Electronic Properties of Transferable Atomically Thin MoSe$_2$/h-BN Heterostructures Grown on Rh(111)

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ABSTRACT: Vertically stacked two-dimensional (2D) heterostructures composed of 2D semiconductors have attracted great attention. Most of these include hexagonal boron nitride (h-BN) as either a substrate, an encapsulant, or a tunnel barrier. However, reliable synthesis of large-area and epitaxial 2D heterostructures incorporating BN remains challenging. Here, we demonstrate the epitaxial growth of nominal monolayer (ML) MoSe$_2$ on h-BN/Rh(111) by molecular beam epitaxy, where the MoSe$_2$/h-BN layer system can be transferred from the growth substrate onto SiO$_2$. The valence band structure of ML MoSe$_2$/h-BN/Rh(111) revealed by photoemission electron momentum microscopy (kPEEM) shows that the valence band maximum located at the K point is 1.33 eV below the Fermi level ($E_F$), whereas the energy difference between K and Γ points is determined to be 0.23 eV, demonstrating that the electronic properties, such as the direct band gap and the effective mass of ML MoSe$_2$, are well preserved in MoSe$_2$/h-BN heterostructures.

KEYWORDS: two-dimensional materials, two-dimensional semiconductors, MoSe$_2$, epitaxial growth, h-BN substrates

Distinct electronic$^1$ and optical properties$^{2,3}$ make atomically thin two-dimensional materials and transition metal dichalcogenides (TMDs)$^{4,5}$ attractive for fundamental research and practical applications. The lack of dangling bonds at their surface makes integration into van der Waals (vdW) heterostructures$^6$ possible, further extending their reach.

Most of the vdW heterostructures being studied today incorporate hexagonal boron nitride (h-BN) as a substrate$^{7,8}$ and encapsulation layer, where the atomically flat surface of h-BN crystals and the low defect density allow the intrinsic properties of 2D materials to be accessed. Moreover, the wide band gap of h-BN in the UV range makes it promising as a tunnel barrier, whereas its dielectric properties also allow it to sustain high electric fields before breakdown.$^9$ However, the reliable preparation of large-area heterostructures remains challenging. The common approach consists of preparing them by mechanical exfoliation and transfer processes, which can introduce residues and contaminants at the interface while the process itself is not scalable.

Chemical vapor deposition (CVD) has been proposed for growing various 2D materials with good quality, but the use of

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various precursors for different material systems may increase complexity. However, molecular beam epitaxy (MBE) can provide a promising alternative route and exhibits several potential advantages including the use of an ultrahigh vacuum (UHV) environment, high-purity sources, and the capability for in situ growth monitoring using reflection high-energy electron diffraction (RHEED). The concept of vdW epitaxy was first proposed by Koma et al. in the 1990s, and a wide variety of 2D materials have been studied since then. However, the MBE growth of 2D vdW heterostructures such as MoSe2/h-BN needs further study, and methods for transferring the resulting heterostack from the metallic substrate also need to be developed.

Here, both the h-BN substrate and the two-dimensional semiconductor MoSe2 are synthesized using scalable methods. We benefit from the previous development of the synthesis of large-scale monolayer (ML) h-BN nanomesh on Rh(111) and demonstrate the growth of atomically thin MoSe2 on ML h-BN/Rh(111) substrates by MBE. There were no intermediate chemical states detected in the X-ray photoelectron spectroscopy (XPS) resulting from hybridization. Surprisingly, the 3D nanomesh morphology of BN disappears during MoSe2 growth, resulting in an atomically flat surface over the length of the substrate, with each layer preserving its lattice constant, in contrast with the previous work on MoSe2/h-BN/Ru(0001) systems. We have also succeeded in transferring the resulting stacks onto insulating substrates. The ML MoSe2/h-BN heterostructure after transfer shows photoluminescence (PL) with the main peak at 1.57 eV at room temperature. We further reveal the electronic properties of ML MoSe2/h-BN heterostructures by photoemission electron momentum microscopy (kPEEM) and perform density functional theory (DFT) calculations to understand the observed effects.

RESULTS

Growth of Atomically Thin MoSe2/h-BN Heterostructures. Wafer-scale monolayer h-BN featuring a nanomesh structure was grown on Rh(111) using CVD in a UHV environment. The h-BN/Rh(111) wafer was cut into 1 × 1 cm² pieces and transferred into a separate MBE system. The growth of MoSe2 was monitored in situ using RHEED. At the growth start, the streaks from epitaxial h-BN/Rh(111) were observed along two different azimuths, [10−10] and [11−20], respectively. Satellite patterns representing the nanomesh structures of h-BN/Rh(111) can be observed on top of the (00) specular streak. During growth, MoSe2 streaks emerge and remain unchanged until the end of the growth. We estimate that the growth time for a complete monolayer is ~30 min. At this point, we can observe both streaks from the substrate and MoSe2 along the [11−20] azimuth. The streak spacing indicates that the as-grown MoSe2 film retains the crystal lattice registry without showing detectable strain from the substrate, as expected from vdW epitaxy. This finding is also consistent with results obtained from scanning tunneling microscopy, showing that the as-grown epitaxial MoSe2 films were modulated by the underlying h-BN while the lattice constants for each layer were preserved. On the other hand, we noticed that in addition to the main MoSe2 streaks shown along the [10−10] azimuth, additional faint streaks also appeared between the main streaks. These could be attributed to the misoriented MoSe2 domains.

We have further examined pristine h-BN and as-grown heterostructures using low-energy electron diffraction (LEED). We can clearly observe a transition from the six-fold superstructure spots related to the h-BN/Rh(111) nanomesh (Figure 1c) to six smeared spots. An aligned six-fold pattern with a larger lattice constant has also appeared, corresponding to the formation of epitaxial MoSe2, whereas the ring pattern in Figure 1d indicates the presence of misoriented domains, in line with RHEED observations. From the LEED intensity distribution analysis, the fraction of aligned MoSe2 can be estimated to be about 42% (Supporting Information section 2). Both MoSe2 and h-BN have preserved their pristine lattices, which are evidenced by the peak intensity distribution of the RHEED spots.
although the lattice mismatch is as large as ∼32% considering epitaxy in the (111) planes.

**Spectroscopic Analysis of MoSe$_2$/h-BN Heterostructures.** The XPS survey of as-grown MoSe$_2$/h-BN/Rh(111) is shown in Figure 2a. The spectrum exhibits a rich feature from both the Rh substrate and the MoSe$_2$/h-BN heterostructure. The Mo 3d$_{3/2}$ and Se 3d$_{3/2}$ core-level spectra shown in Figure 2b,c, respectively, exhibit characteristic binding energies of 233.1 and 55.7 eV, with the stoichiometric analysis indicating a Se-deficient film (Supporting Information section 3). In the Mo 3d core-level region, the Se 3s core-level peak at 231.7 eV overlaps with the Mo 3d peaks, making precise quantification a challenge. Nevertheless, the two featured peak positions related to Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ can be easily distinguished, with very little or no trace of oxidation on the high binding energy side. In the Se 3d core level, the binding energy splitting due to spin-orbit coupling can also be deconvoluted, as shown in fits on Figure 2c. The results imply that only Mo–Se covalent bonding exists without a detectable trace of intermediate compounds or oxidation at the interface. The signals were mainly from the top layer of MoSe$_2$ and the thicker substrate, we have still observed weak signals corresponding to B 1s and N 1s levels located at binding energies of 190.5 and 398.0 eV, respectively. In another sample with the growth time of 60 min, we estimated the stoichiometry by integrating the peak area and found that the MoSe$_2$ film was Se-deficient, with a thickness corresponding to a nominal bilayer, which is consistent with the estimation from RHEED pattern transition (Supporting Information section 3).

**Photoluminescence spectroscopy** was first performed on as-grown heterostructures at room temperature. No detectable PL signal was seen due to the quenching effect from the metal substrate. We have therefore adapted an electrochemical delamination process to transfer the as-grown heterostructure onto fresh SiO$_2$/Si chips. Raman spectra of as-grown and transferred MoSe$_2$/h-BN are comparable and show $A_{1g}$ modes of MoSe$_2$, at ∼240 cm$^{-1}$ (Supporting Information note 4). The PL spectrum acquired from the transferred ML MoSe$_2$/h-BN heterostructure at room temperature is shown in Figure 2f. The asymmetric spectrum is deconvoluted into two parts. The sharp main peak is located at 792 nm (∼1.57 eV) with a line width of 50 meV, whereas a broad sideband is found at 816 nm (∼1.52 eV). The sideband on the low-energy side can be attributed to emission from defect-bound excitons and possibly originates from the local inhomogeneity of the nominal ML which can broaden the main peak on the low-energy side. On the other hand, the sharp main peak at 1.57 eV at room temperature is consistent with reported values for ML MoSe$_2$, indicating that the PL of transferred ML MoSe$_2$ is not affected by the underlying h-BN, as expected, and that it can be quenched by the Rh substrate. Considering that the emission from trions is supposed to disappear at room temperature due to thermal fluctuations, the emission should be mainly from the neutral excitons. These results demonstrate the good optical properties of the ML MoSe$_2$/h-BN heterostructure.

**Photoemission Electron Momentum Microscopy of the ML MoSe$_2$/h-BN Heterostructures.** We have performed kPEEM to further investigate the electronic properties...
of as-grown ML MoSe$_2$/h-BN heterostructures. Unlike conventional angle-resolved photoelectron spectroscopy, which requires a predefined high-symmetry direction and is usually time-consuming due to the sequential acquisition of the $k$-space photoemission signal by sample rotation, $k$PEEM uses parallel angular detection at a given photoelectron energy in the valence band by spectroscopic imaging of the back focal plane of the PEEM. Therefore, the entire reciprocal space is sampled, which makes $k$PEEM an ideal tool for directly assessing the electronic properties of 2D materials.\textsuperscript{33,34} The three-dimensional imaging not only provides the band structures along high symmetry points but also gives insights into the film quality and band distortion due to interaction with the substrate.\textsuperscript{34,35} Here, $k$PEEM was performed with off-normal vacuum ultraviolet excitation (He I, $h\nu = 21.2$ eV), providing an enhanced transition probability at the normal vacuum ultraviolet excitation (He I, $h\nu$.\textsuperscript{36})

Representative images of the $k$PEEM spectroscopic image series of the heterostructure are shown in Figure 3. The signal originates from a selected area in real space defined by a field aperture of $\sim 20$ $\mu$m diameter, containing mostly monolayer crystals with a fraction of bilayer areas, corresponding to a diameter of $\sim 2$ Å$^2$ in reciprocal space, thereby sampling the whole first surface Brillouin zone. In the set of $k$PEEM images, the six-fold symmetry of the bands is clearly revealed, indicating the preferred epitaxial directions of MoSe$_2$. In the image at an energy of 4.10 eV in Figure 3, the first surface Brillouin zone and the characteristic high-symmetry points $\Gamma$, $K$, and $M$ are depicted. We note that the bright spot at the $\Gamma$ point at the binding energy of 3.1 eV is related to the underlying h-BN, which will be discussed later. In the image stack, we can then perform a cut along the high-symmetry direction $\Gamma$ to $K$ in the binding energy range down to 9.2 eV with respect to $E_F = 0$ eV, allowing us to obtain the full valence band structure of MoSe$_2$/h-BN.

**DISCUSSION**

**Electronic Properties of the MoSe$_2$/h-BN Heterostructures.** To gain an insight into the valence band structure of MoSe$_2$/h-BN, we have first calculated the band structure of free-standing ML MoSe$_2$ by DFT (Figure 4a). Except for the doublet splitting of the valence band induced by spin–orbit coupling, the most significant feature of ML MoSe$_2$ that emerges is the direct band gap where the VBM is at the $\Gamma$ point, while the $\Gamma$ point is located 0.23 eV below the VBM. The full valence band structure of nominal ML MoSe$_2$/h-BN/Rh(111) along $\Gamma$ to $K$, derived from the $k$PEEM image series, is shown in Figure 4b. We have further calculated the second derivative of the $k$PEEM images to enhance the contrast and visibility, especially in the upper valence band region (Figure 4c). In the MoSe$_2$/h-BN heterostructure, the h-BN bands coexist with MoSe$_2$ bands. The $\pi$-band of h-BN, which is expected to disperse from the energy of 8.4 eV at $\Gamma$ point and up to the energy of 2.4 eV at $K$ point, is hardly distinguishable as it is masked by the MoSe$_2$ band structure. In the monolayer MoSe$_2$/h-BN sample, however, the band structure of h-BN is much more clearly resolved (Supporting Information section 5). This observation of a close-to-ideal h-BN band structure is in contrast with the electronic band structure of the h-BN nanomesh on Rh or Ru, where split bands can be observed because of the differences in the interfacial distances between the “pore” and “wire” regions of the nanomesh.\textsuperscript{31} Overall, the valence band structure of MoSe$_2$/h-BN resembles those of the free-standing counterpart, without any evidence of interlayer hybridization.

We now focus on the upper valence band dispersions of the MoSe$_2$/h-BN heterostructure in the momentum space along the $\Gamma$ to $K$ direction. First, we do not observe the spin-splitting but a broad band at the $K$ point, likely due to the limited energy resolution (100 meV) provided by the microscope settings used in the experiment as well as the contribution from the misoriented domains. The $K$ point at a binding energy of 1.33 eV below $E_F$ indicates that the as-grown MoSe$_2$ is unintentionally n-doped, as observed for a majority of reported MoSe$_2$ atomically thin films.

Only one band at an energy of $\sim 1.56$ eV at the $\Gamma$ point is observed, thus indicating that the signal is mainly from the top ML MoSe$_2$ and that the band features of h-BN are absent in the upper valence band structure. Additionally, we compare the band maximum at $\Gamma$ and $K$ points and observe that the VBM located at the $K$ point is higher than that of the $\Gamma$ point by 0.23 eV (Supporting Information section 6). While this value matches our PBE-DFT calculations for free-standing MoSe$_2$ within the range of error, it is lower than the previously reported value of 0.38 eV for ML MoSe$_2$ grown on bilayer graphene on SiC.\textsuperscript{31} This could be due to the use of different substrates and a lower measurement resolution in our case.

The direct band gap feature of ML MoSe$_2$ is thus preserved in the heterostructure, and the valence band structure is similar to the calculations for free-standing ML MoSe$_2$. The close examination of the experimental and theoretical band structures reveals the presence of a small band compression, often associated with the presence of a substrate.\textsuperscript{34,35,38}
Similarly, the band dispersions along $\Gamma$ to $M$ are also plotted, and the band structures are in line with the theoretical calculations, with the exception of an energy upshift near the $M$ point (Supporting Information section 7). Although the differences are small in our case, this is possibly due to screening by the substrate and charge redistribution at the interface caused by the metallic Rh substrate below the BN monolayer as well as the unintentional n-doping of MoSe$_2$. Additionally, a contribution from the misoriented domains and grain boundaries may also be present distorting the apparent band structure and work function.

To further support our argument that no new hybridization of bands takes place in MoSe$_2$/h-BN heterostructures, we have additionally performed vdW-DFT calculations. The vertical heterostructure was modeled considering a $(3 \times 3)$ MoSe$_2$ supercell ($a_{\text{MoSe}_2} \approx 3.3 \text{ Å}$) on top of a $(4 \times 4)$ h-BN supercell ($a_{\text{h-BN}} \approx 2.5 \text{ Å}$), as sketched in Figure 5a. Our simulations suggest that ML MoSe$_2$ is located $\sim 3.6$ Å above the h-BN plane, with an interlayer interaction of $\sim 90$ meV per f.u. and an adhesive energy of $\sim 9$ meV/Å$^2$ per f.u. (Supporting Information Table 1). This latter value is below the typical adhesive energy of vdW-layered materials, estimated to be in the range of 13–21 meV/Å$^2$, thereby indicating a very weak coupling between the two layers in the heterostructure.

Figure 5b shows the charge transfer that takes place in the heterostructure: negative charge density distributes on both h-BN and MoSe$_2$ MLs, whereas positive charge accumulates in the interlayer region. Furthermore, the results of our vdW-DFT calculations presented in Figure 5c suggest that, in the heterostructure, the h-BN electronic states exist only below the energy of 0.7 eV below the VBM, as indicated by the dashed line. Therefore, MoSe$_2$ band edges are retained upon heterostructure formation, and the ML feature such as the direct band gap is thus preserved (Supporting Information Figures 8 and 9).

It is not clear why the nanomesh structure disappears with the deposition of MoSe$_2$, resulting in an atomically flat interface. The decoupling of h-BN from Rh occurs early in the MBE growth process as described in the Supporting Information section 5. This was not the case for the MoSe$_2$/h-BN/Ru system deposited by MBE, where the nanomesh structure is unchanged even after the growth, and the electronic properties of MoSe$_2$ are modulated by the morphological variations due to the strong interaction with Ru. A similar disappearance of the nanomesh structure as in our case was observed for the graphene/h-BN/Rh(111)
system, where the decoupling was assisted by the interfacial carbon formation between BN and Rh during the CVD growth of graphene. Here, we saw no evidence for the existence of the interfacial layer, and further investigation of the exact growth mechanism is required. Nevertheless, this route can be highly advantageous for utilizing technologically attractive qualities of the atomically flat, free-standing layers of MoSe$_2$ and other TMDs.

CONCLUSION

In conclusion, we demonstrate the growth of MoSe$_2$/h-BN heterostructures on Rh(111) with preferential lattice alignment via vdW epitaxy. The electronic properties of nominal ML MoSe$_2$/h-BN were directly revealed by kPEEM, showing the direct band gap with the VBM located at the $\Gamma$ point and the electronic structure of the as-grown MoSe$_2$ remains preserved in the presence of the underlying h-BN, as confirmed by first-principles calculations. This work provides deep insights into the growth of TMDs on h-BN with highly attractive optoelectronic properties of pristine monolayer semiconductors.

METHODS

Material Growth. The growth was carried out in an Omicron MBE with $\sim 10^{-10}$ mbar base pressure. 1 $\times$ 1 cm$^2$ h-BN/Rh(111)/YSZ/Si(111) substrates were outgassed at up to 500 $^\circ$C for 12 h prior to growth. The growth was conducted at 350 $^\circ$C with a fixed Se/Mo ratio of $\sim$40 and a Mo deposition rate of $\sim$0.1 Å/min; the temperature was monitored using a pyrometer, and the flux for each cell was calibrated using a quartz crystal microbalance. After growth, the sample was postannealed in situ at the same temperature with Se flux at 400 $^\circ$C for 20 min. A RHEED camera (STABi Co.) was used to monitor the growth in situ. The LEED and photoelectron diffraction experiments were performed in the surface science laboratory at the University of Zurich.

XPS and Raman Spectra and PL Characterizations. The XPS spectra were obtained ex situ in a commercial ULVAC-PHI Versa Probe II system with a laboratory Al Kα X-ray source ($h\nu = 1486.6$ eV), and the C 1s core-level peak at 284.8 eV was used as the reference for determining the binding energies. Peak identification and fitting was processed in PHI’s MultiPak processing software. The PL and Raman spectra were measured using a 532 nm wavelength laser in a Renishaw Raman confocal microscope.

Photoemission Electron Momentum Microscopy. The experimental details of the instrument and kPEEM measurements can be found in previous reports.

First-Principles Simulations. Our calculations were performed within the DFT framework, as implemented in the SIESTA code. In order to describe the exchange and correlation effects, we used the generalized gradient approximations of Perdew, Burke, and Ernzerhof (PBE) for free-standing MoSe$_2$ and several vdW density functionals (BH, C09, DRSLL, KBM, LMKLL) for the MoSe$_2$/h-BN heterostructure. Spin–orbit coupling was included only in the calculations of the band structure of free-standing MoSe$_2$. Core electrons were replaced with relativistic Troullier–Martins pseudo-potentials, whereas valence electrons were described with a TZ$_{\text{c}}$ plus double polarization (TZDP) basis set in conjunction with a mesh cutoff of 450 Ry. The basis set superposition error was systematically corrected following the counterpoise scheme. The Brillouin zone was sampled with the equivalent of 30 $\times$ 30 $\times$ 1 k-points per MoSe$_2$ unit cell during geometry relaxation runs and 120 $\times$ 120 $\times$ 1 k-points for the calculations of the electronic density of states. Tolerance on forces during relaxations was set to 15 meV/Å; lattice constants were set to be equal to that of the ML MoSe$_2$, and a 29 Å thick vacuum region was included to separate periodic replicas.

ASSOCIATED CONTENT

Supporting Information

Additional experimental details, supporting figures and table as described in text (PDF)

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Notes

The authors declare no competing financial interest.

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