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Layer-dependence of the electronic band alignment of few-layer MoS₂ on SiO₂ measured using photoemission electron microscopy

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Tailoring band alignment layer-by-layer using heterojunctions of two-dimensional (2D) semiconductors is an attractive prospect for producing next-generation electronic and optoelectronic devices that are ultra-thin, flexible, and efficient. 2D layers of transition metal dichalcogenides (TMDs) in laboratory devices have already shown favorable characteristics for electronic and optoelectronic applications. Despite these strides, a systematic understanding of how band alignment evolves from monolayer to multilayer structures is still lacking in experimental studies, which hinders development of novel devices based on TMDs. Here we

report on the local band alignment of monolayer, bilayer, and tri-layer MoS₂ on a 285-nm-thick SiO₂ substrate using a new approach to probe the occupied electronic states based on photoemission electron microscopy and deep ultraviolet light. Local measurements of the vacuum level and the valence band edge at the Brillouin zone center show that the addition of layers to monolayer MoS₂ increases the relative work function, and pushes the valence band edge toward the vacuum level. We also deduced n-type doping of few-layer MoS₂ and type-I band alignment across monolayer-to-bilayer and bilayer-to-trilayer lateral junctions. Conducted in isolation from environmental effects owing to the vacuum condition of the measurement and an insulating SiO₂ substrate, this study shows a new metrology to uncover electronic properties *intrinsic* to MoS₂ semiconducting layers and emerging 2D crystals alike.

I. INTRODUCTION

The design and implementation of semiconductor homo- and heterojunctions are cornerstones of today's growing electronic and optoelectronic industries. In addition to a tunable band gap and carrier control via spin and valley degrees of freedom,^{1,2,3,4} heterojunctions based on atomic layers of transition metal dichalcogenides (TMDs) have displayed a wide range of favorable properties in laboratory devices, well-suited to electronic and optoelectronic applications.^{5,6,7} Layered TMDs exhibit high on-off ratios in field effect devices,^{8,9,10,11} high photoluminescence quantum efficiency,^{12,13} high percentages of light absorption,¹⁴ high photogain and photoresponse.^{15,16}

In order to obtain high performances in most of the above-mentioned devices, the efficient injection of charge (or energy) across contacts and control of carrier transport across

heterojunctions require accurate determination of band alignment, including offsets of the work function, valence band maximum, and conduction band minimum. While there has been tremendous progress in the growth of TMD-based heterostructures for charge transport and optical measurements, information about their band alignment is not readily available. This is due in part to their electronic structures being sensitive to the number of layers and the stacking orientation.^{17,18,19,20} Measurement of the band alignment has been further complicated by poor screening of interactions with the supporting substrate and physisorbed or chemisorbed gas molecules, obscuring the electronic properties intrinsic to TMD layers.^{21,22,23} For MoS₂, a prototypical TMD, alignment of the electronic states at the junctions between layers of different thickness have been reported in studies of surface potentials typically using scanning Kelvin probe microscopy (SKPM) and electrostatic force microscopy (EFM).^{24,25,26,27,28,29,30} However, SKPM and EFM studies have yet to quantify the surface potential offsets at the junctions, or even just to achieve a clear consensus on whether the work function rises or falls as layer number is increased. Authors have ascribed incongruous results from SKPM and EFM, often performed in ambient conditions, to hydrophilicity of the MoS₂ surface.^{27,31,32} In this context, an accurate measurement of the electronic band alignment on a technologically relevant substrate, without any influence from the environment is a vital parameter for developing TMD heterostructures for novel optoelectronic devices.^{33,34} The requirement for quantitative determination of the electronic band alignment *intrinsic* to few-layer TMDs also necessitates that measurements be performed on TMD specimens supported by a substrate that interacts minimally with the overlying TMDs, preferably an insulator. This condition precludes the use of electron-based spectroscopy tools, such as photoemission spectroscopy, due to the limitations imposed by

sample charging. We overcome this restriction by using photoemission electron microscopy (PEEM) with deep-ultraviolet (DUV) illumination as an excitation source.

In the work reported here, we studied the band alignment of a model TMD system, few-layer MoS₂ supported on 285-nm-thick SiO₂ grown on a Si wafer, in an ultra-high vacuum environment using PEEM. Local determination of the vacuum level, valence band edge at the Brillouin zone (BZ) center, and ionization energy of monolayer (1ML), bilayer (2ML), and trilayer (3ML) MoS₂ were obtained from the local photoemission spectra (PES) and the photon-energy-dependent photoemission yield (PEY). We observed that with the addition of layers, the vacuum level and, hence, the work function increased relative to 1ML MoS₂. The valence band edge also advanced toward the vacuum level with increasing layer number. Based on these results, we constructed a band diagram of 1ML, 2ML, and 3ML MoS₂, which shows type-I band alignment across monolayer-to-bilayer and bilayer-to-trilayer lateral junctions. We also determined that few-layer MoS₂ on 285-nm-thick SiO₂ is n-type, which we inferred from the reported work function of 1ML MoS₂ supported on a Si wafer. Our successful application of PEEM using deep-ultraviolet (DUV) light to measure the band alignment of semiconducting TMD crystals on a nominally insulating substrate, all the while encountering minimal charging of the sample, presents new insight into their electronic properties.

II. EXPERIMENTAL PROCEDURE

All MoS₂ flakes were synthesized using a slightly modified version of a well-established chemical vapor deposition (CVD) technique that proceeds via sulfurization of a MoO₂ precursor.³⁵ The more common CVD technique using MoO₃ was not chosen because of its tendency to grow large-area 1ML with very scant 2ML nucleation.³⁶ Synthesis of MoS₂ with

MoO₂ precursors and higher growth temperatures produced larger multilayer regions³⁷ ideal for a layer-dependent PEEM study of MoS₂. 285-nm-thick SiO₂ thermally grown on a highly-doped silicon wafer (p-type, 12.0-16.0 Ω·cm) was chosen as a substrate material to produce optical contrast for as-grown structures.^{38, 39} The layer number of each MoS₂ region was verified using Raman spectroscopy.⁴⁰ To remove adsorbed water from the sample surface, samples were annealed for ~12 hours at ~300°C in ultrahigh vacuum (UHV) prior to PEEM measurement.

PEEM measurements were conducted in a LEEM-III system (Elmitec Elektronenmikroskopie GmbH) coupled to a continuous-wave, tunable DUV light source comprised of a pressurized Xe lamp (Energetiq, EQ-1500 LDLS), a Czerny–Turner monochromator (Acton research, SP2150), and refocusing optics (fused silica and calcium fluoride/silica achromat lenses).⁴¹ The spectral width of the DUV light was set to 50-100 meV throughout the wavelength range used for the measurement ($\lambda = 175\text{--}350$ nm, $h\nu \approx 3.6\text{--}7$ eV). Acquisition times for images were typically on the order of a few minutes (< 5 min.), and complete spectra required hours (3-18 hrs.) to obtain. The photon flux of our tunable DUV source provided a sufficient signal-to-noise ratio of photoemission intensity to enable fitting of local photoemission spectra for this study. The field of view for photoemission images and spectral maps was 100 μm with a diameter of 600 pixels, corresponding to a pixel size of ~150 nm/pixel.

During acquisition of photoemission spectra, we used an electron filter on the LEEM-III instrument to sweep through the kinetic energies of the photoemitted electrons. No aperture restricted the emission angle of the photoelectrons. Thus, the data presented here correspond to emission-angle integrated spectra. The leading (left) and trailing (right) edges of PES spectra yield information about the location of the vacuum level and the valence band edge at the center of the BZ, respectively (see Fig. 1(c)). Similar to conventional analysis of XPS/UPS spectra,

lines are fit to these edges and the intersects of the fitted lines with the baseline of the spectra are determined. These intersects specify the locations of the vacuum level and the valence band edge. The energy resolution of our electron energy filter was set to 0.5 eV, which results in a broadening of the PES spectral width by 0.5 eV. This broadening due to the resolution of the electron energy filter is corrected for *post facto* by shifting the leading and trailing edges of the spectra, similar to the procedure outlined in ref. 42. Maps of the vacuum level and the highest occupied states were obtained by fitting the PES spectra at each pixel (obtained at a fixed photon energy) and by correcting for the dispersion of the electron energy filter using a known surface (in this case, the SiO₂ background). Local variation in the vacuum level yields the work function variation.

Ionization energy maps were obtained from PEY curves recorded at each pixel as a function of photon energy using a monochromator in tandem with our DUV light source. The electron energy filter was not used for PEY measurements. We determined ionization energy pixel-by-pixel from the minimum photon energy above which photoemission is observed (photoemission threshold) in the photon-energy scan. The standard deviation of the signal acquired with lower energy photons (below the photoemission threshold) was used as a criterion to define the photoemission threshold at each pixel.⁴³

III. RESULTS AND DISCUSSION

The PEEM measurements and an optical image of 1ML, 2ML, and 3ML MoS₂ grown on 285-nm-thick SiO₂ are shown in Fig. 1. The data in Figs. 1(a), (c), and (d) were acquired using photons with $\lambda = 185$ nm (6.70 eV). Figure 1(a) shows the vacuum level map, where the relative vacuum levels, E_{vac} , of 1ML, 2ML, 3ML, and multilayer MoS₂ as well as that of the SiO₂

substrate are clearly distinguishable. The vacuum level of the SiO₂ substrate lies ~0.5 eV lower in energy than that of 1ML MoS₂. The thickness of the MoS₂ flakes is verified from the optical contrast shown in Fig. 1 (b), and is further confirmed from the Raman spectra at the locations highlighted by the green, yellow, and orange dots corresponding to 1ML, 2ML, and 3ML.⁴⁰ The crystallographic alignment between layers can be inferred from the relative orientations of the triangular edges.⁴⁴ Most flakes display 2H or 3R stacking with random stacking orientation for thicker parts of the flakes.⁴⁵

Figure 1(c) shows representative PES spectra for 1ML, 2ML, and 3ML regions indicated by the black dotted line in the Fig. 1(a). The leading (left) edge and trailing (right) edge of PES spectra, which yield information about the location of E_{vac} and valence band edge at the center of the BZ, are indicated by tick marks in Fig. 1(c). With increasing layer number, E_{vac} (left edge of the PES peak) and the valence band edge (right edge of the PES peak) are shifted higher in kinetic energy for MoS₂. The variation of the local E_{vac} shown in Figs. 1(a) and (c) establishes a layer-dependent surface potential in MoS₂. In Fig. 1(c) the PES intensity from 1ML MoS₂ appears higher than that of 2ML and 3ML MoS₂. Note that the relative intensities between MoS₂ regions with different thicknesses varied as function of photon energy. We postulate that this enhancement of the photoemission intensity results from the difference of the photoemission cross section for different thicknesses of MoS₂ at the particular photon energy used in the measurement.^{46,47,48,49}

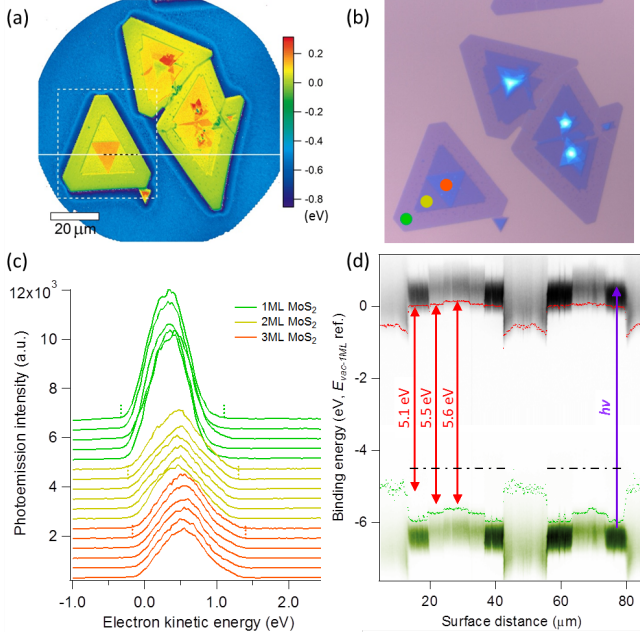


FIG. 1. The (a) vacuum level, E_{vac} , map, (b) the optical image, (c) the representative photoemission spectra, and (d) the alignment of the electronic states of MoS₂ flakes grown on SiO₂. (a), (c), and (d) were acquired using photons with $\lambda = 185$ nm ($h\nu = 6.70$ eV). The color scale bar for (a) is in eV. The black dotted line and the white solid line in (a) illustrate the locations where the photoemission spectra shown in (c) and (d) were obtained from. In (c) the leading edges of E_{vac} (left edge) and the valence band edge (right edge) are indicated by tick marks. In (d), the alignments of E_{vac} and the valence band edges of 1ML, 2ML, and 3ML MoS₂ are indicated by the red and green dots. Superimposed images are the photoemission intensity map. The widths of superimposed photoemission intensity profiles correspond to the widths of their respective photoemission spectra. The black dash dot lines illustrate the energy of the Fermi level deduced from the work function of 1ML MoS₂ reported in ref. 51 and red bidirectional arrows represent results for the ionization energy obtained using PEY.

Combining information concerning E_{vac} , the valence band edge, and the photon energy enables us to examine the alignment of the electronic states across 1ML, 2ML, and 3ML MoS₂. PES

spectra at each pixel along the white line in Fig. 1(a) were extracted and are presented as surface band alignment in Fig. 1(d). Higher PES intensities appear darker in color. The green photoemission intensity map represents the initial filled state, which is inferred by offsetting the black PES spectra by the photon energy used for the PES measurement ($\lambda = 185$ nm, or $h\nu = 6.70$ eV). The energy of the valence band edge is thereby expressed in terms of the electron binding energy with respect to the vacuum level of 1ML MoS₂ by considering the following relationship:

$$(BE_{rel})_{1ML MoS_2} = (KE_{rel})_{1ML MoS_2} - h\nu,$$

where $(BE_{rel})_{1ML MoS_2}$ and $(KE_{rel})_{1ML MoS_2}$ are the binding energy and the kinetic energy relative to 1ML MoS₂, respectively. This difference in binding energy between the vacuum level and valence band edge at the BZ center is the ionization energy as measured using PES. Because we use low-energy photons in our measurement, the highest occupied states measured reflect the valence band edge near the Γ -point.

The vacuum level alignment is presented via red dots in Fig. 1(d). These values were extracted from the leading edge of the PES spectra (the left edge in Fig. 1(c)) shifted 0.25 eV higher in electron kinetic energy (i.e. toward the right edge) to account for energy broadening due to the moderate electron energy resolution of the measurement (~ 0.5 eV). The alignment of the valence band edge at BZ center is presented in green dots, whose values were extracted from the trailing edge of the PES spectra (the right edge in Fig. 1(c)). Again, the trailing edge of the PES spectra was shifted to lower kinetic energy by 0.25 eV to account for energy broadening. The magnitude of the ionization energies for 1ML, 2ML, and 3ML MoS₂ that were determined from the PEY map shown in Fig. S2⁵⁰ are represented by red arrows in Fig. 1(d). Ionization energy measurements are obtained from PEY spectra by analyzing the threshold energy of illumination

at which photoemission occurs. For metals, this threshold energy corresponds to the work function of the metal, while for a semiconductor lacking states at the Fermi level this threshold energy corresponds to the ionization energy- the difference in energy between the vacuum level and valence band edge.

Assuming a 4.49 eV work function for monolayer MoS₂,^{51,52} and that the Fermi level is aligned between 1ML, 2ML, and 3ML MoS₂ within a single crystalline flake, the location of the Fermi level is shown by the black dash-dot lines illustrated in Fig. 1(d). The latter assumption is reasonable given a lack of chemical bonding between MoS₂ and the underlying SiO₂,⁵³ and the van der Waals interlayer coupling between MoS₂ layers.⁵⁴ Refs. 51 and 52 measured work function values for 1ML MoS₂ specimens (4.49 eV and 4.52 eV, respectively) that received little exposure to ambient conditions and were annealed in inert environments, consistent with the conditions of our measurement. Further assuming that the optical band gap values of 1ML, 2ML and 3ML MoS₂ are ~1.9 eV, ~1.6 eV, and ~1.4 eV,¹⁷ our experimental data suggest that the Fermi-level of the MoS₂ flake is above mid-gap, indicating n-type character. This result is consistent with the n-type conductivity commonly found in monolayer MoS₂ on SiO₂ and bulk 2H-MoS₂.^{55,56} Another important aspect of Fig. 1(d) is the abrupt transitions of both E_{vac} and the valence band edge at the junctions between MoS₂ regions of different thicknesses. Band bending at the heterojunctions between TMDs with different layer numbers has been observed, but at the nanometer scale.³⁴ Fig. 1(d) confirms that such band bending is absent at the larger length scale probed in the present PEEM experiment. Further details of the band alignment are discussed in the following.

From Fig. 1(d) it appears that the ionization energy we measured from PEY⁵⁰ (red arrow) and the ionization energy we deduced from the PES spectra (green dots) do not agree for 1ML and

2ML MoS₂, deviating significantly (~0.9 eV) for 1ML MoS₂. In contrast, they show reasonable agreement for 3ML MoS₂. These discrepancies in 1ML and 2ML MoS₂, we believe, are largely due to the photoemission signal of the underlying SiO₂ substrate. Figure 1(d) shows that the measured ionization energy of SiO₂ is lower than that of MoS₂. Therefore, we expect the PEY intensity of the MoS₂ flakes at the lower photon energy (longer wavelength) range would be overwhelmed by the photoelectrons from SiO₂. Furthermore, a general trend of a longer probing depth with longer wavelength photons could increase the relative contribution of the underlying SiO₂ in the photoemission intensity.⁵⁷ This scenario is supported by PES spectra acquired for photons with $\lambda = 200$ nm where additional spectral weight from the SiO₂ substrate is visible in the PES spectra, beyond that of MoS₂.⁵⁸ We note that 1ML and 2ML MoS₂ show larger additional spectral weights than does 3ML, in which the SiO₂ signal is mostly attenuated. Overall, reasonable agreement of the ionization energy of 3ML MoS₂ evaluated from the PES and PEY measurements supports the validity of the energy scale used in our analysis. Because results from PES spectra for MoS₂ are reliable regardless of the MoS₂ thickness, we continue our discussion of the band alignment based on the PES data taken with higher-energy photons ($\lambda = 185$ nm).

Clear distinction between 1ML, 2ML, and 3ML regions in the E_{vac} map in Fig. 1(a) allows for quantifying variation in the local work function. The histogram of the extracted E_{vac} values and the plot of relative work function are presented in Figs. 2(a) and (b). We fit the E_{vac} distribution in Fig. 2(a) with Voigt functions. The FWHM of each fit component corresponds to the error in relative work function values plotted in Fig. 2(b). We note that, because our PES measurements using PEEM do not have an absolute energy scale, the E_{vac} measurements are reported relative to that of 1ML MoS₂.

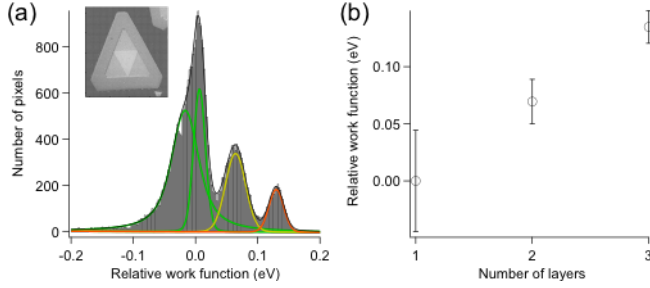


FIG. 2. Determination of the work function variation in a MoS₂ flake. (a) Histogram of E_{vac} obtained for the imaged MoS₂ island shown in the inset. (b) The relative work function of 1ML, 2ML, and 3ML MoS₂. The error bars in the relative work function are the widths of the fitted peaks in (a). Incomplete removal of the dispersion background necessitated that the relative work function distribution of 1ML MoS₂ be fit with two components shown in green. Thus, the error bar in Fig. 2(b) for 1ML MoS₂ corresponds to the FWHM of the overall fit composed of the superposition of the two green peaks.

From Fig. 2(b), we found that the relative work function increases by ~ 70 meV with each additional MoS₂ layer. Thus, if the work function of 1ML MoS₂ is 4.49 eV,^{51,52} our results suggest that those of 2ML and 3ML MoS₂ are 4.55 eV and 4.63 eV, respectively. The trend of work function increase with increasing number of layers has not been established amongst SKPM and EFM studies of MoS₂. Both increasing and decreasing work function with increasing layer number have been reported. One may surmise that hydrophilicity of MoS₂ and the effects of ambient conditions account for this inconsistency.²⁷ We also note that to arrive at surface potentials, SKPM uses the capacitive difference between a conducting AFM probe and a charge layer thickness in the sample. For semiconducting crystals suspended on substrates it is not clear to what extent charge layers in the substrate may contribute to stray fields, and whether the substrate and sample have reached thermodynamic equilibrium.⁵⁹ Both can influence SKPM

results. To our knowledge, the only SKPM study to observe work function variation similar to what we observed in the present work was conducted in UHV (the work function increases by ~ 50 meV with each additional MoS₂ layer).⁵² This appears to confirm that the work function increase as a function of the layer number we observed reflects the electronic properties of MoS₂ flakes supported on an insulating substrate, minimally perturbed by environmental effects (thanks to UHV conditions).

Based on the measured variations of the relative work function and valence band edge at the Γ -point of MoS₂, we determine the band alignments across 1ML, 2ML, and 3ML. Figure 3 shows a simplified schematic of the band alignment between MoS₂ and SiO₂. The schematic includes reported band gap values for 1ML, 2ML, and 3ML MoS₂⁵⁵ as well as the energy differences of the valence band edges at the Γ -point versus the K -point ($\Delta E_{\Gamma,K}$) based on theoretical calculations (ref. 60 for 1ML and 2ML, and ref. 61 for 3ML). Also shown in Fig. 3 is the position of the Fermi level deduced from the 4.49 eV work function for monolayer MoS₂ reported in refs. 51 and 52.

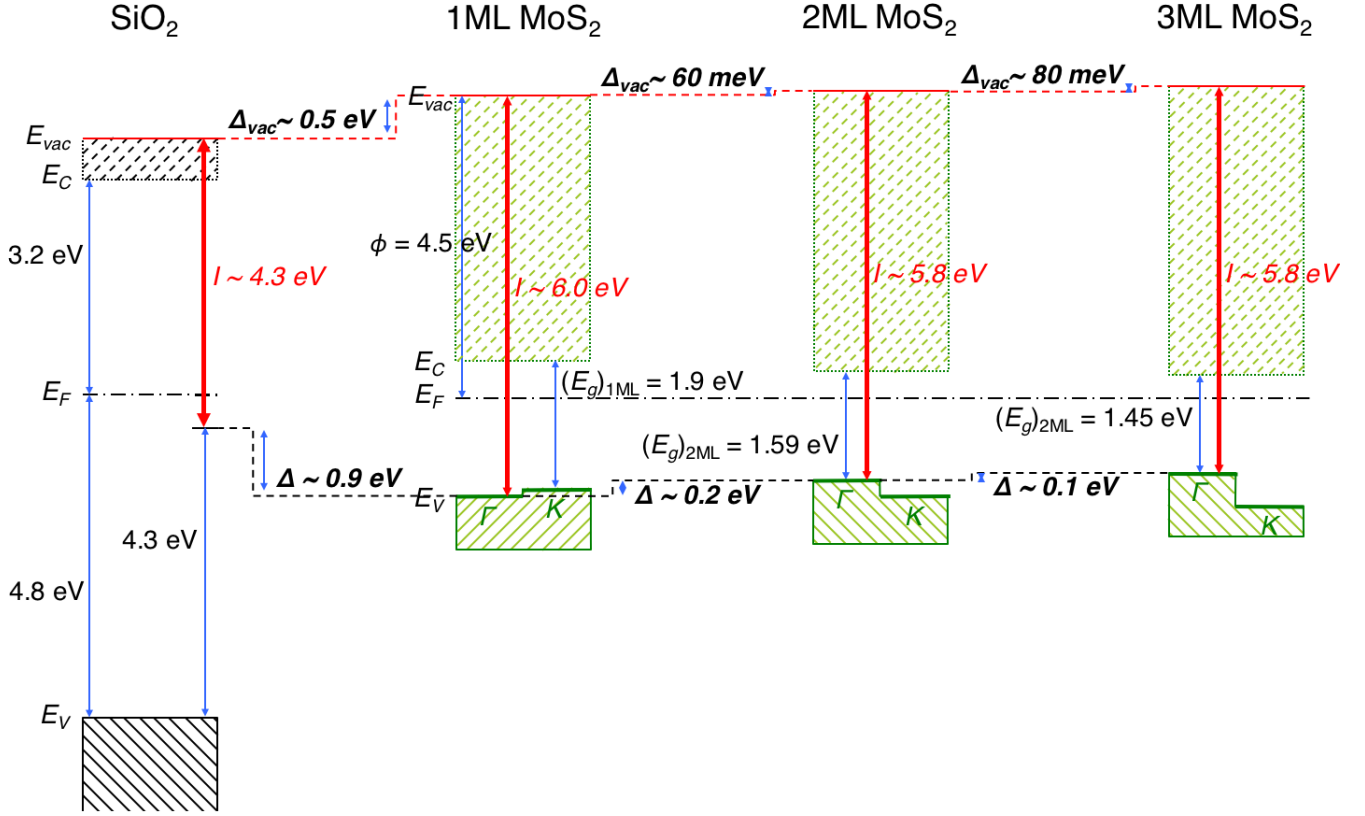


FIG. 3. A simplified band diagram of 1ML, 2ML, and 3ML MoS₂ and SiO₂, which includes quantities measured with PEEM in boldfaced, italicized type. The ionization energies were calculated from PES, and are represented with red arrows and fonts. Other numbers are based on the reported values as described in the main text.

As a whole, Fig. 3 points to some important aspects of the junctions between 1ML, 2ML, and 3ML MoS₂. First, the Fermi-levels of the MoS₂ lie a few 100 meV above mid-gap in all three thicknesses, as described earlier. Because of the similar effective electron and hole masses for 1ML MoS₂ ($m_e^* = 0.54$ and $m_h^* = 0.44$),⁶² we can expect that the Fermi level of the intrinsic 1ML MoS₂ would lie close to the mid gap. This scenario suggests the n-type character of 1ML MoS₂ grown on SiO₂. As the effective electron and hole masses are similar for 2ML and 3ML, they are expected to be n-type as well. The band diagram also suggests type-I band alignment across the

1ML-2ML and 2ML-3ML heterojunctions. This result is in a qualitative agreement with the theoretical calculations by Padilha et al.⁶¹ and Kang et al.,⁶³ and contradicts a scanning photocurrent microscopy study, which suggests a type-II heterojunction between 1ML and multilayer MoS₂ on SiO₂.⁶⁴

One uncertainty in the band diagram (Fig. 3) is the difference in energy of the valence band edges at the Γ -point versus the K -point ($\Delta E_{\Gamma-K}$) in 1ML MoS₂. While we use $\Delta E_{\Gamma-K} = 0.1$ eV based on a theoretical work,⁶⁰ an angle resolved photoemission spectroscopy (ARPES) measurement of 1ML MoS₂ on Au(111) suggests $\Delta E_{\Gamma-K}$ as large as 0.3 eV.^{65,66} Were this so, it would imply that band alignment across the 1ML-2ML MoS₂ heterojunction is type-II. Because ARPES measurements of 1ML MoS₂ on less interacting substrates (thin SiO₂/Si⁶⁷ and graphene/SiC⁴⁹) suggest $\Delta E_{\Gamma-K} = 0.1$ eV, we presume $\Delta E_{\Gamma-K} = 0.1$ eV for 1ML MoS₂ on thick SiO₂. Accordingly, a type-I heterojunction is expected at the 1ML-2ML MoS₂ interface formed on SiO₂. We speculate that the type-II heterojunction found in the scanning photocurrent microscopy study may be the result of light-induced defects or trapped charges at the surface of SiO₂ influencing the band alignment of MoS₂. Further study is needed to gain a comprehensive understanding of the influence of trapped charge. We also note that even $\Delta E_{\Gamma-K} = 0.3$ eV does not alter our assessment of n-type character for 1ML MoS₂.

Additional uncertainty in the band diagram arises due to twist angles between layers and stacking sequence. Though we did not characterize the stacking configuration of our sample, we note that triangular flakes in our sample adopted angles of either 0° or 60° relative to one another (Fig. 1(c)). Theory suggests that is indicative of either of two stable stacking configurations, 2H(AA') or 3R(AB).^{68,69} A recent μ -ARPES study of twisted bilayer MoS₂ on native oxide layers on Si⁷⁰ demonstrates that a twist angle of 60° (2H or AA' stacking) relative to the 3R(AB)

configuration shifts the Γ -point downward in energy by as much as 40 meV, while the K -point appears largely unaffected by twist angles ranging from 0° (3R or AB stacking) to 60° (2H or AA' stacking). Such a shift in energy of the Γ -point would not significantly impact the type-I band alignment we observe across the 1ML-2ML MoS₂ heterojunction, nor alter our assessment of n-type MoS₂.

Figure 3 provides electronic structure information for SiO₂ in addition to that for MoS₂. From Fig. 1(d), E_{vac} of SiO₂ is located at 0.5 eV below that of 1ML MoS₂, while the highest occupied state in SiO₂ lies at -4.8 eV binding energy (with respect to the E_{vac} of 1ML MoS₂). Fig. 3 also shows an 8.0 eV bandgap and 8.6 eV ionization energy for SiO₂, and a Fermi level that sits above mid-gap (4.8 eV above the valence band of SiO₂) based on previous reports.^{71,72} There is type-I band alignment across the lateral MoS₂-SiO₂ heterojunction for which we expect minimal band bending owing to Van der Waals interactions between MoS₂ and the substrate. We note that the 4.3 eV energy difference between E_{vac} and the highest occupied state in SiO₂ is significantly smaller than the expected ionization energy of SiO₂ (8.6 eV).⁷²

We postulate the highest occupied state shown in the PES spectra from SiO₂ (Fig. 1(d)) corresponds to defects in SiO₂. From photoluminescence studies, oxygen deficiency centers (ODCs)⁷³ have been shown to produce emission bands 4.3 eV above the valence band of SiO₂.^{74,75,76,77} Defects in SiO₂ are also observed in the DUV photoemission spectra of glassy SiO₂ and quartz implanted with metals ions.^{78,79} In Fig. 3, the highest occupied state probed in our experiment (see Fig. 1(d)) is located at 4.3 eV below the vacuum level of SiO₂, and coincides well with an energy level of ODCs. Over the course of our PES measurements we observed the photoemission intensity from the SiO₂ substrate to vary as a function of the photon wavelength in a manner consistent with the photoemission intensity variation reported in refs. 78 and 79.

Photoemission experiments on insulating materials are generally not reported because of sample charging, which obscures the interpretation of the spectra or image. In this regard, this report presents a unique case where photoemission microscopy and spectroscopy can be performed on MoS₂ flakes supported on nominally-insulating 285-nm-thick SiO₂. Similar PEEM measurements of 2D crystals on thick SiO₂ are reported, but they were conducted with the aid of additional grounding^{80,81} or alkali metal doping⁸² to alleviate charging. Furthermore, PEEM imaging of an insulator surface free of image distortion or charging was once demonstrated on a SiO₂ film using a supplemental electron source in addition to the UV illumination.⁸³ These works suggest that PEEM of 2D semiconducting layers supported by insulating substrates is possible, provided there are means to compensate for charge accumulation at the sample surface.

To verify that the PES spectra presented here are minimally influenced by charging, we recorded PES spectra as a function of photon energy, and confirmed that the spectral width increases linearly with a slope close to unity.⁸⁴ This result confirms that there is no additional elongation of the spectral width as a function of the photon energy, which is one signature of sample charging. We attribute the apparent absence of charging to two factors: the low photoelectron current of our measurement technique, and the dissipation of photoholes responsible for surface charging by photoactive defects in SiO₂ moving charges to and from the MoS₂ flakes. We note that illumination of a similar sample using a He discharge lamp ($h\nu = 21.2$ eV) resulted in instant charging, likely because of the higher photoelectron current produced at the higher excitation energy. Further experimental verification of the charging behavior of MoS₂ flakes on SiO₂ using a He lamp is provided in Supporting Information.

Electron spectroscopy is a powerful tool for studying electronic properties of materials, but it is generally limited to conductive materials. This limitation has hampered the study of electronic

properties intrinsic to 2D crystals supported on insulating substrates in order to minimize electronic perturbation. The work presented here resolves this quandary for 2D crystals research, and suggests that a new approach based on PEEM and DUV illumination may be used to study the electronic properties intrinsic to other 2D crystals supported on SiO_2 .

IV. CONCLUSION

In summary, a study of the electronic state alignment in monolayer, bilayer and tri-layer MoS_2 on a 285-nm-thick SiO_2 substrate have been presented. The layer dependence of the photoemission spectra showed a trend of increasing work function and shifting of the valence band edge at Brillouin zone center toward the vacuum level with increasing layer thickness. Based on our measurements, we proposed the band alignment between MoS_2 layers. We deduced that MoS_2 is n-type, and showed type-I band alignment across monolayer-to-bilayer and bilayer-to-trilayer lateral junctions. Our results demonstrate that photoemission electron microscopy coupled to a deep ultraviolet light source is a powerful tool to evaluate the electronic properties of MoS_2 with minimal environmental influence, and can be employed to study other 2D layered semiconductors and metals. The band alignment derived in the present work is essential information for building electronic and optoelectronic devices based on atomically thin MoS_2 .

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