Hybridization and localized flat band in the WSe2/MoSe2 heterobilayer

Lama Khalil1, Debora Pierucci1, Emilio Velez-Fort2, José Avila3, Céline Vergnaud2, Pavel Dudin3, Fabrice Oehler1, Julien Chaste1, Matthieu Jamet2, Emmanuel Lhuillier4, Marco Pala1 and Abdelkarim Ouerghi1,∗

1 Université Paris-Saclay, CNRS, Centre de Nanosciences et de Nanotechnologies, F-91120, Palaiseau, France
2 Université Grenoble Alpes, CEA, CNRS, Grenoble INP, IRIG-Spintec, F-38054, Grenoble, France
3 Synchrotron-SOLEIL, Université Paris-Saclay, Saint-Aubin, BP48, F-91192 Gif sur Yvette, France
4 Sorbonne Université, CNRS, Institut des NanoSciences de Paris, INSP, F-75005 Paris, France

E-mail: abdelkarim.ouerghi@c2n.upsaclay.fr

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Abstract

Nearly localized moiré flat bands in momentum space, arising at particular twist angles, are the key to achieve correlated effects in transition-metal dichalcogenides. Here, we use angle-resolved photoemission spectroscopy (ARPES) to visualize the presence of a flat band near the Fermi level of van der Waals WSe2/MoSe2 heterobilayer grown by molecular beam epitaxy. This flat band is localized near the Fermi level and has a width of several hundred meVs. By combining ARPES measurements with density functional theory calculations, we confirm the coexistence of different domains, namely the reference 2H stacking without layer misorientation and regions with arbitrary twist angles. For the 2H-stacked heterobilayer, our ARPES results show strong interlayer hybridization effects, further confirmed by complementary micro-Raman spectroscopy measurements. The spin-splitting of the valence band at K is determined to be 470 meV. The valence band maximum (VBM) position of the heterobilayer is located at the Γ point. The energy difference between the VBM at Γ and the K point is of −60 meV, which is a stark difference compared to individual single monolayer WSe2 and monolayer WSe2, showing both a VBM at K.

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(VBM) position, excitonic spectrum and spin–orbit coupling (SOC) strength [16]. Most interestingly, quasi-lattice-matched heterobilayers such as 1H-WSe2/1H-MoSe2 exhibit a range of twist angles which gives rise to moiré superlattices [17–20] and host a variety of correlated particle physics [21]. For selected twist angles, the electronic band structure can even exhibit a nearly flat band dispersion [22] with enhanced electron–electron correlations. Although these theoretical prospects are appealing, the experimental exploration TMD-based moiré phenomena is particularly challenging, as it requires both the exact knowledge of the relative heterobilayer misorientation in real space and a fine energy and momentum resolution in reciprocal space.

Recently, a scanning tunneling spectroscopy study has successfully imaged moiré flat bands in WSe2/WS2 superlattices [23]. Previous scanning tunneling microscopy studies have also established site-dependent electronic structures in TMD moiré superlattices [20, 22, 24]. However, the direct visualization of flat band near the Fermi level of TMD heterobilayer structures has not been demonstrated. Here, angle-resolved photoemission spectroscopy (ARPES) provides a powerful tool with a direct determination of the electronic structure and the related flat band dispersion in moiré superlattices. However, high-resolution ARPES requires a conductive support and thus imposes additional challenges for the material growth, mostly solved by the use of graphene substrates.

Here, we report the direct observation of the moiré flat band electronic structure in 1 ml WSe2/1 ml MoSe2 vdW heterobilayer (with 1 ml referring to a single monolayer), grown by molecular beam epitaxy (MBE) on graphene substrates. Using ARPES, a flat band is observed near the Fermi level and has a width of several hundred meVs. By combining experimental ARPES measurements with density functional theory (DFT) calculations, we show the coexistence of different domains, namely, the 2H stacking and twisted θ±4-domains (with θ±4 = ±4.0° twist angle). We attribute the existence of the localized valence flat band to these particular sub-sets of twisted θ±4-domains.

Results and discussion

We describe here in brief the sample fabrication procedure; more details can be found in the materials and methods section. The decomposition of a 6H-SiC(0001) substrate at high temperature under atmospheric pressure in an argon atmosphere was used to produce a graphene monolayer with high electron mobility [25–31] (labell ‘Gr’ in figure 1 refers to graphene). The graphene monolayer was obtained by tuning the annealing temperature of the initial SiC substrate [32]. The obtained graphene/SiC substrate was then used to grow 1 ml MoSe2 and 1 ml WSe2 via separate but consecutive vdW epitaxy processes [33–37]. Figures 1(a) and (b) show side and top schematics of the WSe2/MoSe2 heterobilayer in the 2H stacking, respectively. Each MX2 monolayer contains three atomic layers, X-M-X with the transition metal atoms M covalently bounded to six chalcogen atoms X, forming a sandwiched material in a trigonal prismatic structure (1H phase). In figure 1(c), we present the reflection high energy electron diffraction (RHEED) pattern of the initial graphene/SiC substrate. We confirm the monocristalline property of the graphene layer with in-plane six-fold symmetry. Due to the low incidence of the RHEED electron beam, the illuminated area is several tens of microns wide [38].

The RHEED pattern after the first 1 ml MoSe2 growth is shown in figure 1(d). The graphene-related lines have completely disappeared, which indicates an overwhelming surface coverage by MoSe2. The RHEED pattern consists in regular long streaks, which suggests a well-crystallized order and a flat MoSe2 surface. We find that the hexagonal MoSe2 and graphene unit cells are aligned in-plane ([11–20]MoSe2)//[11–20]graphene and [1–100]MoSe2//[1–100]graphene. Figure 1(e) shows the RHEED pattern of the 1 ml WSe2 layer deposited on MoSe2. Due to the near lattice-match (0.18% difference) between MoSe2 (α = 3.288 Å) [39] and WSe2 (α = 3.282 Å) [39] and their similar hexagonal structure, the RHEED pattern is expected to undergo no visible change from MoSe2 to WSe2. The persistence of the elongated streaks, from the early stage right to the end of the WSe2 growth process, suggests a good vdW epitaxy between the 1 ml WSe2 and 1 ml MoSe2, with unit cell alignment. This first picture of the respective layer alignment obtained by RHEED is complemented by the following micro-Raman (μ-Raman), x-ray photoemission spectroscopy (XPS) and ARPES measurements.

Before exploring the electronic properties of the heterobilayer, we probe its characteristic vibrational modes using μ-Raman spectroscopy. Figure 2(a) shows the μ-Raman scattering spectrum obtained in the frequency range of 190–400 cm−1 from the WSe2/MoSe2 heterobilayer, which we compare to two other spectra from 1 ml 1H-MoSe2 and 1 ml 1H-WSe2, respectively. According to the group theory analysis for monolayer MX2, the irreducible representation decomposition of the vibrational modes can be expressed by Γ = A2g(IR) + A1g(R) + E2g(R) + E1g(IR + R) [40]. For pristine MoSe2 (blue curve), the out-of-plane mode A1g and the in-plane mode E1g are observed at 240.5 cm−1 and 284.4 cm−1, respectively. The absence of the Raman peak related to interlayer interactions around 350 cm−1 confirms the single monolayer thickness of the reference 1H-MoSe2 film. Similarly, the reference 1H-WSe2 spectrum (red curve) displays the A1g Raman peak at 247.3 cm−1 and another mode at about 264.4 cm−1, which corresponds to the second order 2LA(M) mode and involves two-phonon interaction close to the M point of the Brillouin zone. The lack of the Raman peak B2g at about 300 cm−1 is the fingerprint of single 1 ml 1H-WSe2. Finally, spectrum obtained from the heterobilayer (black curve) only consists of the distinctive above-mentioned A1g (MoSe2), E1g (MoSe2), E1g and A1g (WSe2), and 2LA(M) (WSe2) modes, in agreement the previous report of Nayak et al [41]. We note that each of these modes is located at the same vibration frequency as those from the individual 1 ml references. This confirms that the heterobilayer consists of 1 ml MoSe2 and 1 ml WSe2 stacked vertically as a 2H polytype [42, 43].

To investigate the quality of the WSe2/MoSe2 interface, we then conducted a XPS study using a photon energy of 350 eV. Figure 2(b) shows a wide XPS spectrum, revealing the presence of six core level peaks. Four of these peaks are
assigned to the heterobilayer (namely, Mo 3d, Se 3p, Se 3d and W 4f), while the two other peaks are attributed to the graphene/SiC substrate (namely, C 1s and Si 2p). For the Mo 3d, Se 3d and W 4f peaks, we have also recorded high-resolution XPS spectra, as shown in figures 2(c)–(e), respectively. The experimentally measured data are displayed as black circles and the fitted envelopes are represented as solid blue lines. After a shirley background subtraction, the core level spectra were fitted by sums of Voigt functions. The fitting of the Mo 3d peak (figure 2(c)) yields a main doublet (Mo 3d_{5/2} and Mo 3d_{3/2}) with a spin-orbit (SO) splitting = 3.14 eV related to stoichiometric MoSe_2 [44], with the 3d_{5/2} component centered at a binding energy (BE) of 229.1 eV. Beside the Se 3s peaks [45, 46] (Se-Mo at BE = 229.8 eV and Se-W at BE = 230.2 eV), we also notice the presence of a second Mo doublet, shifted by 0.45 eV to lower BEs with respect to the main one, corresponding to defective/substoichiometric MoSe_2 [47]. For the Se 3d core level (figure 2(d)), we observe two doublets (Se 3d_{3/2} and Se 3d_{5/2}) with a SO splitting = 0.86 eV corresponding to two inequivalent Se species. The first doublet at higher BE of 54.9 eV is relative to Se atoms embedded in the WSe_2 monolayer [42, 44, 48], while the second one at lower BE of 54.4 eV corresponds to Se atoms in the MoSe_2 monolayer [42, 49–51]. Similarly, to the Mo 3d peak, the W 4f peak (figure 2(e)) presents two doublets (W 4f_{7/2} and W 4f_{5/2}) with a SO splitting = 2.15 eV): the first one is related to stoichiometric WSe_2 [44] with the W 4f_{7/2} component at a BE of 32.7 eV; the second one at lower BEs (−0.40 eV) corresponds to defective/substoichiometric WSe_2 [52]. In all spectra, we find no signature of any additional component (e.g., carbon or oxygen bounds) [53–55], indicating that our samples are not contaminated. Moreover, the absence of extra peaks indicates that there is no covalent bond between MoSe_2 and WSe_2. This is coherent with the expected vdW epitaxy and corroborates the vdW nature of the WSe_2/MoSe_2 heterobilayer.

Figure 1. (a)–(b) Side and top views of the crystal structure of WSe_2/MoSe_2 heterobilayer in the 2H stacking. The gray, blue and orange spheres refer to molybdenum, tungsten and selenium atoms, respectively. The underlying graphene layer (Gr) is shown as a honeycomb. (c) RHEED pattern of the graphene/Si(0001) substrate, showing two streaky-line patterns attributed to graphene and to the interface layer. (d)–(e) Streaky RHEED patterns obtained during the MoSe_2 and WSe_2/MoSe_2 MBE growth process, acquired along the same azimuth as (c).
interface. The combination of RHEED, μ-Raman and XPS thus confirms the thickness and chemical composition of our heterobilayer.

In the next section, we turn to the local investigation of the electronic band structure of the valence state using nano-ARPES with a small beam size of about 600 nm. Such high spatial resolution will give information relative to the local stacking configuration of our bilayer sample. Figure 3(a) displays a comparison between four valence-band structures along the high symmetry direction ΓK, taken from spatially distinct points on the sample (labelled pt 1 to 4), using an incident photon energy of 100 eV. The sharpness of the different bands is attributed to the high quality of our sample. Near Γ, the bands consist of the W and Mo d_{z^2} and Se p_z orbitals [39, 56–58]. Because of their out-of-plane character, these bands are the most sensitive to the number of layers composing the system, and thus they might exhibit strong hybridization effects. Close to K, the valence band is spin-split by the intrinsic SOC and the lack of inversion symmetry. The observation of two split branches in the valence band at Γ (marked by orange arrows in figure 3(a)) for all panels unambiguously confirms the heterobilayer nature of our sample (see band structure calculations for the heterobilayer in supplementary figure S1). The same band dispersion and structures are obtained at all probed areas (pt 1–4), which supports the spatial homogeneity of the MBE growth.

We remark a lower photoemission intensity near the K point in the nominally gapped region of these electronic spectra, suggesting the existence of localized valence states near the Fermi level. The presence of these localized states can be better visualized by comparing two energy distribution curve (EDC) spectra, figures 3(b)–(c), obtained by integrating the nano-ARPES map (figure 3(a), pt2) in a wave-vector window of 0.05 Å⁻¹ around the Γ point (k∥ = 0 Å⁻¹) and the K point (k∥ = 1 Å⁻¹), respectively. In contrast to the EDC at Γ (figure 3(b), red), the EDC at K (figure 3(c), blue) clearly shows a finite density of localized in-gap states near the Fermi level marked as a black arrow, which suggests the presence of a flat band near the Fermi level.

Thanks to the spatial homogeneity of the sample (figure 3), we can better demonstrate the presence of the states near the Fermi level in the WSe₂/MoSe₂ heterobilayer, using a wider 50 × 50 μm² x-ray beam during the ARPES experiment. By increasing the integration area and the beam flux, we expect to improve the signal to noise ratio and obtain a better visualization of the flat band. This new set of ARPES data was collected with a photon energy of 60 eV. This particular energy value was chosen because the electronic structure of the top-lying valence bands of WSe₂ is mostly derived from the W 4d and Se 3p orbitals, each of which possesses a strongly varying photon-energy-dependent photoionization cross section [59]. By lowering the excitation photon energy from 100 to 60 eV, the photoionization cross section of these orbitals increases, which directly improves the corresponding ARPES signal [60]. Figure 4(a) presents the photoemission intensity map along the Γ–K direction. In figure 4(b), we plot EDCs extracted by integrating the spectrum of figure 4(a) around k∥ = 0 Å⁻¹ (Γ, red curve) and
ferred on a graphene substrate. This monocrystalline CVD
and our WSe$_2$ lateral coherence length for the MBE-grown of 2D materials
typically one order of magnitude larger than the typical 30 nm
WSe$_2$ grown by chemical vapor deposition
two bands due to the insuf-
we report in supplementary

Figure 3.

Figure 3. (a) Comparison between four nano-ARPES maps of the WSe$_2$/MoSe$_2$ heterobilayer, acquired along the high symmetry direction KΓM from spatially distinct points (labelled pt 1 to 4). The incident photon energy is 100 eV. (b)–(c) Energy distribution curve extracted from the ARPES map (a)[pt2], showing the absence and presence of a flat band near the Fermi level, near the Γ (K) point, respectively.

$k_{||} = 1\text{Å}^{-1}$ (K, blue curve). Both the EDC at $K (k_{||} = 1\text{Å}^{-1})$
and the second-derivative spectrum confirm the presence of a localized in-gap flat valence state (indicated by a black arrow
in figure 4(c)) near the Fermi level.

Compared to nano-ARPES data acquired 100 eV
(figure 3), the conventional ARPES obtained at 60 eV
(figure 4(a)), shows a better resolution of the valence band near the $K$ point and the states close to the Fermi level. The measured spin–orbit splitting at $K$ is about 470 meV in good agreement with the DFT calculations (see supplementary figure S1).
The analysis of the $K$-resolved projected density of states (PDOS) (see supplementary figure S2) reveals that the highest band is associated to 1 ml WSe$_2$, whereas the bands related to 1 ml MoSe$_2$ are lower in energy and close to the second band of the WSe$_2$. However, our experimental ARPES data only reveal two bands due to the insufficient energy resolution. For clarity, we report in supplementary figure S3 an ARPES map of a 1 ml WSe$_2$ grown by chemical vapor deposition (CVD) and transferred on a graphene substrate. This monocrystalline CVD WSe$_2$ flake presents a lateral size of about 50–100 μm, which is typically one order of magnitude larger than the typical 30 nm lateral coherence length for the MBE-grown of 2D materials and our WSe$_2$/MoSe$_2$ heterobilayer. Note that 2D materials obtained by epitaxy often presents multiple domains of small lateral dimensions (a few tens nm), in addition to different azimuthal orientations and different thickness. Here, the domain sizes of our WSe$_2$/MoSe$_2$ grown by MBE are well below the resolution of present-generation nano-ARPES instruments, which inevitably results in the spatial averaging of spectra from different domains. This directly affects the collected ARPES data, as we can characterize a single crystal in the case of CVD-
grown WSe$_2$, but only a large assembly of MBE-grown WSe$_2$/MoSe$_2$ heterobilayer domains, even with micro-(figure 4) or nano-sized (figure 3) x-ray ARPES beams. Such differences in spatial homogeneity and sampling lead to a significant experimental broadening of the top valence bands, from 100 meV for the CVD-grown WSe$_2$ monolayer [61] to over 300 meV for our MBE-grown WSe$_2$/MoSe$_2$ heterobilayer.

We now detail the position of the VBM of the WSe$_2$/MoSe$_2$ heterobilayer. From the ARPES (figure 4), we determine the VBM at the $Γ$ point, with 1.19 ev BE (binding energy). The energy difference between the VBM and the top of the valence band at the $K$ point (1.25 eV BE) is $ΔΓK = E_F − E_K = −60$ meV, which is a stark difference compared to individual 1 ml WSe$_2$ and 1 ml MoSe$_2$, showing both a VBM shift from $K$ to $Γ$ [62] (see supplementary figure S3, comparing ARPES and DFT data on monolayer TMD). Note that such an energy shift does not occur for individual 1 ml TMD deposited on graphene, which demonstrates that TMDs and graphene only weakly interact electronically, despite the clean graphene/ TMD interface [61]. This VBM shift from $K$ to $Γ$ has been observed in other heterobilayers [62] and is a firm evidence that the two single TMD layers (MoSe$_2$ and WSe$_2$) are strongly coupled electronically. Combined with our previous characterizations, we can draw now a much clearer picture of our sample, which thus consists in a planar stack of three layers (graphene, 1 ml MoSe$_2$ and 1 ml WSe$_2$), with abrupt vDW interfaces, of which the two TMDs (MoSe$_2$ and WSe$_2$) are strongly hybridized, but weakly coupled electronically to the underlying graphene. In a first approximation, our film thus behaves as a simple heterobilayer, independent of the underlying substrate. This has important consequences on the

$E−E_F = −60$ meV
the electronic band structure will strongly depend on the twist angle between the two TMD layers ($\theta_{\text{WSe}_2/\text{MoSe}_2}$), but only weakly to angular misalignment with the underlying graphene ($\theta_{\text{Gr}/\text{MoSe}_2}$).

In the following, we will detail the importance of the $\theta_{\text{WSe}_2/\text{MoSe}_2}$ value on the band structure of the heterobilayer. In figures 4(c) and (d), we compare the ARPES measurements with DFT calculations conducted for the 3R and 2H stacked heterobilayer. The DFT calculations (see Methods) are performed over the full k-space (see supplementary figure S4). We observe an overall agreement with theoretical DFT calculations computed for 3R and 2H stacking, shown as dashed red and green-colored lines in figures 4(c) and (d) respectively. To lift the ambiguity between the two possible 3R and 2H configurations of the 1 ml WSe$_2$/1 ml MoSe$_2$, we compare their total cohesive energies, defined as the total energy difference per atom between the heterobilayer and the two single monolayers. Our results show that 2H stacking has a lower formation energy than 3R (3meV, see supplementary table 1), so that the cohesive energies are different enough to consider that 2H is the natural stacking configuration in our 1 ml WSe$_2$/1 ml MoSe$_2$ heterobilayers [63].

We now extract the typical hole effective masses, $m^*/m_0$, around the $K$ and $\Gamma$ points, which are of $0.4 \pm 0.1$ and

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**Figure 4.** (a) High-resolution ARPES intensity map for 1 ml WSe$_2$/1 ml MoSe$_2$, acquired along the K$\Gamma$M high symmetry direction with a photon energy of 60 eV. (b) Energy distribution curves obtained at $k_{||} = 0$ Å$^{-1}$ and $k_{||} = 1$ Å$^{-1}$ from the ARPES spectrum in (a), confirming the presence of a flat band around the $K$ point, as observed by nano-ARPES. (c) and (d) Second derivative spectrum obtained from the intensity map in (a), showing the presence of flat bands near the Fermi level. (d) Comparison between experimental ARPES data and theoretical DFT calculations computed for 3R and 2H stacking of 1 ml WSe$_2$/1 ml MoSe$_2$, shown as dashed red and green-colored lines, respectively. The indirect band gap transition is marked as dashed arrow.
1.2 ± 0.1, respectively. The spin-splitting of the valence band at $K$ is determined to be 470 meV. Combining ARPES and DFT, we expect our heterobilayer to show an indirect band gap ($1.31 \text{ eV}$) between the VBM at $\Gamma$ and the conduction band at $K$ (see green dashed arrow in figure 4(d)). While there is a relatively good agreement between the DFT and ARPES, there are also important differences. The most prominent one is a flat band at $E - E_F = -0.5 \text{ eV}$ (with ~390 meV bandwidth), inside the forbidden energy region, near the Fermi level, see figure 4(c). Other bands, located between 2.5 and 3 eV BE, are also not reproduced by the calculations. Therefore, it is likely that the valence band dispersion in our heterobilayer is modulated by the change of the twist angle between the two layers.

To gain more insight into the impact of the twist angle on heterobilayer band dispersion, we acquired three constant ARPES energy maps in the $(k_x, k_y)$ momentum plane, using incident photon energy of 100 eV. The first one showing the graphene Dirac cone at the $K_{Gr}$ point; the second and third ones are obtained at the valence band maxima at the $\Gamma$ and $K_{heterobilayer}$ points, respectively. We can also notice the presence of faint circular features surrounding the horseshoe arc of graphene. These features can be attributed to the $\pi$-band replicas of graphene [64]. For perfect 2H stacking, $\Gamma$, $K_{heterobilayer}$ and $K_{Gr}$ are collinear and the relative angles between graphene, MoSe$_2$ and WSe$_2$ are all 0°. Instead of this perfect alignment, we observe an ‘arc’ of the heterobilayer valence band at $K_{heterobilayer}$ (the red arc drawn in figure 5(c) is a guide to the eye), which indicates that the TMD heterobilayer presents a range of rotational misalignment in the $[-4^\circ, +4^\circ]$ interval [34]. Such a continuous arc results from the incoherent emission from a large population of separate domains; each arbitrary rotated within the twist angle interval; sampled together by the relatively large ARPES beam size ($50 \mu m$). The presence of arbitrarily rotated domains is a typical feature of the weak vdW bonding between the components of the heterobilayer. Based RHEED and ARPES measurements, we conclude that the sample consist in ‘mostly

Figure 5. Constant energy maps in the $(k_x, k_y)$ momentum plane, acquired with an incident photon energy of 100 eV. (a) is acquired in the vicinity of the Dirac point of graphene. (b)–(c) are obtained around the valence maxima at $\Gamma$ and $K_{heterobilayer}$ of the heterobilayer, respectively. (d) Illustration of local moiré stackings (A, B, C) in the moiré cell (solid black line) of WSe$_2$/MoSe$_2$ with twist angle $\theta_{WSe2/MoSe2} = 2.6^\circ$. 
aligned’ crystals. Experimentally, the in-plane crystal orientation is not exact and that there exists a small angular spread around the expected value, which we interpret as twist angle between the WSe₂ and MoSe₂ monolayers.

Considering that our sample hosts a significant population of misaligned layers with respect to the 2H stacking, it is not surprising to observe discrepancies between the experimental band structure and the DFT simulation. In TMD heterostructures assembled from closely related twisted heterobilayer, MX₂/MX₂ with a small difference in lattice constant or orientation, theoretical investigations show that the band structure strongly depends on the intra-layer twist angle [65–68]. Unlike graphene bilayer with precise ‘magic’ angles [69], the valence flat bands theoretically predicted in TMD heterobilayers results from hole localization at the moiré high symmetry points due to moiré-induced band gap fluctuations [67]. Assuming the distance between these high symmetry moiré stacking is large enough compared to coulomb interactions (i.e. low twist angle), the holes will localize due to the band gap fluctuations in spatially separated pockets and behave as localized independent defects. Consequently, their corresponding energy dispersion shapes as a flat band in reciprocal space. In addition, there is no specific twist angle value associated to this type of flat band but rather a limited continuous interval centered at \( \theta = 0^\circ \). In the case of 2H stacked WSe₂/MoSe₂, LDA calculation leads to a moiré potential with amplitude about 10 meV for flat band states associated with WSe₂. For this system, the highest valence moiré band is flat and energetically isolated from other bands when the twist angle \( \theta \) is less than 5.6°. Figure 5(d) shows an example of a moiré configuration for \( \theta_{WSe₂/MoSe₂} = 2.6^\circ \) (\( \theta_{WSe₂/MoSe₂} = 0^\circ \) being the conventional 2H stacking). The resulting hexagonal moiré cell (solid black line) hosts a variety of local stacking, including the conventional 2H at position B but also other high symmetry stacking at positions A and C. Note that small positive or negative twist angle variations (a few degrees) around \( \theta_{WSe₂/MoSe₂} = 0^\circ \) only affect the size of the Moiré cell but not the type of high symmetry stackings. The theoretical twisted angle values leading to a flat band scenario in MoSe₂/WSe₂ [68] are \( \theta = 1.6^\circ \) and 2.6°, which falls in our experimental interval for WSe₂/MoSe₂, \( \theta_{±4} = ± 4.0^\circ \), as determined by ARPES. Still, the experimental bandwidth of the flat band is about 390 meV, which is much higher than the expected bandwidth predicted by the theory (between a few tens of meV to a couple of hundred meV) [68, 70]. This experimental bandwidth value can be attributed to the simultaneous sampling of multiple domains with small lateral dimensions with respect to the spatial resolution of present-generation nano-ARPES instruments, (see the discussion of figures 3 and 4), which experimentally results in the broadening of all the flat bands states. Additionally, the superposition of signals from domain with different \( \theta_{WSe₂/MoSe₂} \) misorientation angles, each with a slightly different theoretical flat band energy position respect to the Fermi level from DFT results [68, 70], also mathematically results in the broadening of the flat band alone.

Conversely, in the case of a specific ‘magic’ angle flat band scenario, the in-plane mosaic spread combined with the relatively large lateral probe size of the ARPES beam would lead a small signal to noise ratio for the ARPES flat band signal, proportional to the low probability of sampling this particular ‘magic’ twist angle value in the total population. In contrast, the flat band scenario described in [67, 68] is more robust, as it can occur in a range of twist angle, and thus be captured at much higher signal to noise ratio in our mosaic sample. We therefore conclude that it is very likely that the flat band dispersion observed in our WSe₂/MoSe₂ heterobilayer originates from localized states created by the moiré pattern and the corresponding twist angle between the two TMD lattices.

Conclusion

In summary, we have demonstrated the direct MBE growth of 1 ml WSe₂/1 ml MoSe₂ heterobilayer on graphene via a van de Waals epitaxy process. The high-resolution XPS measurements showed the absence of any contamination and revealed sharp and abrupt van de Waals interface between all materials. Our study of the electronic band structure by ARPES revealed an in-plane mosaic spread with twist angles as large as ±4°. A detailed analysis shows that the heterobilayer is strongly coupled electronically. We note the existence of a flat band, positioned inside the bandgap in the vicinity of the Fermi level, which should not exist for perfectly stacked layers. The comparison with theoretical work gives compelling evidence that this flat band relates to twist-dependent moiré superlattices between the two TMD layers. This observation of such flat band near the Fermi level opens a promising route to engineer the band structure of similar twisted heterobilayer systems.

Materials and methods

Growth of the 1 ml WSe₂/1 ml MoSe₂ heterobilayer

The heterobilayer was grown by MBE in a ultrahigh vacuum (UHV) reactor with a base pressure in the low 10⁻¹⁰ mbar range. Before the growth, the graphene substrate was thermally cleaned in the UHV chamber at a temperature of 800°C for 30 min. The heterobilayer growth temperature was 470°C. The direct Se flux measured at the sample position using a retractable gauge was 10⁻⁶ mbar. The Mo/W deposition rate, measured with a quartz balance, was 1.1 Å min⁻¹ corresponding to the growth of one WSe₂/MoSe₂ layer in 2 min and 30 s. Each monolayer was annealed at 780°C under Se during 15 min to improve crystalline quality. Finally, the heterobilayer was capped with an amorphous Se layer deposited at room temperature to prevent any degradation of the film during air transfer.
μ-Raman measurements

The μ-Raman measurements were conducted at room temperature with a x100 objective and a 532 nm laser excitation, using a commercial confocal Horiba micro-Raman microscope. The laser beam was focused onto a small spot having a diameter of ~1 μm on the sample and its incident power was about 5 μW. In our configuration, this laser power is sufficiently low to avoid any shift of the Raman modes on all samples.

DFT calculations

Bandstructure simulations of the 2H stacked WSe2-MoSe2 vdW heterobilayer were obtained by performing DFT simulations via the Quantum ESPRESSO suite [69], including SOC and vdW forces. Relevant parameters and models are detailed in the supplementary information.

Band structure of the WSe2/MoSe2 heterobilayer

The ARPES experiments were conducted at the ANTARES beamline of the SOLEIL synchrotron light source (Saint-Aubin, France). We used linearly horizontal polarized photons of 60 eV, 100 eV and 350 eV and a hemispherical electron analyzer with vertically-confining entrance slit to allow band mapping. The total angle and energy resolutions were 0.25° and 10 meV. All XPS and ARPES measurements were performed at 70 K.

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Data availability statement

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Contributions

EV, MJ and CV fabricated the samples. LK, DP, AO, JA, and PD carried out the nano-XPS/ARPES experiments. JC, characterized the samples by means of μ-Raman spectroscopy. MP, carried the DFT calculations. All authors analyzed the results and contributed to the scientific discussions and manuscript preparation.

ORCID iDs

Fabrice Oehler @ https://orcid.org/0000-0003-1020-160X
Julien Chaste @ https://orcid.org/0000-0001-8384-0133
Matthieu Janet @ https://orcid.org/0000-0002-8247-4677
Abdelkarim Ouerghi @ https://orcid.org/0000-0002-1898-2765

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