

PAPER

Substrate dependent electronic structure variations of van der Waals heterostructures of MoSe_2 or $\text{MoSe}_{2(1-x)}\text{Te}_{2x}$ grown by van der Waals epitaxy

To cite this article: Horacio Coy Díaz *et al* 2017 *2D Mater.* **4** 025094

View the [article online](#) for updates and enhancements.

Related content

- [Molecular beam epitaxy of the van der Waals heterostructure \$\text{MoTe}_2\$ on \$\text{MoS}_2\$: phase, thermal, and chemical stability](#)
Horacio Coy Díaz, Redhouane Chaghi, Yujing Ma *et al.*
- [Multimodal spectromicroscopy of monolayer \$\text{WS}_2\$ enabled by ultra-clean van der Waals epitaxy](#)
C Kastl, C T Chen, R J Koch *et al.*
- [2D Materials Advances: From Large Scale Synthesis and Controlled Heterostructures to Improved Characterization Techniques, Defects and Applications](#)
Zhong Lin, Amber McCreary, Natalie Briggs *et al.*

Recent citations

- [Electronic Properties of Transferable Atomically Thin \$\text{MoSe}_2/\text{h-BN}\$ Heterostructures Grown on \$\text{Rh}\(111\)\$](#)
Ming-Wei Chen *et al*
- [Telluride-Based Atomically Thin Layers of Ternary Two-Dimensional Transition Metal Dichalcogenide Alloys](#)
Amey Apte *et al*
- [Unraveling the Structural and Electronic Properties at the \$\text{WSe}_2\$ -Graphene Interface for a Rational Design of van der Waals Heterostructures](#)
Stefano Agnoli *et al*



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.



PAPER

Substrate dependent electronic structure variations of van der Waals heterostructures of MoSe₂ or MoSe₂(1-x)Te_{2x} grown by van der Waals epitaxyHoracio Coy Diaz¹, Yujing Ma¹, Sadhu Kolekar¹, José Avila^{2,3}, Chaoyu Chen^{2,3}, Maria C Asensio^{2,3} and Matthias Batzill¹¹ Department of Physics, University of South Florida, Tampa, FL 33647, United States of America² Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin-BP 48, Gif sur Yvette Cedex 91192, France³ Université Paris-Saclay, L'Orme des Merisiers, Saint Aubin-BP 48, Gif sur Yvette Cedex 91192, FranceE-mail: mbatzill@usf.edu**Keywords:** heterostructure, interface, electronic structure**Abstract**

Substrate induced variation of the electronic structure of MoSe₂ monolayers is studied. MoSe₂ is directly grown by van der Waals epitaxy on MoS₂ and highly ordered pyrolytic graphite (HOPG). In this article, we give a review of growth of transition metal dichalcogenides (TMDCs) by van der Waals epitaxy and discuss previously found evidence for the modifications of the electronic structure of TMDCs by van der Waals substrates. Using angle resolved photoemission spectroscopy and scanning tunneling microscopy/spectroscopy we determine the dispersion of the valence band and the band gap, respectively. For MoSe₂ on graphite the valence band resembles that expected for free standing single layer MoSe₂, however, the substrate induces a narrowing of the overall band gap. For MoSe₂ on MoS₂ evidence for hybridization of the valence band maximum between the monolayer and the substrate are presented. Such hybridization, results in an alignment of the valence band maximum (VBM) of MoSe₂ with the binding energy of the VBM of the MoS₂-substrate at the Γ -point. Furthermore, the VBM at the Γ -point is very close in energy to that of the VBM at the K-point. The effective electron mass around the Γ -point is also much decreased for MoSe₂ on MoS₂- compared to HOPG-substrates or free standing MoSe₂ monolayers. This indicates that in TMDC heterostructures interlayer interactions significantly modify the electronic structure and the resulting properties are in between those of free-standing monolayer and bulk materials. In an attempt to control the electronic states incorporation of Te by formation of MoSe₂(1-x)Te_{2x} has been investigated. While shifts in the core level position are observed, the VBM states are found to be very similar to those of pure MoSe₂.

1. Introduction

Van der Waals heterostructures promise to enable the combination of diverse materials with atomically sharp interfaces [1, 2]. The weak interlayer interactions suggest that very different materials can be stacked or grown on top of each other with disregard of lattice-matching conditions that are otherwise limiting the material combination for high quality epitaxial films of '3D' materials [3].

The research in van der Waals heterostructures has received renewed interest since the advent of mechanical exfoliation of single- or few-layer materials and their 'arbitrary' reassembling into heterostructures [4]. This relatively simple and inexpensive approach led to the

discovery of fundamental physical behaviors [5–7], proof-of-principle device fabrications [8–13], and characterization of optical responses in van der Waals heterostructures [14–19]. At the same time efforts are underway to directly grow van der Waals heterostacks [20–37] and their lateral heterojunctions [38, 39]. The two main growth methods are chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) [1, 40]. Advantages of CVD growth are the lower cost, as well as the larger achievable grains and possibly lower defect concentrations enabled by the higher growth temperatures and pressures in CVD compared to MBE. MBE may, however, have advantages in the relative easy combination of materials, doping, formation of alloys, and growth of chemically less stable van der Waals materials,

which require ultra-high vacuum (UHV) conditions for growth and handling, i.e. generally MBE is more flexible. In this article, we review the initial work done as early as the 1990's on van der Waals epitaxy. Then we highlight key aspects developed recently on how the properties in van der Waals heterostructures are modified from those of single component bulk materials and/or the properties of free-standing single monolayers. This review is followed by original work on MBE grown MoSe_2 and mixed $\text{MoSe}_x\text{Te}_{2-x}$ monolayer materials supported on MoS_2 and highly ordered pyrolytic graphite (HOPG).

2. Brief review of van der Waals epitaxy and properties of van der Waals heterostructures

Van der Waals epitaxy [3, 41] is not a new concept but has attracted renewed interest in recent years. Van der Waals epitaxy refers to the crystallographically aligned growth of layered materials on a substrate, where the two materials may be exhibiting a large lattice mismatch. In this context, we call layered materials any material that exhibits strong in-plane covalent and ionic bonding and only weak, mostly van der Waals interactions between its layers. The substrate may be another layered, 'van der Waals' material, or the surface of a 'bulk-3D' material. Here, we are concerned with van der Waals heterostructures, i.e. systems where the growth substrate is also a layered material and thus we exclusively discuss purely van der Waals heterostructures. Although the main point of van der Waals epitaxy is that the weak interaction between the grown layer and the substrate results in no forced registry of the overlayer onto the substrate lattice, i.e. both the substrate and the overlayer maintain their bulk lattice constants, it is called 'epitaxy' because the grown film has a rotational registry with the substrate. Thus, all nucleated grains should have the same crystallographic orientation so that, in an ideal case, a single domain epitaxial film is formed upon coalescence of the grains.

Early studies of van der Waals heterostructures were primarily conducted in Japan by the Koma-group and in Germany by the Jaegermann-group. In these studies a variety of layered transition metal dichalcogenides (TMDCs) and post-transition metal (In, Sn, Ga) selenides were grown on bulk van der Waals substrates by MBE or metalorganic vapor deposition [42–47]. One point of interest was the interlayer band alignment and formation of quantum well states in such atomically sharp interfaces with weak chemical interactions [48–52]. In these studies the band alignment was mainly characterized by photoemission spectroscopy. Noteworthy is an angle resolved photoemission study that demonstrated the change of band structure of WS_2 as a function of layers [53]. In this study WS_2 was grown on HOPG and it was observed that for monolayer WS_2 the valence band maximum is located at the K-point and not at the Γ -point as in the bulk. This drastic change in the electronic structure was correctly interpreted

as a consequence of the interlayer interaction. This work did not receive much interest in 2001 when it was published. Only the recent optical photoluminescence measurements on TMDCs that demonstrated the transition from an indirect- to a direct- band gap semiconductor, as TMDC is thinned to single layer by mechanical exfoliation [54], renewed the interest in the direct measurement of k-space resolved band structure of TMDCs. NanoARPES studies in a photoemission electron microscope (PEEM) on exfoliated flakes [55] as well as ARPES studies of TMDCs grown by MBE on graphene [56, 57] have been performed and are in agreement with the earlier studies. The effects of interlayer interaction in TMDCs on their electronic structure may be divided into two aspects. One effect is due to the interaction of the frontal orbitals between layers, which are commonly the chalcogen p-orbitals, causing a variation of the part of the valence band that is p-derived [58, 59]. For Mo- and W- chalcogenides these are the states at the Γ -point. Consequently, for monolayer the binding energy of the valence band maximum at the Γ -point is increased, and thus moving the valence band maximum (VBM) from the Γ -point in bulk or bi-layer materials to the K-point for the monolayer. Another effect is observed in heterostructures of van der Waals materials in particular TMDCs on conducting substrates, i.e. materials with free charge carriers. In such heterostructures it has been observed that screening effects by the substrate electrons can modify the electronic structure of the TMDCs [60–63]. In particular, such screening will result in a band renormalization which causes a narrowing of the band gap of the TMDCs. In addition to these interlayer interactions, quantum confinement effects in monolayers become important that results in a widening of the band gap for monolayers compared to bulk materials [64].

The aforementioned interlayer orbital interactions reshape the electronic and optical properties for monolayers compared to bulk materials. However, it may also be important in heterostructures when two dissimilar TMDCs are being combined. In heterostructures some interaction between the frontal orbitals is still expected and thus these interactions should modify the electronic structure compared to free-standing monolayers. However, while in a homostructure the spatial relationship between orbitals of the two layers are all the same, in heterostructures the lattice mismatch between the individual layers gives a variety of relative spatial relationships of frontal orbitals from the two layers. In general, lattice mismatched 2D materials will form a moiré structure, where the relative atom positions between the two layers varies within the moiré unit cell. The formation of moiré unit cells in van der Waals epitaxy was first reported from low energy electron diffraction (LEED) for $\text{WS}_2/\text{MoTe}_2(0001)$ [65]. Since then, moiré structures have been observed in STM studies of TMDCs grown on various van der Waals substrates. The variation of the coordination between the atoms in two layers within the moiré unit cell thus suggests that the electronic structure may

also be modulated within the unit cell. Density functional theory calculations have shown that, depending on the interlayer coordination such an electronic structure modulation should exist [66, 67]. Recent scanning tunneling spectroscopy (STS) on a $\text{MoS}_2/\text{WSe}_2$ heterostructure has shown that the electronic structure for such a TMDC heterostructure is indeed modified with a variation amplitude of 0.15 eV for the band gap within the moiré unit cell [68]. In another recent study, micro ARPES was used to characterize the interlayer hybridization in $\text{MoSe}_2/\text{WSe}_2$ heterostructures fabricated by mechanical exfoliation and careful alignment of the monolayer flakes [69]. Evidence of hybridization in the heterostructure at the Γ -point was found. In addition to the bands that were assigned to monolayer MoSe_2 and WSe_2 , a third band was observed. This new band has been assigned to interlayer hybridization. It was suggested that this hybridization occurs in commensurate regions while the pure monolayer bands are observed in regions where the two layers are incommensurate. Although the observed hybridization band is at lower binding energy than the valence band maxima of the monolayer materials, it is still at a slightly higher binding energies than the valence band maximum at K. Thus, the heterostructure of $\text{MoSe}_2/\text{WSe}_2$ remains a direct band gap material. In summary, both recent STS and micro-ARPES studies on TMDCs heterostructures demonstrate that a naïve picture for van der Waals heterostructures that describes the electronic structure as the sum of the properties of the individual layers, does not hold. Instead the properties of heterostructures are modified by interlayer interactions. This should also be observed in directly grown TMDC heterostructures by MBE, while TMDCs grown on non-TMDCs, like HOPG, should not exhibit the same hybridization effects at the Γ point of the TMDCs. Generally speaking, interlayer hybridization can only be observed where orbitals overlap in momentum and energy which enables hybridization at the Γ point of two TMDCs, but gives rise to different hybridization effects in very dissimilar materials such as graphene/TMDCs [70].

Here we investigate the properties of MBE grown MoSe_2 monolayers. We find strong dependence of the electronic structure of MoSe_2 on the substrates. In particular, we find evidence of the VBM to be energetically aligned to the VBM of the substrate at the Γ point if grown on another TMDC (i.e. MoS_2). Furthermore, the band dispersion at the Γ point is modified for monolayers on MoS_2 compared to HOPG substrates, with the former exhibiting more ‘bulk’ like dispersion and the latter more ‘monolayer’ like dispersion. We also expand our studies to selenide/telluride alloys and investigate the formation of $\text{MoSe}_{2(1-x)}\text{Te}_{2x}$ solid solutions by MBE.

3. Experimental methods

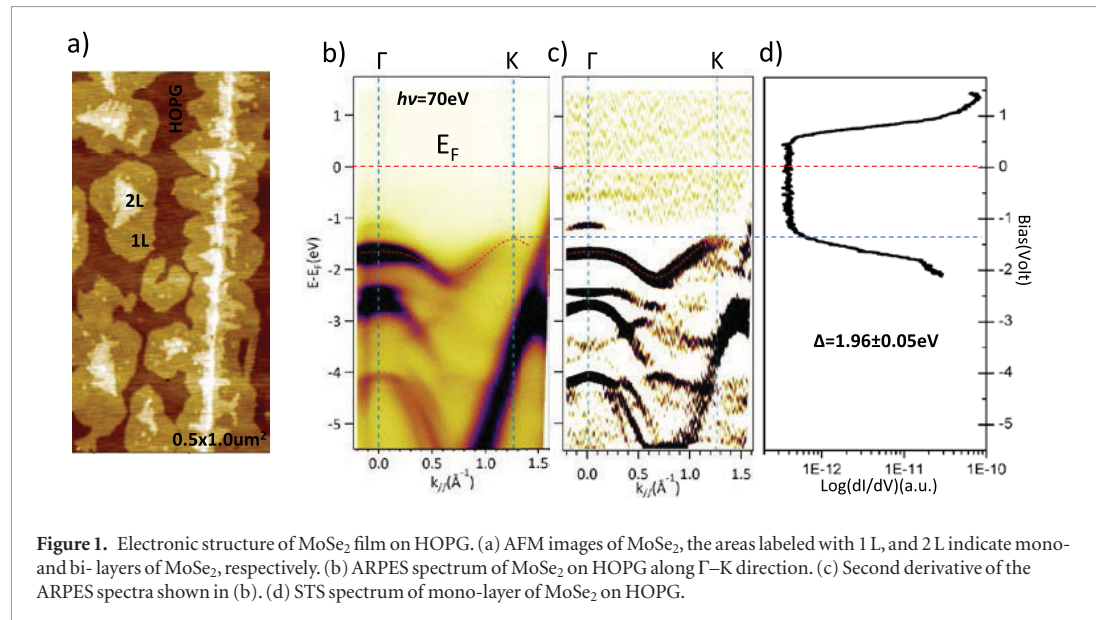
All the experiments were conducted in UHV. The substrates for growth of MoSe_2 or $\text{MoSe}_{2(1-x)}\text{Te}_{2x}$ were commercial HOPG, and synthetically grown single crystalline MoS_2 . These substrates were cleaved in air

and immediately introduced into the vacuum chamber. The growth chamber had a base pressure of 10^{-9} Torr. Before growth, the substrates were outgassed for 4 h at 300 °C. For growth of mono- to few-layer films, Mo was evaporated from a home-built water-cooled e-beam evaporator. For the evaporant a 2 mm diameter, high purity Mo-rod was used. Atomic selenium was supplied by a valved, hot-wall selenium cracker source, while tellurium was evaporated from a water-cooled effusion cell. The films were grown with chalcogen flux 10 times higher than that of molybdenum flux, at a growth temperature of 300 °C. The growth rate was controlled to be slow with about 1 h for a monolayer. The growth rate varied slightly for different substrates, suggesting that the sticking of the Mo-containing precursors may be different on different substrates. Particularly for HOPG the growth rate was only about $\frac{3}{4}$ that for the growth on MoS_2 substrates under otherwise identical growth conditions.

After completion of the growth, the sample was transferred *in situ* to the analysis chamber with help of a magnetically coupled transfer arm. The mu-metal analysis chamber was equipped with an Omicron Sphera-II electrostatic analyzer for photoemission spectroscopy. For x-ray photoemission spectroscopy (XPS) a Mg/Al dual anode x-ray source and for ultraviolet photoemission spectroscopy (UPS) a VUV He-discharge lamp was used. The analysis chamber also hosts a room temperature scanning tunneling microscope (STM) (Omicron STM 1). Additional analysis was performed in a separate variable temperature STM that allowed cooling of the sample to 15 K with a closed-cycle cryostat. The samples were transferred into the variable temperature STM in a vacuum suitcase without exposing them to air. The pressure in the vacuum suitcase was maintained at $\sim 10^{-8}$ Torr with an ion getter pump during transfer. STM imaging and local STS was acquired with a cut PtIr- tip. For dI/dV spectroscopy a lock-in amplifier with a modulation voltage of 7 mV and reference frequency of 995 Hz was used. Finally, for a few selected samples Micro-ARPES measurements were performed at the ANTARES beamline in SOLEIL synchrotron in France. The beam spot size was $\sim 120 \mu\text{m}$. The angular and energy resolution of the beamline at a photon energy of 40 eV are $\sim 0.2^\circ$ and $\sim 10 \text{ meV}$, respectively. All ARPES data were collected with the sample at 300 K.

4. Results and discussion

MoSe_2 films are grown by MBE on van der Waals substrates and characterized without exposure to air. In addition, MoSe_2 films could also be doped with Te by co-deposition of Se and Te. Samples were characterized by XPS, UPS, scanning tunneling microscopy and spectroscopy at the University of South Florida as well as by ARPES at the ANTARES beamline at SOLEIL synchrotron in France. We first concentrate on the question how the van der Waals substrate influences the electronic structure of MoSe_2 . Then, how Se



substitution by Te affects the stability and electronic structure.

4.1. Electronic structure of MoSe₂ on HOPG- versus MoS₂- substrates

MoSe₂ has been grown on HOPG- and MoS₂- substrates. While the MoS₂ substrate was single crystalline, HOPG is naturally polycrystalline, however, the grains are large enough to enable micro-ARPES measurements. The main question we want to address in this study is the influence of the substrate on the electronic structure of MoSe₂. The conductive nature of HOPG may cause a strong band renormalization, i.e. narrowing of the band gap compared to free-standing MoSe₂, while for MoSe₂/MoS₂ heterostructure hybridization of chalcogen states at the Γ -point may result in a band edge modifications compared to free-standing MoSe₂.

Large scale ambient air atomic force microscopy images of MoSe₂ grown on HOPG, shown in figure 1(a), indicate the preferential nucleation and growth at step edges. Before completion of the first layer, the second layer nucleates and thus ARPES measurements show a mixture of single- and bi-layer MoSe₂. It is well established that only the monolayer of MoSe₂ has a direct band gap at the K-point and that for bilayer the VB-edge at the Γ -point is lower in binding energy than that at the K-point. This behavior is reproduced in the ARPES data shown in figure 1(b). Since both mono- and bi-layer are measured simultaneously the ARPES data shows a superpositioning of the electronic structure of both. Since the monolayer coverage is much larger than the bilayer region the ARPES spectra is dominated by the monolayer and the bilayer region only contributes weakly. Nevertheless, at the Γ -point we resolve two bands. A strong intensity band with at a binding energy of 1.64 eV, which is assigned to the monolayer regions and a faint band at a binding energy of 1.14 eV, which is assigned to the bilayer region. Thus, we measure a

shift of the VBM from the monolayer to the bilayer at the Γ -point of 0.5 eV. This agrees well with previously reported differences of the VBM at the Γ -point of ~ 0.47 eV in ARPES measurements for mono- and bi-layer materials [56]. Importantly, for the monolayer the VBM at the Γ -point is around ~ 0.23 eV below the VBM at the K-point, while for the bilayer, the VBM is ~ 0.27 eV above the VBM at the K-point, assuming the K-point is the same for mono- and bi-layer MoSe₂. Furthermore, the band shape at the Γ -point is relatively flat for the monolayer, indicating a higher effective mass for holes in the monolayer than for bi-layer or bulk MoSe₂. From a parabolic fit of the band at the Γ -point we estimate an effective mass of $3.07 \pm 0.08 m_e$ for monolayer MoSe₂ on HOPG. Photoemission only probes the filled states, thus to obtain information of the band gap we performed STS on monolayer MoSe₂ on HOPG, shown in figure 1(d). The binding energy of the VBM agrees well with the ARPES data and the CBM is measured at ~ 0.5 eV above the Fermi-level indicating an n-type doping of the MoSe₂ monolayer. The band gap determined from STS is $\sim 1.96 \pm 0.05$ eV. This is $\sim 10\%$ smaller than the band gap reported for MoSe₂ on bilayer graphene/SiC of 2.16 eV [60]. This smaller band gap of MoSe₂ monolayer on HOPG may be a consequence of a larger band renormalization on HOPG compared to graphene.

Now we turn to single layer MoSe₂ grown on MoS₂ substrates. On MoS₂, MoSe₂ nucleates more uniformly (it still maybe a heterogeneous nucleation process, but MoS₂ may have more nucleation sites than HOPG), and thus a more homogeneously covered surface is obtained with almost complete monolayer and only small fraction of bilayer as the *in situ* STM image in figure 2(a) shows. Consequently, the ARPES data in figures 2(b) and (c) is almost entirely from the single layer MoSe₂ and contribution of second layer is almost negligible. Also, the photon energy of 70 eV is extreme surface sensitive and thus most of the sig-

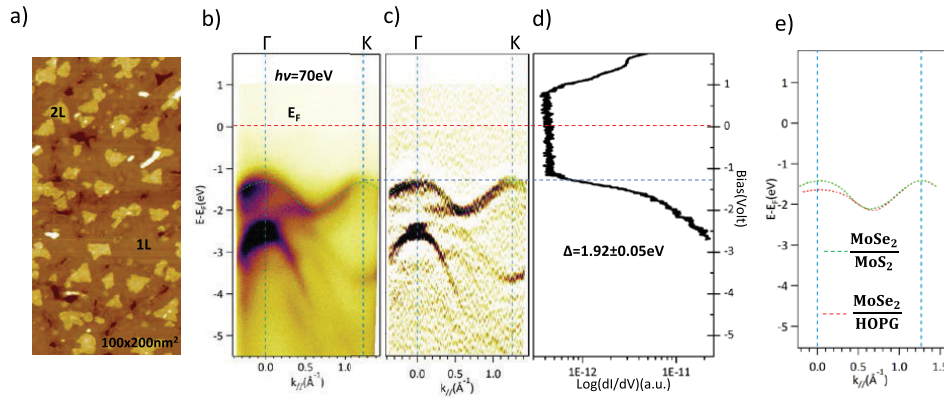


Figure 2. Electronic structure of mono-layer of MoSe₂ on MoS₂. (a) Large scale STM image of MoSe₂ mono- and bi-layers of MoSe₂ are labeled with 1 L and 2 L, respectively. (b) ARPES spectrum for MoSe₂ on MoS₂ along Γ -K direction. (c) Second derivative of data in panel (a). (d) STS spectrum of mono-layer of MoSe₂. (e) Comparison between the VBM for MoSe₂ grown on HOPG (see figure 1) and MoS₂.

nal is from the MoSe₂ surface layer. For this sample, we measure the VBM at almost the same binding energy at the Γ - and K- points. Very weak contribution from the 2nd layer islands can be found at smaller binding energy at the Γ -point. Fitting a parabolic dispersion to the VBM at the Γ -point allows us to estimate the effective mass to $0.82 \pm 0.01 m_e$. STS measurements, shown in figure 2(d), of this sample indicates a band gap of $1.92 \pm 0.05 \text{ eV}$.

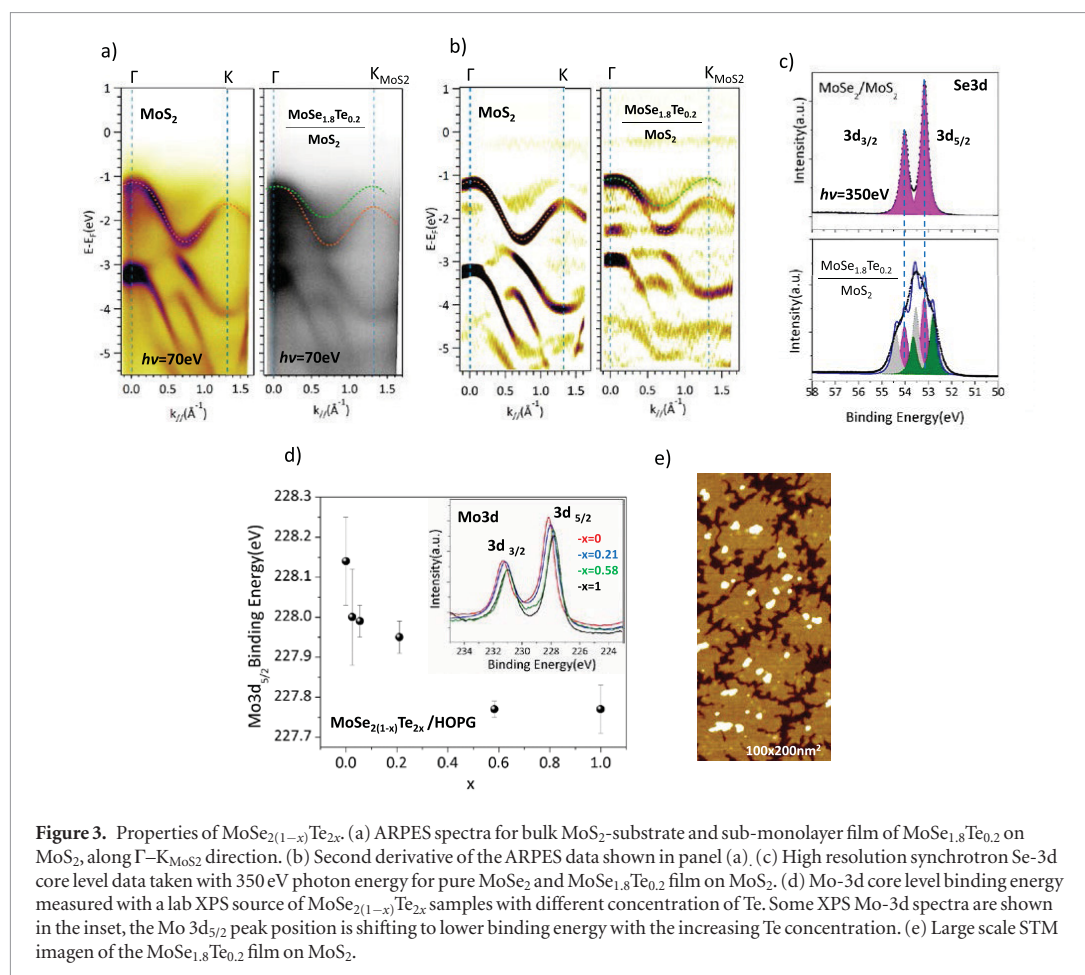
There are clear differences in the band structure of single layer MoSe₂ on HOPG compared to MoS₂ as summarized by the VBM traces for MoSe₂ on these two substrates, shown in figure 2(e). This variation of the electronic structure indicates differences in the substrate interactions. A flatter band of MoSe₂ monolayers at Γ on a HOPG- compared to a MoS₂- substrate is consistent with retaining the properties of freestanding MoSe₂, i.e. weak interlayer hybridization. The significantly lower binding energy of the VBM at Γ compared to K also agrees with the expectations for free-standing MoSe₂. Thus, the main difference between free-standing MoSe₂ and MoSe₂/HOPG is a reduced band gap due to band-gap renormalization by the conducting substrate. In contrast, MoSe₂ on MoS₂ has its VBM at Γ raised to almost the same energy as the VBM at K. Furthermore, it disperses more than expected for freestanding MoSe₂. These effects can be attributed to hybridization of the Se p-states with the S p-states from the substrate. In bi-layer or bulk hybridization of chalcogen p-states at the Γ -point are partially responsible for the change from a direct to an indirect band gap due to the lowering of the binding energy and thus raising the VBM at Γ - above the VBM at the K-point. For the MoSe₂/MoS₂ heterostructure, it appears that the hybridization is not as strong and only raises the VBM for MoSe₂ at the Γ -point roughly to the same energy as the VBM at K. Such a hybridization also changes the dispersion of the Γ -point, resulting in significantly lower effective mass compared to MoSe₂ on HOPG. Finally, hybridization of electronic

states suggests that these states overlap in momentum and energy. This would imply that the MoSe₂ p-derived band is energetically aligned with the MoS₂ p-states of the substrate. This effect cannot be clearly seen for the full monolayer film at the used photon energy because the substrate bands are not visible. The alignment of the monolayer VBM binding energy to those of the substrate at the Γ -point is better seen on the samples discussed in the next section because they only exhibit a partial monolayer and thus both substrate and monolayer are observed in the same spectrum.

4.2. Properties of MoSe₂(1-x)Te_{2x}

The flexibility of MBE in co-deposition of different elements also enables in principle the direct growth of solid solutions of isostructural TMDCs and thus the tuning of the properties of TMDC monolayers. There already exist a few studies that examine the properties of solid solution TMDCs. For example, for the MoS_xSe_{2-x} system it has been shown that by changing the S to Se ratio the photoluminescence, i.e. the optical gap can be continuously tuned between the values of the pure chalcogenides [71–77]. In addition of tuning gaps, alloying may also affect the chemical stability. Generally, air-stability and aging of synthesized monolayer materials is a concern for TMDCs [78]. Often the chemical stability of materials correlates with the band gap, with wide band gap materials being more stable than narrow band gap or metals. This is certainly also the case for Mo-chalcogenides, with the chemical (air) stability decreasing in the order of MoS₂, MoSe₂, to MoTe₂. MoTe₂ easily oxidize if exposed to air [29] while both MoS₂ and MoSe₂ monolayers are stable in air at room temperature for some time, but eventually also start to degrade. Step edges or defects in these materials are likely the starting points for such degradation.

To investigate chemical stability of Te-doped MoSe₂ and the electronic properties of doped samples we have grown MoSe₂(1-x)Te_{2x} samples by co-evaporation of



Se and Te. MoTe_2 has different phases including the 2H-structure of MoSe_2 . Thus, the mixed $\text{MoSe}_{2(1-x)}\text{Te}_{2x}$ is expected to be a solid solution of MoSe_2 and 2H- MoTe_2 . Addition of Se to MoTe_2 stabilizes the semi-conducting 2H phase and suppress the formation of metallic 1T or 1T' phases. In previous studies of MBE growth of pure MoTe_2 we found that small amounts of the 1T' phase was present, predominantly at edges of grown islands [29]. We also found that these MBE grown MoTe_2 films were very reactive and easily oxidized upon exposure to air. The metallic edges may contribute to the ready oxidation. Here, we found that addition of Se makes these films more chemically stable in air, possibly due to a suppression of a 1T' phase formation.

We performed ARPES measurements on a single $\text{MoSe}_{2(1-x)}\text{Te}_{2x}$ sample with about 10% Te, i.e. $\text{MoSe}_{1.8}\text{Te}_{0.2}$. Surprisingly, the band that comprises the VBM appeared very similar compared to pure MoSe_2 in the ARPES data. Figure 3(a), shows ARPES of the MoS_2 substrate and for submonolayer of $\text{MoSe}_{1.8}\text{Te}_{0.2}$. The submonolayer amount of $\text{MoSe}_{1.8}\text{Te}_{0.2}$ allows us to see both the signal from the substrate as well as the monolayer. It is apparent that the VBM of the monolayer and the MoS_2 substrate overlap at the Γ -point, which strengthens the suggestion that this overlap enables the hybridization of these states and effectively aligns the Γ -point of the monolayer to the binding energy of the

Γ -point of the MoS_2 substrate. This alignment of the binding energies of the VBM at the Γ -point may contribute to the very similar VB for the $\text{MoSe}_{1.8}\text{Te}_{0.2}$ sample as for the pure MoSe_2 monolayer on MoS_2 substrates.

Te is less electronegative than Se, which is responsible for the chemical shift of the Mo core levels from 228.14 eV to 227.77 eV as the composition is changed from pure MoSe_2 to pure MoTe_2 . Figure 3(d) shows the change in the core-level position as a function of Te-doping. Interestingly the Mo-peak appears to shift rigidly without indication of a significant broadening or even multiple components that could be associated with different number of Se and Te ligands to each Mo-atom. While there is a clear peak shift for Mo, the Se and Te peak position remains almost unaltered within the resolution limit of our laboratory XPS. High resolution synchrotron core level data taken with 350 eV photon energy for pure MoSe_2 and $\text{MoSe}_{1.8}\text{Te}_{0.2}$ indicate however a peak broadening of the Se peak after incorporation of $\sim 10\%$ Te into MoSe_2 . While for pure MoSe_2 the Se can be fit with a single spin-orbit split core level doublet, after Te incorporation the Se peak requires at least 3 doublets for obtaining a reasonable fit. Such broadening indicates that the Se core level shows some sensitivity to the local environment and dependence on the number of Te-ligands to the adjacent Mo-atom.

5. Conclusions

Recent interest in van der Waals heterostructures has sparked renewed research efforts in van der Waals epitaxy by MBE of layered TMDCs, which enables the combination of materials with diverse properties regardless of their lattice matching. Many van der Waals materials grow epitaxially, i.e. the grown layers are in rotational registry with that of a van der Waals substrate. This enables, for example, ARPES measurements for MoSe₂ films on MoS₂ single crystal substrates. ARPES data indicates that the valence band maximum of MoSe₂ is modified depending on the substrate. On MoS₂ substrates, the VBM at the Γ -point is almost at the same binding energy as at the K-point for monolayer MoSe₂. In contrast, on HOPG the difference in binding energy of the VBM at Γ - and K-points is similar to that expected for free-standing monolayer MoSe₂. This difference may be understood in terms of hybridization between the chalcogen p-orbitals of the substrate with those of the monolayer. This hybridization of monolayer with that of the substrate also results in an alignment of the VBM at the Γ -point of the MoSe₂ monolayer to the binding energy of the VBM position of MoS₂. No such alignment of binding energies is observed for MoSe₂ on HOPG. The hybridization of the MoSe₂ monolayer with the MoS₂ substrate is also reflected by the band dispersion, which shows a more bulk-like dispersion of the VBM at the Γ -point. The different properties of MoSe₂ monolayers depending on the substrate clearly shows that interlayer interactions need to be considered in defining the properties of van der Waals heterostructures.

Acknowledgment

The authors acknowledge support from the National Science Foundation under Award DMR-1701390 and ECCS-1608654. The Synchrotron SOLEIL is supported by the Centre National de la Recherche Scientifique (CNRS) and the Commissariat à l'Energie Atomique et aux Energies Alternatives (CEA), France.

References

- [1] Novoselov K S, Mishchenko A, Carvalho A and Castro Neto A H 2016 2D materials and van der Waals heterostructures *Science* **353** 461
- [2] Jariwala D, Sangwan V K, Lauhon L J, Marks T J and Hersam M C 2014 Emerging device applications for semiconducting two-dimensional transition metal dichalcogenides *ACS Nano* **8** 1102–20
- [3] Koma A 1999 Van der Waals epitaxy for highly lattice-mismatched systems *J. Cryst. Growth* **201** 236
- [4] Geim A K and Grigorieva I V 2013 Van der Waals heterostructures *Nature* **499** 419–25
- [5] Dean C R et al 2013 Hofstadter's butterfly and the fractal quantum Hall effect in moiré superlattices *Nature* **497** 598–602
- [6] Ponomarenko L A et al 2013 Cloning of Dirac fermions in graphene superlattices *Nature* **497** 594–7
- [7] Ma Q et al 2016 Tuning ultrafast electron thermalization pathways in a van der Waals heterostructure *Nat. Phys.* **12** 455
- [8] Liu C H, Clark G, Fryett T, Wu S F, Zheng J J, Hatami F, Xu X D and Majumdar A 2017 Nanocavity integrated van der Waals heterostructure light-emitting tunneling diode *Nano Lett.* **17** 200–5
- [9] Vu Q A et al 2017 Tuning carrier tunneling in van der Waals heterostructures for ultrahigh detectivity *Nano Lett.* **17** 453–9
- [10] Wang F, Wang Z, Xu K, Wang F, Wang Q, Huang Y, Yin L and He J 2015 Tunable GaTe-MoS₂ van der Waals p-n junctions with novel optoelectronic performance *Nano Lett.* **15** 7558–66
- [11] Padilha J E, Fazzio A and da Silva A J R 2015 van der Waals heterostructure of phosphorene and graphene: tuning the schottky barrier and doping by electrostatic gating *Phys. Rev. Lett.* **114** 066803
- [12] Huo N J, Kang J, Wei Z M, Li S S, Li J B and Wei S H 2014 Novel and enhanced optoelectronic performances of multilayer MoS₂-WS₂ heterostructure transistors *Adv. Funct. Mater.* **24** 7025–31
- [13] Lopez-Sanchez O, Llado E A, Koman V, Morral A F I, Radenovic A and Kis A 2014 Light generation and harvesting in a van der Waals heterostructure *ACS Nano* **8** 3042–8
- [14] Schaibley J R, Rivera P, Yu H Y, Seyler K L, Yan J Q, Mandrus D G, Taniguchi T, Watanabe K, Yao W and Xu X D 2016 Directional interlayer spin-valley transfer in two-dimensional heterostructures *Nat. Commun.* **7** 13747
- [15] Chen H L et al 2016 Ultrafast formation of interlayer hot excitons in atomically thin MoS₂/WS₂ heterostructures *Nat. Commun.* **7** 12512
- [16] Peng B, Yu G N, Liu X F, Liu B, Liang X, Bi L, Deng L I, Sum T C and Loh K P 2016 Ultrafast charge transfer in MoS₂/WSe₂ p-n heterojunction *2D Mater.* **3** 025020
- [17] Rivera P, Seyler K L, Yu H Y, Schaibley J R, Yan J Q, Mandrus D G, Yao W and Xu X D 2016 Valley-polarized exciton dynamics in a 2D semiconductor heterostructure *Science* **351** 688–91
- [18] Rivera P et al 2015 Observation of long-lived interlayer excitons in monolayer MoSe₂-WSe₂ heterostructures *Nat. Commun.* **6** 6242
- [19] Fang H et al 2014 Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides *Proc. Natl Acad. Sci. USA* **111** 6198–202
- [20] Samad L, Bladow S M, Ding Q, Zhuo J Q, Jacobberger R M, Arnold M S and Jin S 2016 Layer-controlled chemical vapor deposition growth of MoS₂ vertical heterostructures via van der Waals epitaxy *ACS Nano* **10** 7039–46
- [21] Choudhary N, Park J, Hwang J Y, Chung H S, Dumas K H, Khondaker S I, Choi W B and Jung Y 2016 Centimeter Scale Patterned Growth of Vertically Stacked Few Layer Only 2D MoS₂/WS₂ van der Waals Heterostructure *Sci. Rep.* **6** 25456
- [22] Zhang Q, Chen Y X, Zhang C D, Pan C R, Chou M Y, Zeng C G and Shih C K 2016 Bandgap renormalization and work function tuning in MoSe₂/hBN/Ru(0001) heterostructures *Nat. Commun.* **7** 13843
- [23] Zhao M, Liu M M, Dong Y Q, Zou C, Yang K Q, Yang Y, Zhang L J and Huang S M 2016 Epitaxial growth of two-dimensional SnSe₂/MoS₂ misfit heterostructures *J. Mater. Chem. C* **4** 10215–22
- [24] Ben Aziza Z, Henck H, Pierucci D, Silly M G, Lhuillier E, Patriarche G, Sirotti F, Eddrief M and Ouerghi A 2016 van der Waals epitaxy of GaSe/graphene heterostructure: electronic and interfacial properties *ACS Nano* **10** 9679–86
- [25] Aretouli K E, Tsoutsou D, Tsipas P, Marquez-Velasco J, Giamini S A, Kelaidis N, Psycharis V and Dimoulas A 2016 Epitaxial 2D SnSe₂/2D WSe₂ van der Waals heterostructures *ACS Appl. Mater. Interfaces* **8** 23222–9
- [26] Li X F et al 2016 Two-dimensional GaSe/MoSe₂ misfit bilayer heterojunctions by van der Waals epitaxy *Sci. Adv.* **2** e1501882
- [27] Tsoutsou D, Aretouli K E, Tsipas P, Marquez-Velasco J, Xenogiannopoulou E, Kelaidis N, Giamini S A and Dimoulas A 2016 Epitaxial 2D MoSe₂ (HfSe₂) semiconductor/2D TaSe₂ metal van der Waals heterostructures *ACS Appl. Mater. Interfaces* **8** 1836–41

- [28] Liu X L, Balla I, Bergeron H, Campbell G P, Bedzyk M J and Hersam M C 2016 Rotationally commensurate growth of MoS₂ on epitaxial graphene *ACS Nano* **10** 1067–75
- [29] Coy Diaz H, Chaghi R, Ma Y and Batzill M 2015 Molecular beam epitaxy of the van der Waals heterostructure MoTe₂ on MoS₂: phase, thermal, and chemical stability *2D Mater.* **2** 044010
- [30] Li X F et al 2015 Van der Waals epitaxial growth of two-dimensional single-crystalline GaSe domains on graphene *ACS Nano* **9** 8078–88
- [31] Vishwanath S et al 2015 Comprehensive structural and optical characterization of MBE grown MoSe₂ on graphite, CaF₂ and graphene *2D Mater.* **2** 024007
- [32] Miwa J A, Dendzik M, Gronborg S S, Bianchi M, Lauritsen J V, Hofmann P and Ulstrup S 2015 Van der Waals epitaxy of two-dimensional MoS₂-graphene heterostructures in ultrahigh vacuum *ACS Nano* **9** 6502–10
- [33] Jiao L et al 2015 Molecular-beam epitaxy of monolayer MoSe₂: growth characteristics and domain boundary formation *New J. Phys.* **17** 053023
- [34] Yuan X et al 2015 Arrayed van der Waals vertical heterostructures based on 2D GaSe grown by molecular beam epitaxy *Nano Lett.* **15** 3571–7
- [35] Aretouli K E, Tsipis P, Tsoutsou D, Marquez-Velasco J, Xenogiannopoulou E, Giamini S A, Vassalou E, Kelaidis N and Dimoulas A 2015 Two-dimensional semiconductor HfSe₂ and MoSe₂/HfSe₂ van der Waals heterostructures by molecular beam epitaxy *Appl. Phys. Lett.* **106** 143105
- [36] Yan A, Velasco J Jr, Kahn S, Watanabe K, Taniguchi T, Wang F, Crommie M F and Zettl A 2015 Direct growth of single- and few-layer MoS₂ on h-BN with preferred relative rotation angles *Nano Lett.* **15** 6324–31
- [37] Robinson J A 2016 Growing vertical in the flatland *ACS Nano* **10** 42–5
- [38] Huang C, Wu S, Sanchez A M, Peters J J P, Beanland R, Ross J S, Rivera P, Yao W, Cobden D H and Xu X 2014 Lateral heterojunctions within monolayer MoSe₂-WSe₂ semiconductors *Nat. Mater.* **13** 1096–101
- [39] Duan X et al 2014 Lateral epitaxial growth of two-dimensional layered semiconductor heterojunctions *Nat. Nanotechnol.* **9** 1024–30
- [40] Lv R, Robinson J A, Schaak R E, Sun D, Sun Y, Mallouk T E and Terrones M 2015 Transition metal dichalcogenides and beyond: synthesis, properties, and applications of single- and few-layer nanosheets *Acc. Chem. Res.* **48** 56–64
- [41] Koma A 1992 Van der Waals epitaxy- a new epitaxial growth method for a highly lattice mismatched system *Thin Solid Films* **216** 72–6
- [42] Ohuchi F S, Parkinson B A, Ueno K and Koma A 1990 van der Waals epitaxial growth and characterization of MoSe₂ thin films on SnS₂ *J. Appl. Phys.* **68** 2166–75
- [43] Ueno K, Takeda N, Sasaki K and Koma A 1997 Investigation of the growth mechanism of layered GaSe *Appl. Surf. Sci.* **113/4** 38–42
- [44] Ohuchi F S, Shimada T, Parkinson B A, Ueno K and Koma A 1991 Growth of MoSe₂ thin films with Van der Waals epitaxy *J. Cryst. Growth* **111** 1033–7
- [45] Schlaf R, Tiefenbacher S, Lang O, Pettenkofer C and Jaegermann W 1994 van der Waals epitaxy of thin InSe₂ films on MoTe₂ *Surf. Sci.* **303** L343–7
- [46] Yamada H, Ueno K and Koma A 1996 Preparation of GaS thin films by molecular beam epitaxy *Japan. J. Appl. Phys.* **35** L568–70
- [47] Lang O, Schlaf R, Tomm Y, Pettenkofer C and Jaegermann W 1994 Single crystalline GaSe/WSe₂ heterointerface grown by van der Waals epitaxy. I. Growth conditions *J. Appl. Phys.* **75** 7805–13
- [48] Schlaf R, Lang O, Pettenkofer C and Jaegermann W 1999 Band lineup of layered semiconductor heterointerfaces prepared by van der Waals epitaxy: charge transfer correction term for the electron affinity rule *J. Appl. Phys.* **85** 2732–53
- [49] Lang O, Klein A, Pettenkofer C, Jaegermann W and Chevy A 1996 Band lineup of lattice mismatched InSe/GaSe quantum well structures prepared by van der Waals epitaxy: absence of interfacial dipoles *J. Appl. Phys.* **80** 3817–21
- [50] Schlaf R, Pettenkofer C and Jaegermann W 1999 Band lineup of SnS₂/SnSe₂/SnS₂ semiconductor quantum well structure prepared by van der Waals epitaxy *J. Appl. Phys.* **85** 6550–6
- [51] Kreis C, Traving M, Adelung R, Kipp L and Skibowski M 2000 Tracing the valence band maximum during epitaxial growth of HfS₂ and WSe₂ *Appl. Surf. Sci.* **166** 17–22
- [52] Kreis C, Werth S, Adelung R, Kipp L, Skibowski M, Voss D, Krueger P, Mazur A and Pollmann J 2002 Surface resonances at transition metal dichalcogenide heterostructures *Phys. Rev. B* **65** 153314
- [53] Klein A, Tiefenbacher S, Eyert V, Pettenkofer C and Jaegermann W 2001 Electronic band structure of single-crystal and single-layer WSe₂: influence of interlayer van der Waals interactions *Phys. Rev. B* **64** 205416
- [54] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Atomically thin MoS₂: a new direct-gap semiconductor *Phys. Rev. Lett.* **105** 136805
- [55] Jin W C et al 2013 Direct measurement of the thickness-dependent electronic band structure of MoS₂ using angle-resolved photoemission spectroscopy *Phys. Rev. Lett.* **111** 106801
- [56] Zhang Y et al 2014 Direct observation of the transition from indirect to direct bandgap in atomically thin epitaxial MoSe₂ *Nat. Nanotechnol.* **9** 111–5
- [57] Mo S K, Hwang C, Zhang Y, Fanciulli M, Muff S, Dil J H, Shen Z X and Hussain Z 2016 Spin-resolved photoemission study of epitaxially grown MoSe₂ and WSe₂ thin films *J. Phys.: Condens. Matter* **28** 454001
- [58] Cheng Y, Zhua Z and Schwingenschlögl U 2012 Role of interlayer coupling in ultra thin MoS₂ *RSC Adv.* **2** 7798–802
- [59] Bradley A J et al 2015 Probing the role of interlayer coupling and Coulomb interactions on electronic structure in few-layer MoSe₂ nanostructures *Nano Lett.* **15** 2594–9
- [60] Ugeda M M et al 2014 Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor *Nat. Mater.* **13** 1091–5
- [61] Bruix A et al 2016 Single-layer MoS₂ on Au(111): band gap renormalization and substrate interaction *Phys. Rev. B* **93** 165422
- [62] Diaz H C, Addou R and Batzill M 2014 Interface properties of CVD grown graphene transferred onto MoS₂(0001) *Nanoscale* **6** 1071–8
- [63] Coy-Diaz H, Bertran F, Chen C Y, Avila J, Rault J, Le Fevre P, Asensio M C and Batzill M 2015 Band renormalization and spin polarization of MoS₂ in graphene/MoS₂ heterostructures *Phys. Status Solidi RRL* **9** 701–6
- [64] Kuc A, Zibouche N and Heine T 2011 Influence of quantum confinement on the electronic structure of the transition metal sulfide TS₂ *Phys. Rev. B* **83** 245213
- [65] Tiefenbacher S, Pettenkofer C and Jaegermann W 2000 Moiré pattern in LEED obtained by van der Waals epitaxy of lattice mismatched WS₂/MoTe₂(0001) heterointerfaces *Surf. Sci.* **450** 181–90
- [66] Terrones H, López-Urías F and Terrones M 2013 Novel hetero-layered materials with tuneable direct band gaps by sandwiching different metal disulfides and diselenides *Sci. Rep.* **3** 1549
- [67] Kang J, Li J, Li S-S, Xia J-B M and Wang L-W 2013 Electronic structural moiré pattern effects on MoS₂/MoSe₂ 2D heterostructures *Nano Lett.* **13** 5485–90
- [68] Zhang C, Chuu C-P, Ren X, Li M-Y, Li L-J, Jin C, Chou M-Y and Shih C-K 2017 Interlayer couplings, Moiré patterns, and 2D electronic superlattices in MoS₂/WSe₂ hetero-bilayers *Sci. Adv.* **3** e1601459
- [69] Wilson N R et al 2017 Determination of band offsets, hybridization, and exciton binding in 2D semiconductor heterostructures *Sci. Adv.* **3** e1601832
- [70] Coy Diaz H, Avila J, Chen C, Addou R, Asensio M C and Batzill M 2015 Direct observation of interlayer hybridization and Dirac relativistic carriers in graphene/MoS₂ van der Waals heterostructures *Nano Lett.* **15** 1135–40

- [71] Feng Q, Mao N, Wu J, Xu H, Wang C, Zhang J and Xie L 2015 Growth of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ($x = 0.41\text{--}1.00$) monolayer alloys with controlled morphology by physical vapor deposition *ACS Nano* **9** 7450–5
- [72] Feng Q *et al* 2014 Growth of large-area 2D $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ semiconductor alloys *Adv. Mater.* **26** 2648–53
- [73] Umrao S, Jeon J, Jeon S M, Choi Y J and Lee S 2017 A homogeneous atomic layer $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy prepared by low-pressure chemical vapor deposition, and its properties *Nanoscale* **9** 594–603
- [74] Rajbanshi B, Sarkar S and Sarkar P 2015 The electronic and optical properties of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ and $\text{MoS}_{2(1-x)}\text{Te}_{2x}$ monolayers *Phys. Chem. Chem. Phys.* **17** 26166
- [75] Yang L, Fu Q, Wang W, Huang J, Huang J, Zhang J and Xiang B 2015 Large-area synthesis of monolayered $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ with a tunable band gap and its enhanced electrochemical catalytic activity *Nanoscale* **7** 10490–7
- [76] Mann J *et al* 2014 2 dimensional transition metal dichalcogenides with tunable direct band gaps: $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayers *Adv. Mater.* **26** 1399–404
- [77] Kang J, Tongay S, Li J and Wu J 2013 Monolayer semiconducting transition metal dichalcogenide alloys: stability and band bowing *J. Appl. Phys.* **113** 143703
- [78] Gao J, Li B, Tan J, Chow P, Lu T-M and Koratkar N 2016 Aging of transition metal dichalcogenide monolayers *ACS Nano* **10** 2628–35