure 5.5: Hf 4f (a) and Se 3d (b) CL decompositions of S_{5-1} , S_{5-2} and S_{5-3} after the Se-annealing treatment. The take-off angle is 25° and the substrate is a n-type GaP(111)_B. (c) UPS measurement, evolution of the VBM energy with the Se-annealing treatment and the growth temperature, and (d) the associated threshold energy measurement for determining the work function. The spectrum are recorded using a He I radiation.

sample	ΔE_{CL}	ΔE_V	$E_F - E_{VBM}$	Φ
2.5 ML 250°C			0.22	5.06
2.8 ML 250°C/680°C	-112.8	-0.49	1.03	5.22
2.2 ML 350°C			0.97	5.21
2.4 ML 350°C/650°C	-112.79	-0.48	1.08	5.06
1.9 ML 450°C			1.08	5.22
2.4 ML 450°C/680°C	-112.75	-0.44	1.04	5.23

Table 5.3: evolution of the band offset, the VBM energy and the work function with the growth conditions

We then calculate the valence band discontinuity at the GaP/HfSe₂ interface after Se-annealing for S₅₋₁, S₅₋₂ and S₅₋₃ using the Waldrop method as already presented in section 4.3, which stands from the equation:

$$\Delta E_V = \Delta E_{CL} + (E_{P\ 2p}^{GaP} - E_V^{GaP}) - (E_{Hf\ 4f}^{HfSe_2/Cg} - E_V^{HfSe_2/Cg})$$

The $(E_{P\ 2p}^{GaP} - E_V^{GaP})$ value measured on a deoxidized GaP(111)_B substrate by XPS at $\theta=75^\circ$ equals 128.00 ± 0.05 eV, while we get $(E_{Hf\ 4f}^{HfSe_2/Cg} - E_V^{HfSe_2/Cg}) = 15.69 \pm 0.05$ eV recorded on a thick HfSe₂ (~15 ML) grown at 450°C and Se-annealed on a graphene substrate (Figure 5.6a). The ΔE_{CL} value is extracted by measuring the binding energy difference between the Hf 4f and P 2p CLs on samples S₅₋₁, S₅₋₂ and S₅₋₃ with a take-off angle $\theta=25^\circ$. As presented in Table 5.3, the mean value of ΔE_{CL} is -112.77 ± 0.05 eV whatever the growth temperature, inducing an average ΔE_V of -0.47 ± 0.1 eV. Therefore, the final arrangement of the n-type GaP(111)_B/HfSe₂ heterojunction (Figure 5.6b) exhibits a type-I band alignment with a strong charge transfer at the interface giving rise to a potential step ΔV varying from 0.55 eV at 350°C to 0.68 eV at 250°C and 0.69 eV at 450°C.

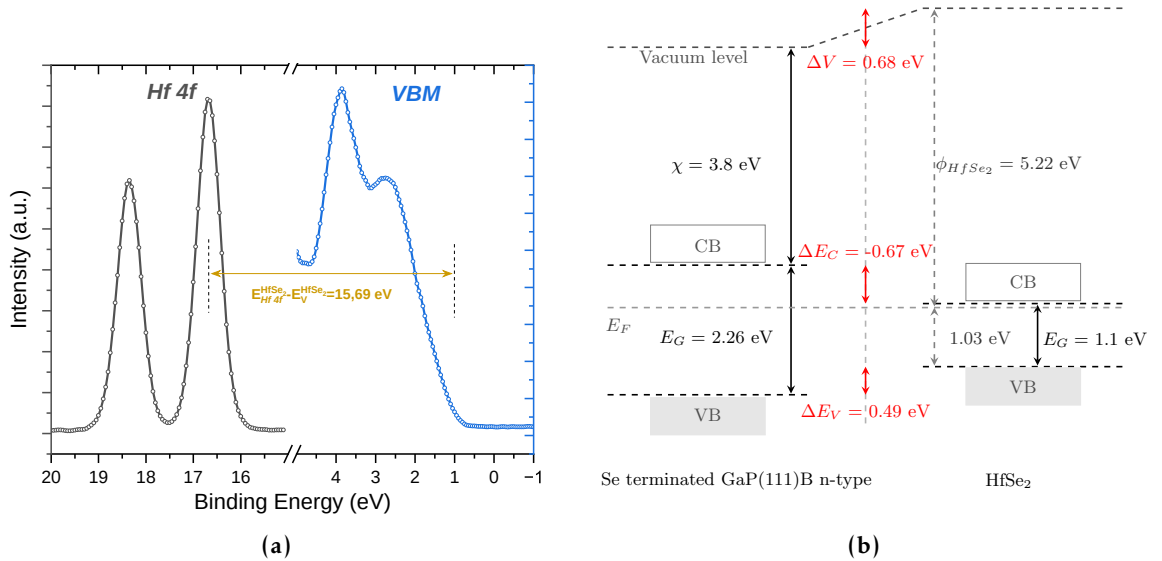


Figure 5.6: (a) $E_{Hf\ 4f}^{HfSe_2} - E_V^{HfSe_2}$ measured in a 15 MLs HfSe₂ sample grown on a graphene substrate at 450°C and Se-annealed. (b) Band structure schematic of a 2.8 MLs HfSe₂/n-GaP(111)_B heterojunction grown at 250°C and Se-annealed.

5.1.3 Impact of the growth rate V_{Hf} and the selenium/hafnium ratio Se:Hf

In the previous section, we set the hafnium growth rate V_{Hf} at $0.0013\text{--}0.0017$ Å/s $\pm 15\%$ for a large selenium overpressure of $P_{Se} = 4\text{--}5 \times 10^{-6}$ Torr, which results in a Se:Hf growth rate ratio higher than 500. In this section, we propose to study the impact of a stronger V_{Hf} or a lower P_{Se} on HfSe₂ growth. The sample S₅₋₄ is a 2.6 ML HfSe₂ grown with a ten times higher Hf growth rate ($V_{Hf} = 0.013$ Å/s), while

the sample S₅₋₅ is a 2.9 ML HfSe₂ grown with a lower Se overpressure of $P_{\text{Se}}=5 \times 10^{-8}$ Torr for a growth rate of $V_{\text{Hf}}=0.0018$ Å/s. Both samples have been grown at 250°C and further annealed under a large Se flux. In Figure 5.7a, the RHEED pattern of S₅₋₄ after the growth shows a strong degradation of the crystal quality with the appearance of a faint circular pattern around the specular spot coupled to blur 1×1 vertical streaks. On the other hand, the use of a low selenium flux during the growth of S₅₋₅ also induces the degradation of the RHEED pattern (Figure 5.7c), with a low intensity associated with the emergence of spots along the vertical streaks. This stands as the first indication on the unsuitability of high transition metal growth rate or low selenium overpressure for good quality HfSe₂ growth. However, the post-growth annealing treatment greatly improves both RHEED patterns (Figure 5.7b & 5.7d), with an increase of the contrast, the thinning of the 1×1 pattern and the suppression of circles and spots. It results in RHEED patterns similar to that of sample S₅₋₁.

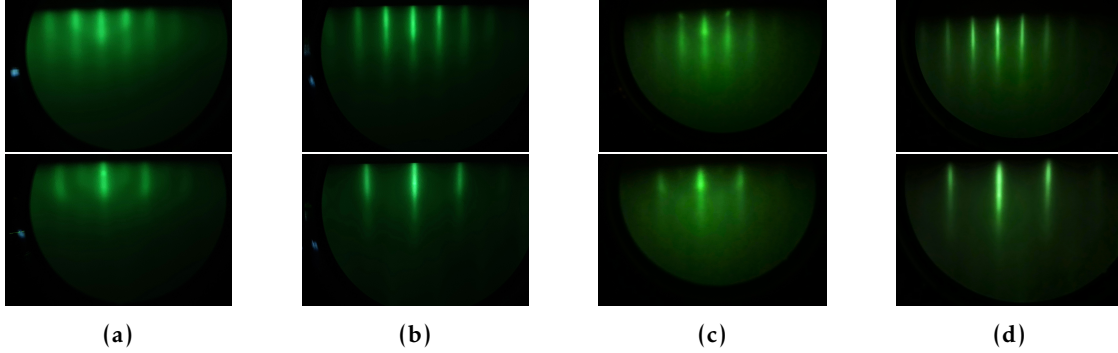


Figure 5.7: RHEED pattern along $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$ for a 2.6 ML HfSe₂ growth at 250°C with $V_{\text{Hf}}=0.013$ Å/s (a) before and (b) after the Se-annealing treatment (S₅₋₄). RHEED patterns of a 2.9 ML HfSe₂ growth at 250°C with $P_{\text{Se}}=5.2 \times 10^{-8}$ Torr (c) before and (d) after the Se-annealing (S₅₋₅).

The comparison of XPS measurements for the growth at low (S₅₋₁) and high V_{Hf} (S₅₋₄) in Figure 5.8a and 5.8b shows similar Hf 4f and Se 3d CLs after annealing, with identical FWHMs (0.59 eV for Hf 4f and 0.68 eV for Se 3d) and Se:Hf intensity ratios.

On the other hand, the reduction of the Se overpressure before annealing (S₅₋₅) induces the formation of an additional component in Hf 4f at low binding energy (16.13 eV) that we associate to metallic Hf-Hf bonding (Figure 5.8c). This component is suppressed after annealing, resulting in the same Hf 4f and Se 3d CLs as S₅₋₁. To support these observations, the evolution of the VBM energy (Figure 5.8d) highlights the suppression of a metallic component on S₅₋₅ ($E_{\text{VBM}} \sim 0$ eV) with the Se-annealing, which results in an n-type HfSe₂ layer strongly similar to S₅₋₁ ($E_{\text{VBM}}=0.96$ eV). In addition, the measured work function after annealing the S₅₋₅ sample is identical to the S₅₋₁ one ($\Phi=5.2 \pm 0.05$ eV), evidencing the homogenisation effect induced by the subsequent Se-annealing step.

XRD measurements on both samples after annealing (Figure 5.8e & 5.8f) show a slight improvement of the $2\theta_{\chi/\varphi(100)}$ FWHM for a low Se overpressure, resulting in an increase of the average grain size up to 21.2 nm (Table 5.4), while a high V_{Hf} does not alter the (100) peak whatsoever.

Besides, the in-plane disorientation is slightly increased for both samples with a spread angle around 1.30° instead of 1.18° . Here, the influence of the Hf growth rate or the Se overpressure is overtaken by the effect of the Se-annealing treatment, at least in terms of composition and grain size. The HfSe₂ growth on GaP(111)_B has appeared less challenging than WSe₂, probably due to its single 1T phase. The use of a strong Se overpressure is still preferred to limit the formation of potential metallic clusters, yet a strong V_{Hf} can be considered to hasten the growth process.

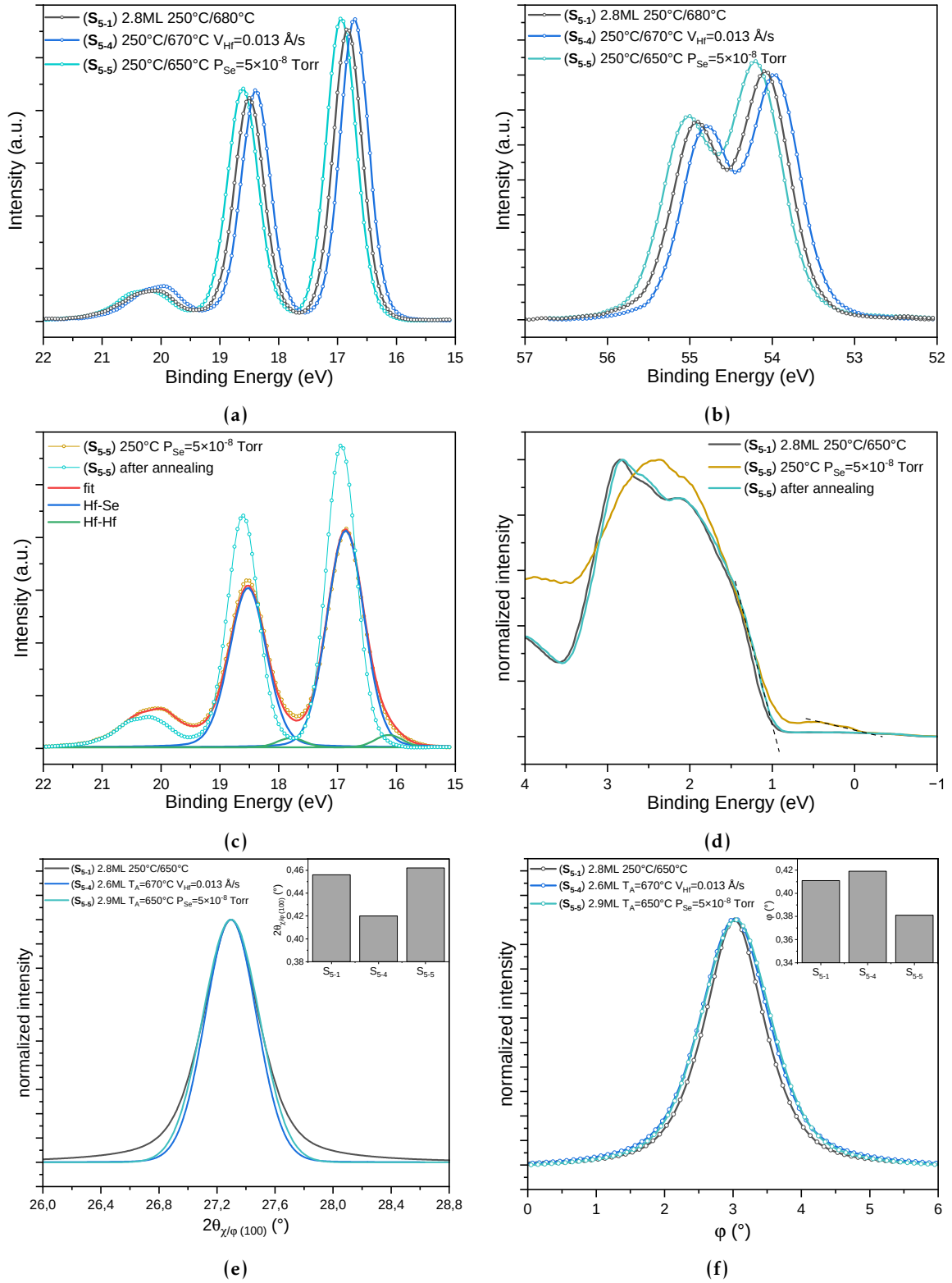


Figure 5.8: Evolution of the Hf 4f (a) and the Se 3d (b) CLs of S₅₋₄ and S₅₋₅ after Se-annealing, considering S₅₋₁ as a reference. (c) Hf 4f CL decomposition of S₅₋₅ before annealing coupled with the CL shape after annealing. The takeoff angle is 25° and the substrate is a n-type GaP(111)_B. (d) UPS measurement of S₅₋₅, evolution of the VBM energy before and after the Se-annealing treatment. The spectrum are recorded using a He I radiation. (e) Normalized 2θ_{χ/φ(100)} scans of S₅₋₁, S₅₋₄ and S₅₋₅ after annealing, and (f) the associated normalized HfSe₂ (110) φ scan.

T_G	φ (110) IB	(100) FWHM	(100) IB	Grain size (nm)
(S ₅₋₁) 2.8 ML 250°C/680°C	$1.18 \pm 0.01^\circ$	0.456°	0.411°	19.7 ± 0.1
(S ₅₋₄) 2.6 ML 250°C/670°C $V_{Hf}=0.013 \text{ Å/s}$	$1.30 \pm 0.02^\circ$	0.459°	0.419°	19.3 ± 0.3
(S ₅₋₅) 2.9 ML 250°C/670°C $P_{Se}=5.2 \times 10^{-8} \text{ Torr}$	$1.32 \pm 0.01^\circ$	0.429°	0.381°	21.2 ± 0.1

Table 5.4: In plane spread angle, FWHM and integral breadth of the (100) HfSe₂ peak and the deducted average grain size at different growth conditions.

To summarize, we have demonstrated the epitaxial growth of few layers HfSe₂ on top of a Se-terminated GaP(111)_B substrate. A subsequent Se-annealing treatment is still required, and appeared strongly effective in improving layer crystalline quality, especially for growth at low Se overpressure or high transition metal growth rate. Finally, we stress the systematic formation of a type-I band alignment with a highly n-doping character, regardless of the growth temperature condition.

5.2 First attempts of a WSe₂/HfSe₂ heterostructure growth

In this section, we present the growth of two heterostructures with the different materials studied in this work. We first investigate the growth of a GaP/HfSe₂/WSe₂ heterostructure before inverting the two TMDC layers.

5.2.1 n-type GaP(111)_B-Se/HfSe₂/WSe₂

After the Se-passivation performed on an n-type GaP substrate, which resulted in a clean 1×1 RHEED pattern (Figure 5.9a), the growth of the 2.5 ML HfSe₂ was performed at a growth rate of 0.0015 Å/s and a Se overpressure of $4.3 \times 10^{-6} \text{ Torr}$. As the results obtained in the previous section tend to highlight a similar surface morphology after annealing regardless of T_G , the growth of this HfSe₂ layer has been performed at 450°C with a subsequent annealing step to be in line with the best growth conditions for WSe₂. It results in the formation of a clear 1×1 RHEED pattern with additional spots along the vertical streaks, as evidenced by the Figure 5.9b. In a second time, the WSe₂ growth was performed at 450°C with a subsequent annealing step, a growth rate of 0.0020 Å/s and a Se overpressure of $4.3 \times 10^{-6} \text{ Torr}$ with a targeted thickness of 2 monolayers. This resulted in a rather blur and broad 1×1 RHEED pattern with a progressive loss of intensity (Figure 5.9c), which indicates a rather poor WSe₂ crystal quality.

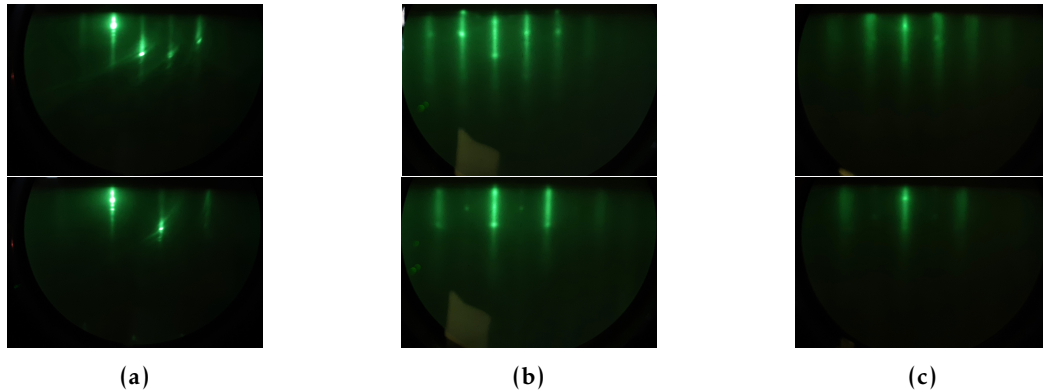


Figure 5.9: RHEED pattern along directions $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$ after (a) the Se-passivation, (b) the annealed HfSe₂ growth and (c) the annealed WSe₂ growth.

The HAADF-STEM images along the $[1-10]$ zone axis tend to validate the formation of 2 ML 1T-HfSe₂ and at least two monolayers of WSe₂, also evidencing the coexistence of both 3R and 2H polytypes

(Figure 5.10a). The observation of a 60° rotation of the 1T-HfSe₂ lines within the same layer also highlights a rather strong in-plane disorientation for both materials (Figure 5.10b). Each layer is well isolated by a clear van der Waals gap, while the substrate/TMDC interface appears degraded with the diffusion of Se species in the outermost P-layers, as already observed at the HfSe₂/GaP interface (Figure 5.3e). We determine a $[11-20]_{\text{WSe}_2} // [11-20]_{\text{HfSe}_2} // [1-10]_{\text{GaP}}$ and $[1-100]_{\text{WSe}_2} // [1-100]_{\text{HfSe}_2} // [11-2]_{\text{GaP}}$ in plane epitaxial relationship, and a $[0001]_{\text{WSe}_2} // [0001]_{\text{HfSe}_2} // [-1-1-1]_{\text{GaP}}$ out of plane relationship.

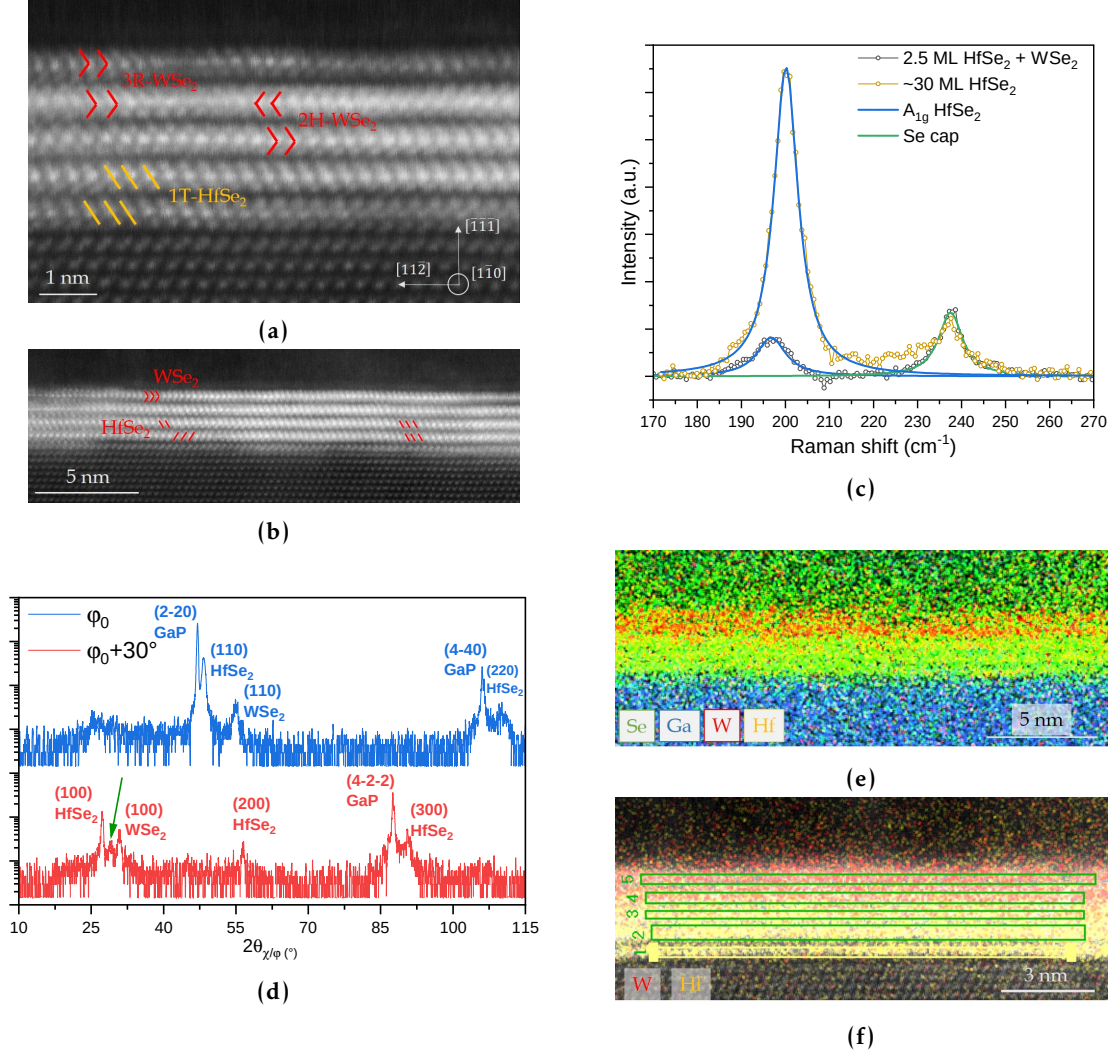


Figure 5.10: (a, b) HAADF-STEM images of a HfSe₂/WSe₂ heterostructure grown on n-type GaP(111)_B-Se. (c) The associated Raman shift with its decomposition and superposed with the Raman shift of a 30 MLs HfSe₂ sample grown on GaP at 250°C and further annealed. (d) The associated grazing incident XRD global $2\theta_{\chi/\phi}$ scan (e) EDX measurements with the superposition of W, Ga, Hf and Se signals. (f) Isolated EDX W and Hf signals superposed to a HAADF-STEM image. The different scanned zones are represented in **green**, while the interface zone is represented in **yellow**.

However, this first analysis based on visual interpretation is further contradicted by Raman spectroscopy (Figure 5.10c), which shows a clear peak at 196.8 cm^{-1} that we attribute to the HfSe₂ A_{1g} vibration mode^{35, 304}, a second one at 237.5 cm^{-1} already associated to the selenium cap, while there is no evidence of a component related to WSe₂. This behaviour is quite unpredicted, as we have previously got Raman spectra for lower WSe₂ thicknesses (Figure 4.24c). As for the HfSe₂ A_{1g} peak, the recent observation of a strong peak at 200.1 cm^{-1} , in better agreement with the literature, on a 30 ML thick

HfSe₂ sample grown on GaP(111)_B at 250°C and further annealed could indicate a change in micro-strain after the additional growth of WSe₂. Besides, we estimate an A_{1g} FWHM of 8 cm⁻¹ and 7 cm⁻¹ in the case of the heterostructure and the 30 ML HfSe₂ sample, respectively, pointing out a degraded crystal quality after the WSe₂ growth. On the other hand, the global 2θ_{χ/φ} scans measured with grazing incident XRD (Figure 5.10d) tends to highlight the dominant formation of HfSe₂, with clear difficulties to observe the (200) and (300) peaks of WSe₂. Moreover, we observe an additional peak between the HfSe₂ (100) and WSe₂ (100) peaks at 29°, which is not linked to either TMDCs, the GaP substrate or the Ga-Se interface.

Thus, EDX measurements presented in Figure 5.10e clearly evidence a strong dominance of the Hf (yellow) species compared to W (red), which leads us to consider a lower WSe₂ thickness. Table 5.5 presents the evolution of the different species atomic proportions in the five zones marked in Figure 5.10f. As expected, stoichiometric HfSe₂ with barely no traces of tungsten is present in the three first zones. The strong proportion of phosphorus and gallium in the first zone is directly linked to the substrate/TMDC interface, though the rather strong presence of P species in the zones 2 to 5 is quite disturbing. When reaching the zones 4 and 5, the proportion of W species is logically increasing, yet never to a stoichiometric level. Moreover, the proportion of hafnium is not decreasing so much, indicating the formation of a (Hf/W)Se_x alloy that we are calling X in the upper layers of this heterostructure. As hafnium and tungsten have close atomic numbers, it is barely impossible to differentiate them in HAADF-STEM images.

Element	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5
Selenium	41.15%	53.34%	53.51%	56.79%	61.33%
Hafnium	18.09%	26.01%	27.54%	20.47%	12.48%
Tungsten	0.59%	0.72%	4.15%	11.61%	13.42%
Phosphorus	22.88%	13.74%	12.12%	9.40%	10.83%
Gallium	17.30%	6.19%	2.67%	1.73%	1.94%

Table 5.5: evolution of the atomic proportion measured by EDX for the different zones presented in Figure 5.10f.

As presented in Figure 5.11a, the W 4f CL exhibits a rather strong asymmetrical behaviour, which can be attributed either to an additional and residual component at higher binding energy, or to the metallic behaviour of a single component. The unchanged normalized W 4f CL regardless of the electron take-off angle tends to validate the presence of a unique metallic component that we link to the X phase observed with EDX. On the other hand, the Hf 4f CL in Figure 5.11b shows clear evidence of an additional component at low binding energy. When normalizing the signals for the three polar angles, it clearly appears that this new component is a surface one, as shown by the enlargement of the peak at θ=25°. Moreover, the UPS measurement in Figure 5.11c shows an evolution of E_{VBM}-E_F from 0.98 eV after the HfSe₂ growth to 0.09 eV after the WSe₂ growth, evidencing a near-metallic character induced by the WSe₂ deposition, while the work function (Figure 5.11d) is not altered with an energy of 5.25 eV. Therefore, we decompose the W 4f CL (Figure 5.11e) into one single asymmetrical component with a binding energy of 32.10 eV, while we fit the Hf 4f CL with one main component at 16.82 eV linked to HfSe₂ and a second asymmetrical one at 16.43 eV linked to the X phase. Thus, we can assume that the 2H phase of WSe₂ can hardly be grown on the trigonal prismatic HfSe₂. It is possible that the 1T' phase of WSe₂ would be more suitable to this heterostructure, yet the selected T_G (450°C) was too high to favour this polytype. The initial roughness of the HfSe₂ layer induced by the rather high T_G used could also favour the formation of the X phase. In an attempt to suppress the alloy component, we propose to invert the two TMDCs, *i.e.* growing first WSe₂ on GaP, and then HfSe₂ on top, resulting in a GaP/WSe₂/HfSe₂ heterostructure.

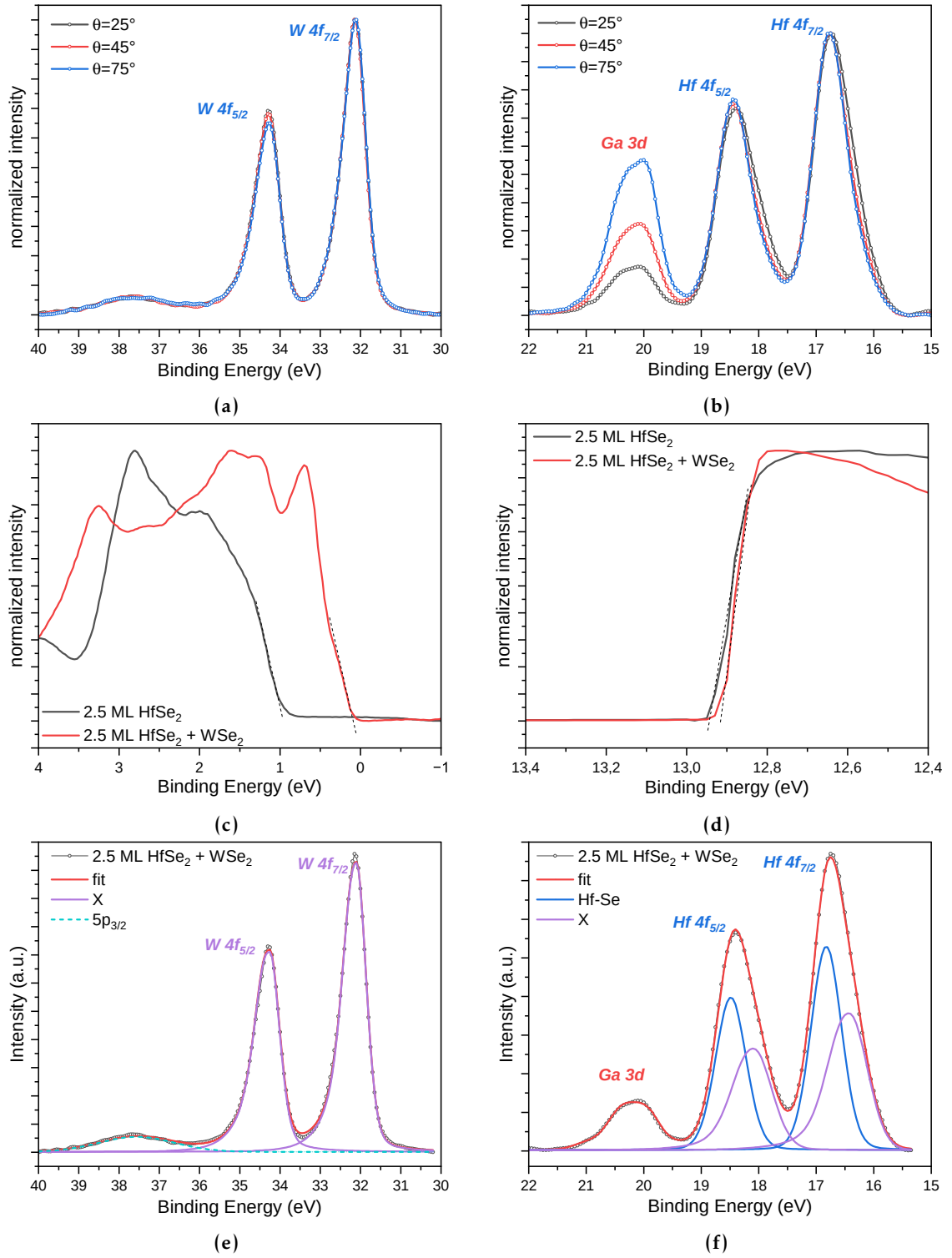


Figure 5.11: Evolution of the normalized (a) W 4f and (b) Hf 4f CLs with the polar angle. Evolution of (c) the VBM energy and (d) the threshold energy before and after the deposition of the WSe₂ layer. (e, f) the decompositions of the W 4f and Hf 4f CLs recorded with a polar angle $\theta = 25^\circ$.

5.2.2 n-type GaP(111)_B-Se/WSe₂/HfSe₂

After the Se-passivation performed on a n-type GaP substrate, the growth of the 3.9 ML WSe₂ is processed at 450°C with a subsequent annealing step, a growth rate of 0.0018 Å/s and a Se overpressure of 5.4×10^{-6} Torr. Taking advantage of the results of the Chapter 4, we apply an intermediate annealing step, which clearly improves the crystallinity of the grown layer, as the final RHEED pattern exhibits a clear 1×1 RHEED pattern with faint additional spots along the vertical streaks (Figure 5.12a). In a second step, the HfSe₂ growth was performed at 250°C with a subsequent annealing step, a growth rate of 0.0017 Å/s and a Se overpressure of 5.3×10^{-6} Torr with a nominal thickness of 5 monolayers. The choice of a low T_G was driven by the optimisation of a 2D growth behaviour, as one hypothesis to explain the formation of the X phase in the previous section was the roughness of the HfSe₂ layer grown at 450°C. The RHEED pattern after a nominal deposited thickness of 0.5 ML HfSe₂ is presented in Figure 5.12b, showing the 1×1 reconstructions of both WSe₂ and HfSe₂ with the duplication of the vertical streaks, evidenced by the RHEED intensity profiles (Figure 5.12e & 5.12f). Considering the WSe₂ lattice parameter of 3.30 Å as a reference, we measure an HfSe₂ lattice parameter of 3.7 Å, which stands in good agreement with the DFT calculation of Gong *et al.*⁴³ ($a \sim 3.65$ Å) or experimental values obtained by Aretouli *et al.*¹⁹⁵ ($a \sim 3.78$ Å). When reaching a nominal thickness of 5 monolayers (Figure 5.12c), the vertical streaks attributed to WSe₂ have totally disappeared, though the intensity of the RHEED signal has drastically decreased. After a subsequent annealing step under Se flux at 650°C (Figure 5.12d), the RHEED contrast is greatly improved, and we observe a clean 1×1 pattern with two additional spots along the $\langle 11-20 \rangle$ direction.

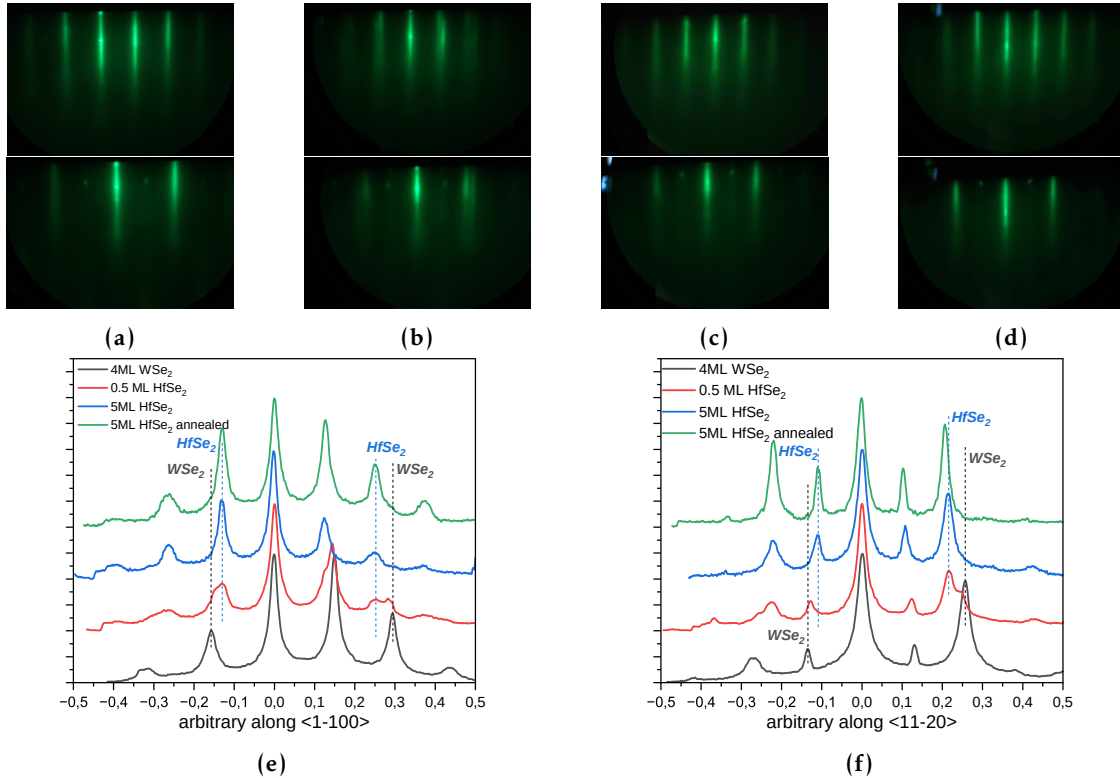


Figure 5.12: RHEED pattern along the $\langle 1-100 \rangle$ and $\langle 11-20 \rangle$ directions after (a) a 4 ML annealed WSe₂ growth, deposition of (b) 0.5 ML (c) 5 ML HfSe₂ at 250°C and (d) the Se-annealing treatment of the 5 ML thick HfSe₂ overlayer. The associated and normalized RHEED intensity profiles along (e) $\langle 1-100 \rangle$ and (f) $\langle 11-20 \rangle$.

Grazing incident XRD measurements φ scans show a perfect alignment of the different reflections associated to WSe₂ and HfSe₂ with the substrate (Figure 5.13a), indicating the good epitaxial relationship of HfSe₂ with the underlying WSe₂ layer and GaP substrate. However, the in-plane angular spread (Figure 5.13b) extracted from the integral breadth of the most intense $\varphi_{(110)\text{HfSe}_2}$ peak is clearly degraded compared to a direct growth on GaP(111)_B, with an integral breadth increasing from 1.18° on S₅₋₁ to 1.88° on this heterostructure. We assume that this degradation is due to the van der Waals gap between WSe₂ and HfSe₂ as well as the propagation of the angular spread inherited from WSe₂ estimated at 1.39°. In addition, as presented in Figure 5.13c, the global $2\theta_{\chi/\varphi}$ scans along two azimuthal directions exhibit the different diffraction peaks already associated to GaP, WSe₂ and HfSe₂ used for the determination of the average grain size.

As shown in Figure 5.13d and Table 5.6, the integral breadth of the (100) WSe₂ peak is slightly increased on the heterostructure compared to the 1.9 ML growth at 500°C with an intermediate annealing (S₄₋₂₆). However, the Williamson-Hall plot in Figure 5.13e highlights an increase of the slope (*i.e.* the micro-strain is increased), while the y-intercept reduces, inducing an increase of the average grain size up to 50 nm. Overall, the grazing incident XRD measurements are in good agreement with what was observed with STM in the precedent chapter (Figure 4.23c). In contrast, we observe in Figure 5.13f a strong reduction of the HfSe₂ (100) peak integral breadth compared to the 2.8 ML grown on GaP(111)_B (S₅₋₁) from 0.347° to 0.241°. Yet, as already discussed in section 5.1.2 (Figure 5.4b), the estimation of the average HfSe₂ grain size using the Williamson-Hall plot is challenging due to the closeness of the HfSe₂ peaks and the more intense GaP ones, leading to a negative value of the y-intercept. Acknowledging the limitations of the different methods, we estimate a minimal HfSe₂ grain size value up to 35 nm with the Scherrer equation, as presented in Table 5.6. In comparison, the WSe₂ (100) peak integral breadth of 0.409° on the heterostructure leads to a grain size calculated with the Scherrer equation around 21 nm. Therefore, we assume that the HfSe₂ grains are significantly larger than the WSe₂ ones on this heterostructure. The strong increase of the HfSe₂ grain size compared to S₅₋₁ is assumed being favoured by the van der Waals interface between the two TMDCs, which would significantly reduce the nucleation density.

T _G	φ (110) IB	(100) IB	Grain size Scherrer (nm)	Grain size W-H (nm)	Strain (Cε)
(S ₄₋₂₆) 1.9 ML 500°C/650°C IA	1.14 ± 0.01°	0.374°	22.8 ± 0.7	42.3 ± 13.3	0.008 ± 0.002
(S ₅₋₁) 2.8 ML 250°C/650°C	1.18 ± 0.01°	0.411°	19.7 ± 0.5		
WSe ₂ hetero	1.39 ± 0.01°	0.409°	20.8 ± 0.2	49.7 ± 36.6	0.011 ± 0.004
HfSe ₂ hetero	1.88 ± 0.02°	0.241°	35.7 ± 0.4		

Table 5.6: In plane spread angle, integral breadth of the (100) HfSe₂ (WSe₂) peak and the deducted average grain size calculated with the Scherrer equation and the Williamson-Hall approach. We use samples S₄₋₂₆ and S₅₋₁ WSe₂ and HfSe₂ as references.

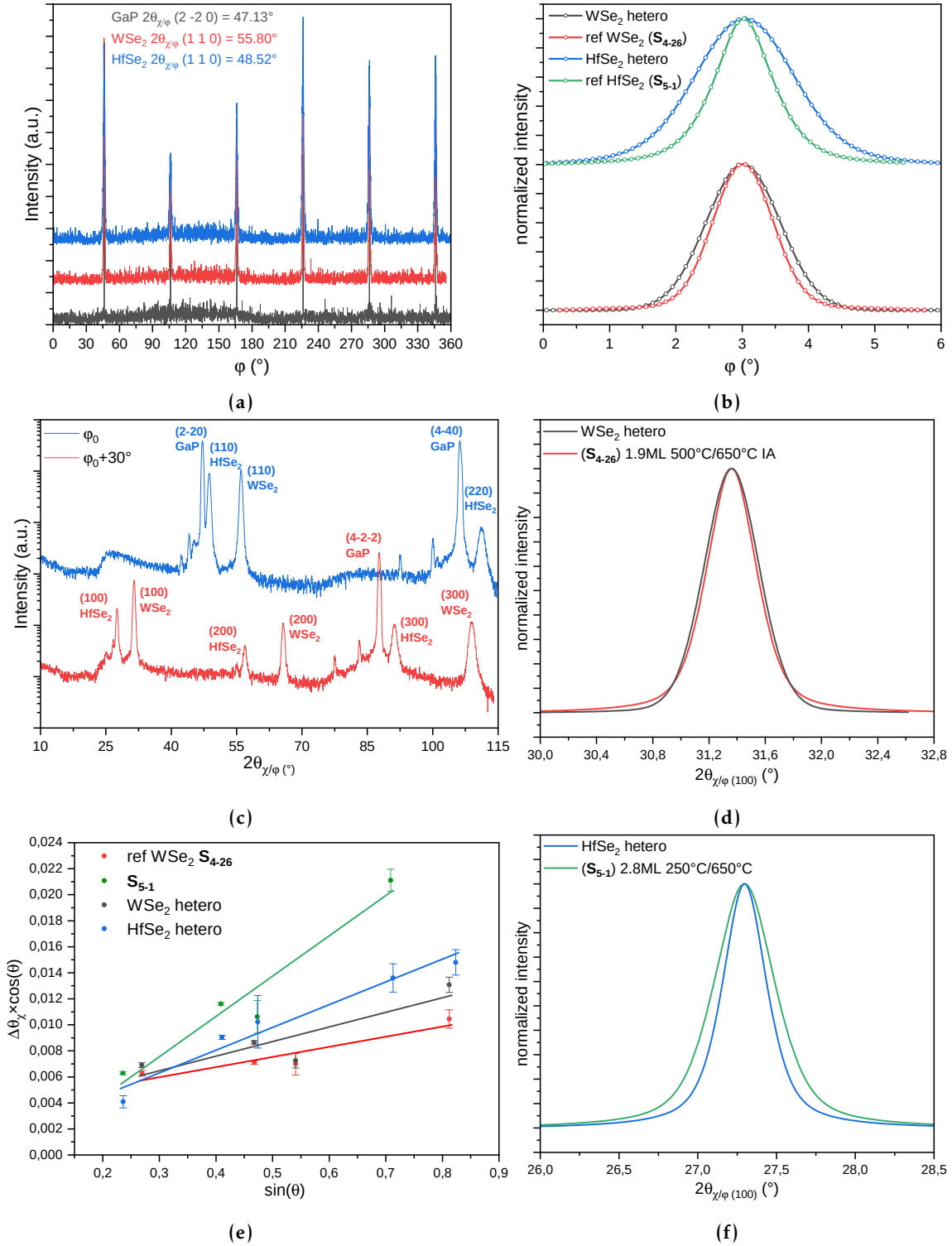


Figure 5.13: XRD measurement on the GaP(111)_B/WSe₂/HfSe₂ heterostructure. **(a)** 360° GaP (2-20) ($2\theta_{\chi/\phi}$ =47.13°), WSe₂ (110) ($2\theta_{\chi/\phi}$ =55.80°) and HfSe₂ (110) ($2\theta_{\chi/\phi}$ =48.52°) azimuthal spectrum and **(b)** the normalized HfSe₂ and WSe₂ ϕ scan, compared to samples S₄₋₂₆ and S₅₋₁ used as references. **(c)** XRD $2\theta_{\chi/\phi}$ spectrum along two azimuthal directions. **(d)** Normalized $2\theta_{\chi/\phi}$ (100) scans of WSe₂ considering sample S₄₋₂₆ as reference and **(e)** The associated Williamson-Hall plots. **(f)** Normalized $2\theta_{\chi/\phi}$ (100) scans of HfSe₂ considering sample S₅₋₁ as reference.

In contrast with what was observed in the previous heterostructure, the XPS W 4f and Hf 4f CLs (Figure 5.14a & 5.14b) exhibit clear Gauss-Lorentz lineshapes, each CL being decomposed with only one doublet at 32.17 eV and 16.71 eV, respectively. The additional peak in W 4f is associated to the Hf 5p_{3/2} peak. The absence of interfacial components is indicative of the formation of a rather sharp WSe₂/HfSe₂ interface with a well-defined van der Waals gap. In addition, while the FWHM of W 4f is similar to what was obtained in section 4.2.2 (0.56 eV), the slight increase of the Hf 4f FWHM up to 0.61 eV is in good agreement with the increase of the spread angle measured with XRD. Besides, the UPS measurement in Figure 5.14c evidences a similar shape of the VBM between the WSe₂/HfSe₂ heterostructure and a multilayer HfSe₂ grown on GaP(111)_B, yet with a decrease of the of $E_{\text{VBM}}-E_{\text{F}}$ value from 0.98 eV to 0.8 eV. As the UPS measurement is surface sensitive, the rather similar shape indicates the effective growth of an HfSe₂ overlayer on top of WSe₂. Moreover, as the WSe₂ layer is assumed being p-type, it can induce a slight charge transfer, resulting in a lower n-type behaviour of the HfSe₂ layer. Finally, the work function (Figure 5.14d) is increased up to 5.34 eV, resulting in an ionization energy $E_{\text{i}}=6.14$ eV.

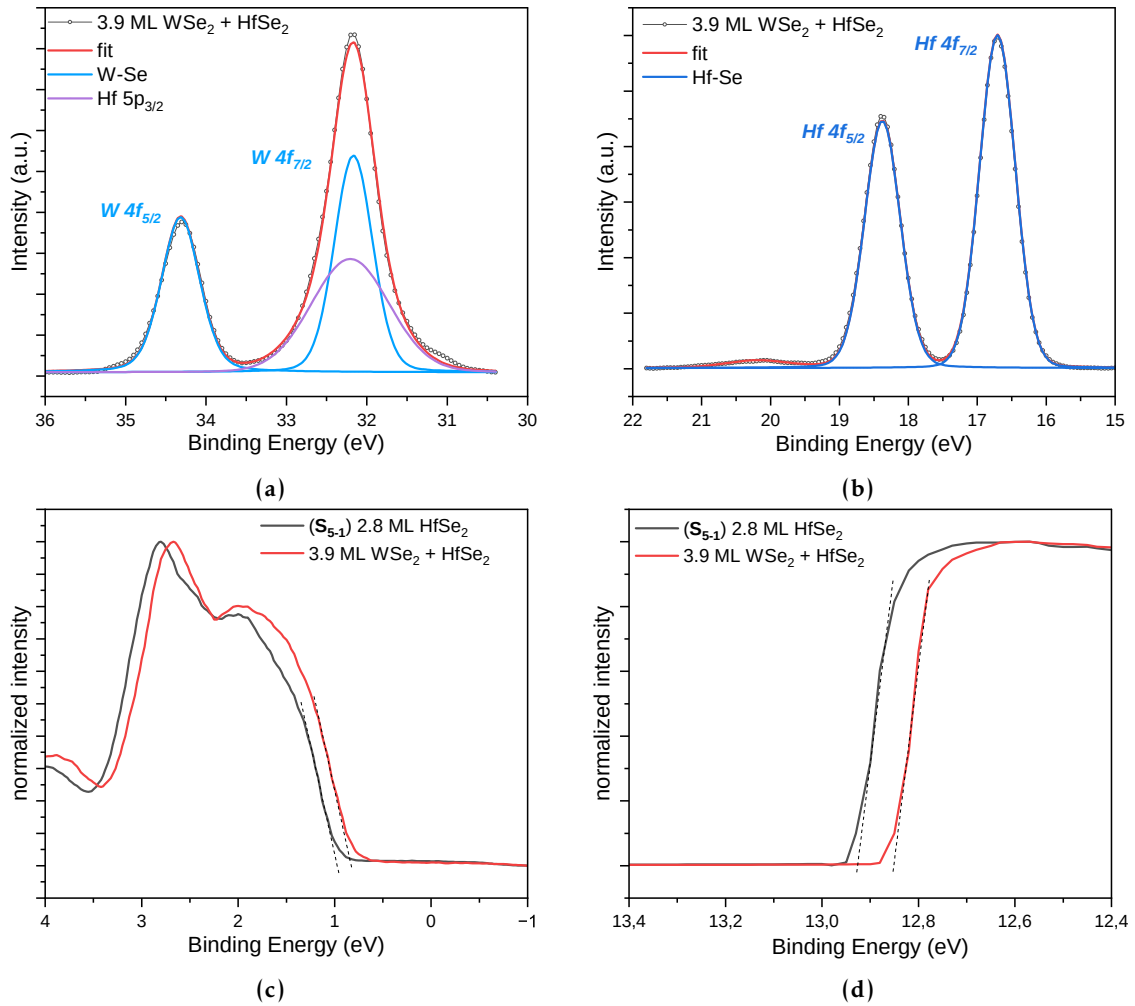


Figure 5.14: Decomposition of (a) the W 4f and (b) the Hf 4f CLs after the heterostructure growth, with a polar angle $\theta=25^\circ$. Evolution of (c) the VBM energy and (d) the threshold energy after a HfSe₂ multilayer growth on GaP(111)_B (black) and on WSe₂ (red).

Considering the XPS results obtained on both heterostructures, we point out a more favourable GaP(111)_B/WSe₂/HfSe₂ stacking.

Finally, we calculate the valence band discontinuity between the GaP substrate and the WSe₂ layer, as well as the one between the WSe₂ and the HfSe₂ layers using the Waldrop method as already presented in section 4.3, which stands from the equation:

$$\begin{aligned}\Delta E_{V_{\text{GaP-WSe}_2}} &= \Delta E_{\text{CL}_1} + (E_{\text{P } 2\text{p}}^{\text{GaP}} - E_{\text{V}}^{\text{GaP}}) - (E_{\text{W } 4\text{f}}^{\text{WSe}_2/\text{GaP}} - E_{\text{V}}^{\text{WSe}_2/\text{GaP}}) \\ \Delta E_{V_{\text{WSe}_2\text{-HfSe}_2}} &= \Delta E_{\text{CL}_2} + (E_{\text{W } 4\text{f}}^{\text{WSe}_2/\text{GaP}} - E_{\text{V}}^{\text{WSe}_2/\text{GaP}}) - (E_{\text{Hf } 4\text{f}}^{\text{HfSe}_2/\text{Cg}} - E_{\text{V}}^{\text{HfSe}_2/\text{Cg}}) \\ \Delta E_{V_{\text{GaP-HfSe}_2}} &= \Delta E_{\text{CL}_3} + (E_{\text{P } 2\text{p}}^{\text{GaP}} - E_{\text{V}}^{\text{GaP}}) - (E_{\text{Hf } 4\text{f}}^{\text{HfSe}_2/\text{Cg}} - E_{\text{V}}^{\text{HfSe}_2/\text{Cg}})\end{aligned}$$

The $(E_{\text{P } 2\text{p}}^{\text{GaP}} - E_{\text{V}}^{\text{GaP}})$ value equals 128.00 ± 0.05 eV, while we get $(E_{\text{Hf } 4\text{f}}^{\text{HfSe}_2/\text{Cg}} - E_{\text{V}}^{\text{HfSe}_2/\text{Cg}}) = 15.69 \pm 0.05$ eV and $(E_{\text{W } 4\text{f}}^{\text{WSe}_2/\text{GaP}} - E_{\text{V}}^{\text{WSe}_2/\text{GaP}}) = 31.71 \pm 0.05$ eV, recorded on a thick HfSe₂ (WSe₂) grown at 450°C and Se-annealed on a Graphene (GaP) substrate. The binding energy differences between W 4f and P 2p CLs (ΔE_{CL_1}), Hf 4f and W 4f CLs (ΔE_{CL_2}), and between Hf 4f and P 2p CLs (ΔE_{CL_3}) are measured on the analysed heterostructure with a take-off angle $\theta = 25^\circ$. As presented in Figure 5.15a, ΔE_{CL_1} amounts to -97.48 ± 0.05 eV, inducing a $\Delta E_{V_{\text{GaP-WSe}_2}}$ of -1.19 ± 0.1 eV, while the ΔE_{CL_2} value for HfSe₂ is measured at -15.46 ± 0.05 eV, resulting in a $\Delta E_{V_{\text{WSe}_2\text{-HfSe}_2}}$ of 0.56 ± 0.1 eV. In complement, we can measure the value ΔE_{CL_3} , which amounts -112.9 ± 0.05 eV and induces a $\Delta E_{V_{\text{GaP-HfSe}_2}}$ of -0.59 ± 0.1 eV in good agreement with the two other results. We can hereby confirm the good coherence of the different ΔE_{V} values. Considering the $E_{\text{VBM}} - E_{\text{F}}$ value of 0.8 eV measured at the surface with UPS, we can propose a final arrangement of the heterostructure in Figure 5.15b, evidencing a staggered gap type-II band alignment with a clear p-n junction between WSe₂ and HfSe₂. If considering the theoretical values of electronic bandgap energy^{49, 296} (~ 1.5 eV) and electron affinity^{43, 72} (~ 3.55 eV) in a multilayer WSe₂, the heterostructure exhibits a strong charge transfer at the WSe₂/HfSe₂ interface with a potential step ΔV about 0.53 eV. Besides, we emphasize a decrease of both $\Delta E_{V_{\text{GaP-WSe}_2}}$ and $\Delta E_{V_{\text{GaP-HfSe}_2}}$ compared to their measurement in section 4.3 (-0.94 eV) and section 5.1.2.2 (-0.49 eV), respectively, evidencing a relatively strong electronic transfer induced by the WSe₂/HfSe₂ heterojunction. It also allows maintaining the staggered type-II band alignment for the GaP/WSe₂ heterojunction for a thicker film with a stronger p-type character ($E_{\text{F}} - E_{\text{VBM}} \sim 0.24$ eV). Overall, we point out the formation of a staggered type-II band alignment between multilayer WSe₂ and HfSe₂ with a clear p-n junction when growing on an n-type substrate. As a broken gap band alignment tend to be more adequate for developing a tunnelling device, the use of an alternative n-type TMDC with a smaller band offset could be considered. For instance, SnSe₂ tends to be a promising candidate to replace HfSe₂, as the ΔE_{CBM} with WSe₂ is estimated at 1.52 eV against 1.05 eV in the current state⁴⁹.

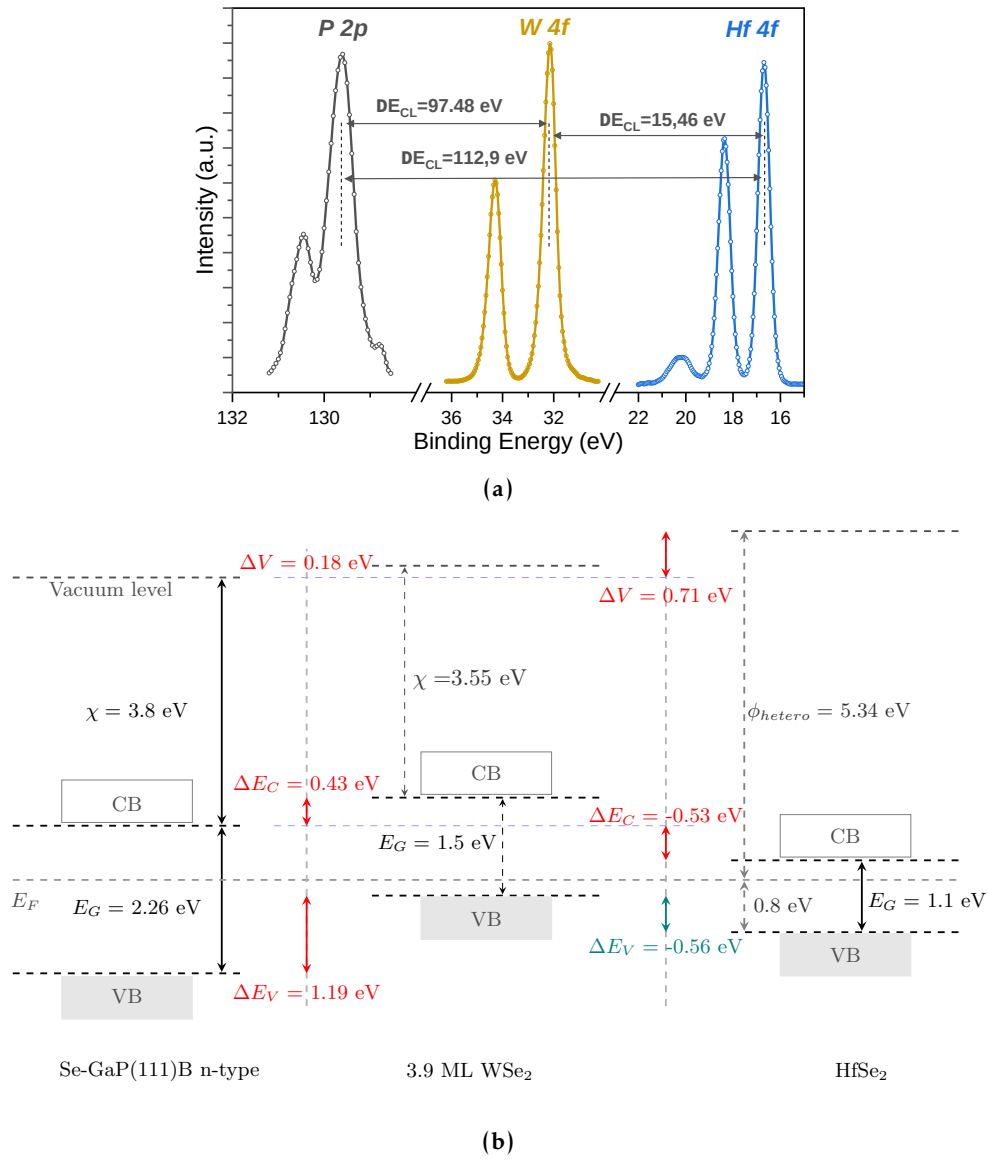


Figure 5.15: (a) ΔE_{CL} measurement with XPS at $\theta=25^\circ$ on the heterostructure and (b) the associated band structure schematic.

Raman spectroscopy (Figure 5.16a) after peeling off the sample for STEM imaging tends to evidence the formation of single phase 2H-WSe₂, with the strong dominance of the A_{1g} contribution at 251.2 cm⁻¹ over the E_{2g}¹ one at 248.9 cm⁻¹. We attribute the weaker peak at 237.8 cm⁻¹ to the selenium protection cap, which is slightly decreasing during the acquisition due to a local vaporisation. Yet, it has been impossible to observe the expected peak at 200 cm⁻¹ attributed to 1T-HfSe₂. Indeed, the STEM and EDX images (Figure 5.16b & 5.16c) exhibit a full oxidation of the HfSe₂ layer through the Se protection layer, while the WSe₂ one is clearly resolved with a clean 2H stacking. The Se layer observed between the WSe₂ and HfO_x layer (Figure 5.16b & 5.16d) can be attributed to the selenium atoms of HfSe₂ being expelled during the oxidation process. Taking into account the XPS and XRD results, we assume that this oxidation has appeared during or after the sample peeling. Yet, it clearly evidences the WSe₂ resistance to oxidation and its promising use in TMDC-based MOS structures. The fast oxidation of HfSe₂ can be also studied and tuned in order to develop thin HfO₂ layers as gate dielectrics of the MOS structure as recently reported in the literature³⁰⁵.

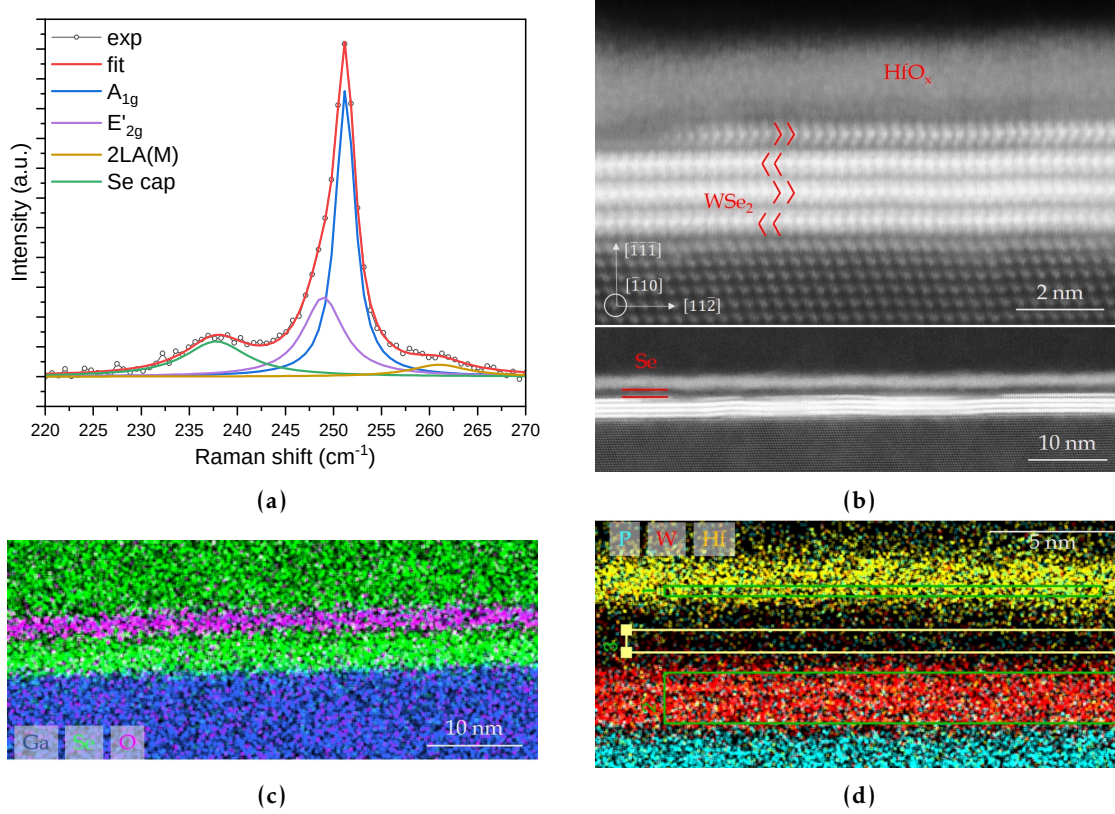


Figure 5.16: (a) Raman spectroscopy measurement on the WSe₂/HfSe₂ heterostructure, (b) the associated HAADF-STEM image along the [-110] zone axis and (c,d) the EDX measurements with the superposition of Ga, Se, O, W, Hf and P signals.

Conclusion

In this Chapter, we have demonstrated the epitaxial growth of few layer HfSe₂ on top of a Se-terminated GaP(111)_B substrate, before studying the formation of a GaP(111)_B/HfSe₂/WSe₂ heterostructure as well as a GaP(111)_B/WSe₂/HfSe₂ one. We have pointed out the effect of the growth and annealing temperatures as well as a high Hf growth rate and a low Se overpressure on the structural and morphological properties, before showing the key role of the growth sequence on the heterostructure properties.

We have evidenced that a low growth temperature of 250°C favours a 2D surface. A subsequent Se-annealing treatment is still required to improve the surface morphology. Following this annealing, the structural properties of the layer are rather independent on T_G in the 250-450°C range. In addition, we point out the systematic formation of a type-I band alignment with a highly n-type doping character.

In a second time, we have demonstrated the clear difficulties in growing a GaP(111)_B/HfSe₂/WSe₂ heterostructure, as this specific stacking tends to promote the mixing of both TMDC layers. It leads to the formation of an interfacial new component X with a metallic behaviour. On the other hand, the GaP(111)_B/WSe₂/HfSe₂ heterostructure has shown promising results with the good alignment of both TMDCs with the GaP substrate, rather low spread angle and grains exceeding 50 nm in size. In addition, XPS and UPS measurement tend to evidence a good van der Waals interface between the two layers. We point out the formation of a staggered type-II band alignment with a clear p-n junction between both TMDCs and a relative strong charge transfer at the WSe₂/HfSe₂ interface.

Conclusion

The goal of this thesis was the epitaxial growth and characterization of WSe_2 , HfSe_2 thin layers and their heterostructure on $\text{GaP}(111)_\text{B}$ by MBE, with a strong focus on their structural, morphological and electronic properties. After reviewing the state of the art linked to TMDCs as well as the different growth and characterization techniques required, the research work was separated in three main axes. First, we have investigated the surface preparation of the $\text{GaP}(111)_\text{B}$ substrate before the epitaxy of few layers WSe_2 by MBE, while that of HfSe_2 as well as the first attempts of $\text{WSe}_2/\text{HfSe}_2$ heterostructure growth were ultimately studied.

Achieving a smooth and fully deoxidized $\text{GaP}(111)_\text{B}$ surface has appeared rather challenging since thermal deoxidation leads to a degradation of the surface morphology. Therefore, we have demonstrated the need for a combination of atomic hydrogen, Hat, and cracked phosphine within a 3-step sequence, while showing the key role of the Hat exposure time on a successful deoxidation. As the optimal process results in serrated atomic step edges, we have tried to improve their morphology by growing a few nanometre thick $\text{GaP}(111)_\text{B}$ buffer layer. However, we have evidenced the difficulty in obtaining flat surfaces, as a too low growth temperature induces the formation of small pyramids, while a too high temperature favours the appearance of triangular nano-holes probably originating from the formation of gallium droplets.

In a second time, we have explored and optimized the selenium termination of the $\text{GaP}(111)_\text{B}$ surface required for a quasi van der Waals growth. We have highlighted a similar morphology before and after the treatment together with a change in chemical environment mainly in the outermost P-surface layer. We have evidenced the reduction of the band bending after treatment, indicating an effective electronic passivation of the surface, although only partial. However, the observation of a sub-surface component in the Se 3d CL has required some process optimisation unveiling the predominant effect of the selenium flux on the presence of this sub-surface component. On the other hand, the temperature has shown little effect between 450°C and 700°C, allowing us to select a passivation temperature close to the TMDC growth one.

Exploiting this promising surface as a substrate, we have demonstrated the epitaxial growth of WSe_2 , pointing out the key role of the growth temperature, the subsequent Se-annealing treatment and to a less extent of the growth rate on the polytype formation, the structural and morphological properties. It appeared that a low growth temperature (T_G) promotes the partial formation of the metastable $1\text{T}'$ phase, coexisting with the dominant 3R stacking in the bilayer regime. The increase of T_G induces a radical change in growth mode from 2D to 3D, resulting in a degradation of the surface roughness, while suppressing the presence of $1\text{T}'$. Besides, it goes along with a reduction of the in-plane disorientation and an improvement of the structural properties. However, increasing the temperature above 500°C

has appeared irrelevant, due to the progressive formation of metallic tungsten clusters even under high selenium flux. A subsequent annealing under selenium flux at 650°C has promoted the suppression of the different features induced by T_G , with a systematic improvement of the morphology and the suppression of the 1T' phase. It results in the formation of a 2H/3R mix phase at 250°C and at 450°C/500°C in the bilayer regime, while promoting a pure 2H phase formation for layers grown at 450°C and 500°C when the thickness exceeds two monolayers. We have highlighted the strong impact of the annealing step in reducing the in-plane disorientation, and the layer micro strain while the effect on the average grain size is more mitigated. Contrarily, a two-step annealing sequence has proven to be effective in increasing the grain size up to ~40-50 nm accompanied with a further decrease of the in-plan disorientation. The annealing treatment does not prevent the formation of metallic tungsten clusters when T_G exceeds 500°C, nor the appearance of an additional P-W bonds. Last, we have confirmed the need of a rather low transition metal growth rate set at 0.002 Å/s in order to avoid the formation of metallic clusters at 450°C, limit the in-plane disorientation and favour the formation of larger grains.

After optimisation, the resulting layers exhibit clear epitaxial relationships with the GaP(111)_B substrate with a well-defined van der Waals interface. We point out the systematic formation of a staggered type-II band alignment between monolayer and bilayer WSe₂ and GaP(111)_B substrate with a highly p-doping character regardless of the substrate doping type. The increase of the film thicknesses has a double effect on the band structure, with a decrease in electronic bandgap altering the band alignment, and an evolution of the WSe₂ doping into ambipolar on n-type GaP substrate. We have unveiled a band-offset difference induced by the substrate doping type with a preferential use of n-type GaP for a more staggered band alignment.

Following the results obtained on WSe₂, the optimisation of the epitaxial growth of HfSe₂ has then been explored starting with the growth a Se-terminated GaP(111)_B substrate, before studying the HfSe₂/WSe₂ heterostructure formation. We have pointed out the effect of the growth and annealing temperatures as well as a high Hf growth rate and a low Se overpressure on the structural and morphological properties of the HfSe₂ epilayer. Whatever T_G , the only phase detected was the 1T one while a low growth temperature of 250°C favours a 2D morphology. A subsequent Se-annealing treatment is still required to improve the surface morphology. In addition, we show the systematic formation of a type-I band alignment with a highly n-doping character at the GaP(111)_B/HfSe₂ interface.

Last, we have demonstrated the clear difficulties in growing a GaP(111)_B/HfSe₂/WSe₂ heterostructure, as this specific stacking results in the mixing of both TMDC layers. It leads to the formation of an upper undesirable compound with a metallic behaviour. On the other hand, the development of a GaP(111)_B/WSe₂/HfSe₂ heterostructure has shown promising results with the good alignment of both TMDCs with the GaP substrate, rather low spread angle and grains exceeding 50 nm in size. In addition, XPS and UPS measurements tend to evidence a good van der Waals interface between the two layers. We point out the formation of a staggered type-II band alignment with a clear p-n junction between both TMDCs and a relative strong charge transfer at the WSe₂/HfSe₂ interface.

These promising results, yet uncompleted, encourage to plan several additional studies. The WSe₂ thickness influence on the stacking formation needs to be further investigated, with the confrontation of our STEM images and Raman spectra with ARPES measurements. Besides, the estimation of the average grain size of HfSe₂ is to be checked or improved with STM imaging. Although the strong oxidation of the HfSe₂ layer compared to WSe₂ has been detrimental to our STEM observation, it could be used and tuned

under O_2 plasma to develop the base of a TMDC MOS structure, as already performed with exfoliated MoS_2 and $HfSe_2$ flakes by Jing et al.³⁰⁵. Regarding the heterojunctions, further growth attempts of the $GaP/HfSe_2/WSe_2$ stacking should be investigated with the $HfSe_2$ layer grown at $250^\circ C$ instead of $450^\circ C$. This will help to determine the origin of the observed interfacial compound. On the other hand, due to the unpredicted oxidation of the $HfSe_2$ layer observed in Chapter 5, the observation of the $GaP/WSe_2/HfSe_2$ heterostructure with STEM should be performed again to confirm the $WSe_2/HfSe_2$ interface quality.

A further critical step would be the characterization of the electrical properties of WSe_2 , $HfSe_2$ layers as well as $WSe_2/HfSe_2$ heterostructures using the 4-probe STM/STS experiment or the 4-probe cryostat in the PCMP platform. This will include the influence of the different TMDC layer thickness on the electronic bandgaps and band offsets. To ease these measurements, a physical mask designed by Corentin Sthioul has been recently installed in the TMDC MBE chamber. It allows the localized growth of the TMDC layers with further deposition of metallic contacts, very suitable for Hall Effect measurements without any etching step. First selective growths of $HfSe_2$ through this mask have been successful, without revealing any material differences with respect to the mask free deposition. The next experiments will consist in properly aligning the metallic contacts on the grown areas. Moreover, the different shapes included in the mask might lead to the *in-situ* formation of TMDC-based vertical or lateral diodes before the contact deposition.

Finally, as a way toward the integration of TMDCs with the silicon technology, the development of epitaxial $GaP(111)/Si(111)$ buffer layers might be considered. This kind of buffer has been successfully grown on $Si(100)$ ³⁰⁶ with further growth of active III-V device layers³⁰⁷. However, on (111) oriented substrates, the main challenge of such growth is the formation of rotational twins, which appeared to degrade the surface quality^{227, 228}.

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calculated 2θ angles values for hexagonal WSe₂, HfSe₂, GaP and GaSe crystals

2H-WSe ₂				1T-HfSe ₂				GaP				GaSe			
<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{th}$	<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{th}$	<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{th}$	<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{th}$
1	0	0	31.01°	1	0	0	27.29°	1	1	1	28.34°	1	0	0	27.29°
1	0	-1	31.59°	1	0	-1	30.71°	2	0	0	32.84°	1	0	-1	27.83°
1	-1	2	33.26°	1	-1	-2	39.36°	2	1	0	36.85°	1	-1	2	29.39°
1	0	3	35.90°	1	1	0	48.24°	2	1	1	40.51°	1	-1	3	31.83°
1	-1	4	39.34°	1	1	1	50.42°	2	-2	0	47.13°	1	-1	4	35.00°
1	-1	5	43.41°	1	-1	-3	51.04°	3	0	0	50.18°	1	-1	-5	38.73°
1	1	0	55.17°	2	0	0	56.31°	3	1	0	53.10°	1	1	0	48.24°
2	-1	1	55.53°	1	1	2	56.60°	3	1	1	55.91°	1	1	1	48.57°
1	1	2	56.62°	2	0	1	58.28°	2	2	2	58.63°	1	1	-2	49.56°
1	1	3	58.39°	2	0	2	63.95°	3	2	0	61.28°	1	1	3	51.18°
1	1	4	60.82°	1	1	-3	66.04°	2	1	3	63.85°	1	1	4	53.38°
1	1	5	63.86°	2	-2	-3	72.86°	4	0	0	68.85°	1	1	5	56.12°
2	0	0	64.65°	3	-1	0	77.25°	4	1	0	71.29°	2	0	0	56.31°
2	-2	1	64.98°	2	1	1	78.94°	4	1	1	73.69°	2	-2	-1	56.61°
2	-2	2	65.96°	3	-2	2	83.96°	3	3	1	76.06°	2	-2	-2	57.50°
2	-2	3	67.59°	3	0	0	90.11°	4	2	0	78.41°	2	0	-3	58.96°
2	-2	4	69.84°	3	-3	1	91.77°	4	2	1	80.74°	2	-2	4	60.97°
2	-2	5	72.69°	3	-2	3	92.25°	3	3	2	83.05°	2	-2	5	63.51°
2	1	0	90.04°	3	-3	2	96.75°	4	2	2	87.64°	2	1	0	77.25°
3	-1	1	90.34°	3	-3	3	105.18°	4	3	0	89.93°	2	1	1	77.50°
3	-1	2	91.23°	2	2	0	109.63°	4	3	1	92.22°	3	-2	2	78.27°
2	1	-3	92.73°	2	2	-1	111.40°	3	3	-3	94.52°	2	1	3	79.54°
3	-1	4	94.83°					4	3	2	99.13°	2	1	4	81.30°
3	-1	5	97.54°					4	-4	0	106.17°	2	1	5	83.56°
3	0	0	106.65°					4	4	1	108.57°	3	0	0	90.11°
3	-3	1	106.96°					4	3	3	111.00°	3	0	1	90.36°
3	-3	2	107.91°									3	-3	2	91.11°
3	-3	3	109.49°									3	0	3	92.35°
3	-3	4	111.73°									3	0	4	94.10°
3	-3	5	114.66°									3	0	5	96.35°
												4	-2	0	109.63°
												2	2	1	109.89°
												4	-2	2	110.69°
												2	2	3	112.03°
												2	2	4	113.92°

theoretical 2θ angles for hexagonal WSe₂, HfSe₂, GaSe and cubic GaP

IMFP, TRFMP, EAL and relative sensitivity factors calculated for XPS measurements

GaP		WSe ₂		HfSe ₂	
N _{Ga}	$2.395 \times 10^{+22} \text{ cm}^{-3}$	N _W	$1.66 \times 10^{+22} \text{ cm}^{-3}$	N _{Hf}	$1.27 \times 10^{+22} \text{ cm}^{-3}$
N _P	$2.395 \times 10^{+22} \text{ cm}^{-3}$	N _{Se}	$3.32 \times 10^{+22} \text{ cm}^{-3}$	N _{Se}	$2.53 \times 10^{+22} \text{ cm}^{-3}$
σ_{Ga}	1.085	σ_{W}	9.8	σ_{Hf}	7.52
σ_{P}	1.192	σ_{Se}	2.294	σ_{Se}	2.294
β_{Ga}	1.012	β_{W}	1.043	β_{Hf}	1.046
β_{P}	1.136	β_{Se}	1.09	β_{Se}	1.09

Atomic densities, photoemission cross-section and asymmetry parameters for GaP, WSe₂ and HfSe₂

$\lambda_{\text{in}}^{\text{W-WSe}_2}$	$\lambda_{\text{tr}}^{\text{W-WSe}_2}$	$\lambda_{\text{in}}^{\text{Se-WSe}_2}$	$\lambda_{\text{tr}}^{\text{Se-WSe}_2}$	$\lambda_{\text{in}}^{\text{Ga-WSe}_2}$	$\lambda_{\text{tr}}^{\text{Ga-WSe}_2}$	$\lambda_{\text{in}}^{\text{P-WSe}_2}$	$\lambda_{\text{tr}}^{\text{P-WSe}_2}$
26.07Å	75.59Å	25.76Å	74.27Å	26.25Å	76.38Å	24.72Å	69.81Å
$L_{\text{TH}}^{\text{W-WSe}_2}$		$L_{\text{TH}}^{\text{Se-WSe}_2}$		$L_{\text{TH}}^{\text{Ga-WSe}_2}$		$L_{\text{TH}}^{\text{P-WSe}_2}$	
21.22Å		20.95Å		21.37Å		20.04Å	

IMFP and EAL for a finite WSe₂ layer on top of GaP

$\lambda_{\text{in}}^{\text{W-WSe}_2}$	$\lambda_{\text{tr}}^{\text{W-WSe}_2}$	$\lambda_{\text{in}}^{\text{Se-WSe}_2}$	$\lambda_{\text{tr}}^{\text{Se-WSe}_2}$	$\lambda_{\text{in}}^{\text{Ga-GaP}}$	$\lambda_{\text{tr}}^{\text{Ga-GaP}}$	$\lambda_{\text{in}}^{\text{P-GaP}}$	$\lambda_{\text{tr}}^{\text{P-GaP}}$
26.07Å	75.59Å	25.76Å	74.27Å	30.41Å	138.10Å	28.60Å	123.80Å
$L_{\text{QA}}^{\text{W-WSe}_2}$		$L_{\text{QA}}^{\text{Se-WSe}_2}$		$L_{\text{QA}}^{\text{Ga-GaP}}$		$L_{\text{QA}}^{\text{P-GaP}}$	
24.81Å		24.51Å		29.44Å		27.65Å	

IMFP and EAL for infinite WSe₂ and GaP layers

$\lambda_{in}^{Hf-HfSe_2}$	$\lambda_{tr}^{Hf-HfSe_2}$	$\lambda_{in}^{Se-HfSe_2}$	$\lambda_{tr}^{Se-HfSe_2}$	$\lambda_{in}^{Ga-HfSe_2}$	$\lambda_{tr}^{Ga-HfSe_2}$	$\lambda_{in}^{P-HfSe_2}$	$\lambda_{tr}^{P-HfSe_2}$
28.13 Å	84.23 Å	27.58 Å	81.75 Å	28.09 Å	84.03 Å	26.44 Å	76.74 Å
$L_{TH}^{Hf-HfSe_2}$		$L_{TH}^{Se-HfSe_2}$		$L_{TH}^{Ga-HfSe_2}$		$L_{TH}^{P-HfSe_2}$	
23.00 Å		22.52 Å		22.97 Å		21.52 Å	

IMFP and EAL for a finite HfSe₂ layer on top of GaP

$\lambda_{in}^{Hf-HfSe_2}$	$\lambda_{tr}^{Hf-HfSe_2}$	$\lambda_{in}^{Se-HfSe_2}$	$\lambda_{tr}^{Se-HfSe_2}$	λ_{in}^{Ga-GaP}	λ_{tr}^{Ga-GaP}	λ_{in}^{P-GaP}	λ_{tr}^{P-GaP}
28.13 Å	84.23 Å	25.78 Å	81.75 Å	30.41 Å	138.10 Å	28.60 Å	123.80 Å
$L_{QA}^{Hf-HfSe_2}$		$L_{QA}^{Se-HfSe_2}$		L_{QA}^{Ga-GaP}		L_{QA}^{P-GaP}	
26.81 Å		26.27 Å		29.44 Å		27.65 Å	

IMFP and EAL for infinite HfSe₂ and GaP layers

S_W/S_{Ga}	7.657	S_{Hf}/S_{Ga}	6.353
S_{Se}/S_{Ga}	1.787	S_{Se}/S_{Ga}	1.916
S_W/S_P	7.243	S_{Hf}/S_P	6.008
S_{Se}/S_P	1.691	S_{Se}/S_P	1.812

Relative sensitivity factors estimation from EAL calculations

Gwyddion treatment for statistical measurements with AFM imaging

The different AFM images are treated using the GwyddionTM software for brief statistical calculations by leveling them using the option "frequency split" with a 33 nm wavelength to artificially suppress the impact of the substrate roughness before marking the remaining grains by threshold as represented in Figure C.1. The generated mask is pasted on the initial AFM image before filtering the grains with a lower threshold of 60 pixels and removing every grain whose are touching the edges of the image.

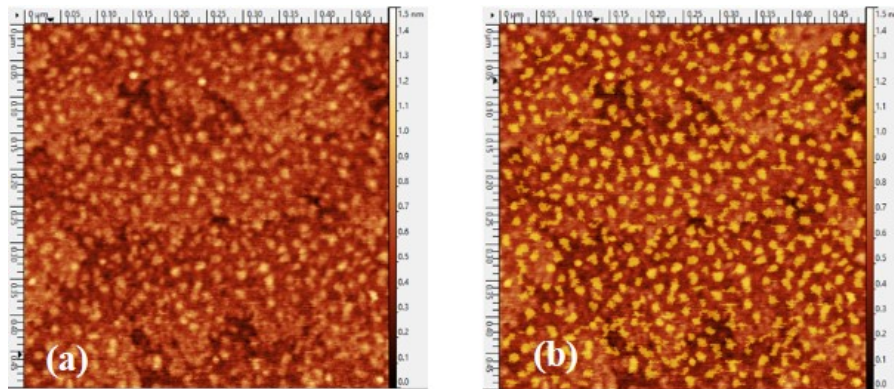


Figure C.1: (a) Initial AFM image. (b) Grain selection for statistical calculation using Gwyddion.

Acronyms

[Numbers](#) | [A](#) | [B](#) | [C](#) | [D](#) | [E](#) | [F](#) | [G](#) | [H](#) | [I](#) | [K](#) | [L](#) | [M](#) | [N](#) | [P](#) | [Q](#) | [R](#) | [S](#) | [T](#) | [U](#) | [V](#) | [X](#)

Numbers

1H Trigonal prismatic. [5](#), [73](#)

1T Octahedral. [5](#), [73](#)

2DMs Two-dimensional Materials. [1](#)

A

AFM Atomic Force Microscopy. [17](#), [48](#), [51](#), [71](#), [107](#)

ALD Atomic Layer Deposition. [13](#)

ARPES Angle Resolved PhotoEmission Spectroscopy. [17](#), [48](#), [77](#)

B

BD Backward Diode. [28](#)

BE binding energy. [67](#)

BEP beam equivalent pressure. [35](#)

BLG Bilayer Graphene. [18](#)

C

CBM Conduction band minimum. [7](#), [23](#)

CDW Charge Density Wave. [18](#), [21](#)

CL Core level. [42](#), [52](#), [54](#), [76](#), [106](#)

CVD Chemical Vapor Deposition. [2](#), [11](#), [75](#)

D

DFT Density Functional Theory. [7](#), [8](#), [23](#)

E

EAL Effective Attenuation Length. [44](#)

ED Esaki Diode. [28](#)

EDX Energy-dispersive X-ray Spectroscopy. [49](#), [116](#)

EDXS Energy-dispersive X-Ray Spectrometer. [49](#)

F

FET Field Effect Transistor. [1](#), [23](#)

FIB Focus Ion Beam. [49](#)

FWHM Full Width at Half Maximum. [40](#), [75](#), [106](#)

G

GGA Generalized gradient approximation. [24](#)

H

H_{AT} Atomic Hydrogen. [31](#), [52](#)

HF High Frequency. [28](#)

HOPG Highly Ordered Pyrolytic Graphite. [15](#), [17](#), [109](#)

HSE Heyd Scuseria Ernzerhof. [90](#)

I

IEMN Insitute of Electronic, Microelectronic and Nanotechnology. [33](#)

IMFP Inelastic Mean Free Path. [42](#)

K

KMC Kinetic Monte Carlo. [15](#)

L

LDA Local Density Approximation. [7](#), [8](#)

LED Light Emitting Diode. [26](#)

LEED Low Energy Electron Diffraction. [21](#), [38](#), [39](#), [53](#), [73](#)

M

MBE Molecular Beam Epitaxy. [2](#), [5](#), [9](#), [13](#), [33](#), [51](#)

MOCVD MetalOrganic Chemical Vapor Deposition. [11](#), [12](#)

MOSFET Metal Oxide Semiconductor Field Effect Transistor. [9](#)

MTB Mirror Twin Grain Boundaries. [21](#), [74](#)

N

NDR Negative Differential resistance. [28](#)

NIST National Institute of Standards and Technology. [45](#)

P

PCMP-PCP multi-physics characterization platform. [49](#), [50](#)

PH₃ Phosphine. [31](#), [51](#)

PL Photoluminescence. [23](#)

PLD Pulsed Laser Deposition. [13](#)

PVCR Peak-to-valley current ratio. [28](#)

Q

QSH Quantum spin Hall effect. [18](#), [25](#)

R

RHEED Reflection High Energy Electron Diffraction. [19](#), [34](#), [38](#), [51](#), [73](#), [105](#)

RTD Resonant Tunnelling Diode. [28](#)

S

sccm standard cubic centimetres per minute. [34](#)

SEM Scanning Electronic Microscope. [49](#)

STEM Scanning Transmission Electronic Microscopy. [45](#), [49](#), [74](#), [107](#)

STM Scanning Tunnelling Microscopy. [17](#), [49](#)

STS Scanning Tunnelling Spectroscopy. [18](#), [23](#), [50](#), [99](#)

T

T_{DEOX} oxide removal temperature. [31](#)

T_G Growth temperature. [15](#)

TM Transition Metal. [5](#)

TMDC Two-dimensional Transition Metal Dichalcogenide. [1](#), [5](#), [33](#), [51](#)

TRMFP Transport Mean Free Path. [44](#)

U

UHV Ultra-high vacuum. [13](#), [33](#), [40](#), [61](#), [71](#), [77](#)

UPS Ultra-violet Photoelectron Spectroscopy. [46](#), [54](#), [84](#), [109](#)

V

V_M Transition Metal growth rate. [15](#)

VBM Valence band maximum. [7](#), [23](#), [46](#), [55](#), [77](#), [109](#)

X

XP X-Ray Photoelectron Diffraction. [45](#), [63](#)

XPS X-Ray Photoelectron Spectroscopy. [40](#), [52](#), [76](#)

XRD X-Ray Diffraction. [18](#), [20](#), [36](#), [79](#), [108](#)

Abstract

Two-dimensional materials (2DMs) offer unique properties primarily due to their crystallographic structure, which consists of weakly coupled layers composed of one to few atomic planes where the atoms are covalently bonded. This specific structure results in the absence of dangling bonds at the surface, allowing the formation of heterostructures without the need to adapt the crystal lattice parameter. Among 2DMs, **transition metal dichalcogenides (TMDCs)** of formula MX₂ (M=metal, X=Se, Te or S) are particularly interesting because, unlike graphene, some of them have band gaps ranging from 0.5 to 2 eV and present a wide variety of band structure alignments. These properties make TMDCs promising candidates for various components, including those based on the inter-band tunnelling effect. Until now, most devices have been manufactured using exfoliated or transferred layers or flakes, which introduces significant issues regarding interface integrity, precise rotational alignment between successive layers, and process reliability.

In the last decade, **Molecular Beam Epitaxy (MBE)** growth has garnered significant interest in developing TMDC-based heterostructures, especially on 2D substrates like graphene, h-BN, or mica, due to the natural van der Waals interface between the epi-layer and the substrate surface. Additionally, a new generation of heterojunctions has emerged using 3D substrates such as insulating Al₂O₃(0001) or AlN(0001), emphasizing the critical importance of surface preparation before growth. Recently, the successful growth of a WSe₂ monolayer as well as that of large-area, highly oriented MoSe₂/WSe₂ heterostructures have been demonstrated on a selenium-passivated GaAs(111)_B surface. This raises new interest in using III-V semiconductors as substrates for TMDC-based optoelectronic and microelectronic device development. However, Monte Carlo simulations have highlighted the necessity of high growth temperatures to enhance the TMDC grain size, which makes GaP a suitable alternative to GaAs, thanks to its similar crystallography and significantly higher thermal stability.

In this work, we study the MBE growth of few-layer WSe₂ and HfSe₂, as well as that of the HfSe₂/WSe₂ heterostructure on a GaP(111)_B substrate. Each step of the process has been investigated, with particular emphasis on the substrate surface preparation, the crystalline quality of the obtained layers and the preservation of the interface integrity of the heterojunction. We show that the use of a combination of atomic hydrogen and cracked phosphine in a three-step deoxidation sequence allows to get a smooth deoxidized GaP(111)_B surface. To favour the formation of a quasi van der Waals gap between the substrate and the TMDC overlayer, selenium termination of the GaP(111)_B surface is then achieved. Thanks to a combination of experimental techniques, we then demonstrate the epitaxy of WSe₂ and HfSe₂ on GaP(111)_B-Se, emphasizing the critical role of the growth temperature and subsequent Se-annealing treatment on the polytype formation, structural and morphological properties. The resulting layers show clear epitaxial relationships with the GaP(111)_B substrate and a well-defined van der Waals interface. WSe₂ reveals a p-type doping and a staggered type-II band alignment with the GaP substrate, while HfSe₂ exhibits a type-I band alignment and a highly n-doped character. Finally, we discuss the challenges in developing a GaP/HfSe₂/WSe₂ heterostructure due to the formation of a (Hf/W)Se_x compound, whereas the GaP/WSe₂/HfSe₂ stacking presents promising results with a staggered type-II band alignment leading to a p-n junction.

Keywords: material science, transition metal dichalcogenides, molecular beam epitaxy, photoelectron spectroscopy, grazing incidence x-ray diffraction, transmission electron microscopy

Résumé

Les **matériaux bidimensionnels (2MDs)** offrent des propriétés uniques principalement dues à leur structure cristallographique, composée de couches faiblement couplées constituées d'un à quelques plans atomiques où les atomes sont liés de manière covalente. Cette structure spécifique entraîne l'absence de liaisons pendantes à la surface, permettant la formation d'hétérostructures sans nécessité d'adaptation du paramètre de maille. Parmi les 2MDs, les **dichalcogénures de métaux de transition (DMTs)**, de formule MX₂ (M=métal, X=Se, Te ou S), sont particulièrement intéressants car certains d'entre eux possèdent des bandes interdites allant de 0,5 à 2 eV et offrent une grande variété d'alignements de bandes. Ces caractéristiques en font, des candidats prometteurs pour le développement de divers composants, notamment ceux basés sur l'effet tunnel inter-bandes. Jusqu'à présent, la plupart des dispositifs ont été fabriqués en utilisant des couches ou des flocons exfoliés ou transférés, introduisant des problèmes significatifs concernant la qualité des interfaces ainsi que la fiabilité du processus.

Au cours de la dernière décennie, la croissance **épitaxiale par jets moléculaires (EJM)** a suscité un grand intérêt pour le développement d'hétérostructures basées sur les DMTs, notamment sur des substrats 2D comme le graphène, h-BN ou le mica en raison de l'interface van der Waals naturelle entre la couche épitaxiée et le substrat. En parallèle, une nouvelle génération d'hétérojonctions a émergé, utilisant des substrats 3D tels que l'Al₂O₃(0001) ou l'AlN(0001), et soulignant l'importance cruciale de la préparation de la surface avant croissance. Ainsi, la croissance d'une monocouche de WSe₂ ou celle d'une hétérostructure MoSe₂/WSe₂ ont été réalisées sur une surface GaAs(111)_B précédemment passivée sous sélénium, suscitant un nouvel intérêt pour l'utilisation de semi-conducteurs III-V comme substrats pour le développement de dispositifs basés sur les DMTs. Cependant, des simulations Monte Carlo ont souligné la nécessité de températures de croissance élevées afin d'améliorer la taille des grains des DMTs, faisant du GaP une alternative appropriée au GaAs, grâce à sa stabilité thermique nettement supérieure.

Dans ce travail de thèse, nous explorons la croissance par EJM de quelques couches de WSe₂ et de HfSe₂, ainsi que celle de l'hétérostructure HfSe₂/WSe₂ sur un substrat GaP(111)_B. Chaque étape du processus a été étudiée, avec une attention particulière à la préparation du substrat, à la qualité cristalline des couches obtenues et à la préservation de l'intégrité de l'interface de l'hétérojonction. Nous montrons que l'utilisation d'une combinaison d'hydrogène atomique et de phosphine craquée dans une séquence en trois étapes permet d'obtenir une surface GaP(111)_B lisse et complètement désoxydée. Pour favoriser la formation d'un quasi-gap de van der Waals entre le substrat et la couche DMT, la terminaison au sélénium de la surface de GaP(111)_B est ensuite réalisée. Grâce à une combinaison de techniques expérimentales, nous démontrons l'épitaxie de WSe₂ et de HfSe₂ sur GaP(111)_B-Se, en soulignant le rôle crucial de la température de croissance et d'un recuit sous Se sur la formation des polytypes, les propriétés structurales et morphologiques. Les couches résultantes présentent des relations épitaxiales claires avec le substrat GaP(111)_B et une interface van der Waals bien définie. WSe₂ présente un dopage de type p et un alignement de bandes de type II avec le substrat GaP, tandis que HfSe₂ révèle un alignement de bandes de type I et un caractère fortement dopé n. Enfin, nous discutons des défis du développement d'une hétérostructure GaP/HfSe₂/WSe₂ en raison de la formation d'un composé (W/Hf)Se_x, tandis que l'empilement GaP/WSe₂/HfSe₂ montre des résultats prometteurs avec un alignement de type II et une jonction p-n claire.

Mots clés : science des matériaux, dichalcogénures de métaux de transition, épitaxie par jets moléculaires, spectroscopie photoélectronique, diffraction des rayons x en incidence rasante, microscopie électronique à transmission
