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Atomic scale depletion region at one dimensional MoSe₂-WSe₂ heterointerface

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Lateral heterojunctions based on two dimensional (2D) transition metal dichalcogenides (TMDCs) potentially realize monolayer devices exploiting 2D electronic structures and the functions introduced by the presence of 1D heterointerfaces. Electronic structures of a lateral MoSe₂-WSe₂ junction have been unveiled using scanning tunneling microscopy and spectroscopy. A smooth and narrow depletion region exists despite a defect-rich heterointerface deviating from the preferred zigzag orientations of the TMDC lattice. From the characteristics of the depletion region, a high carrier concentration and high internal electric fields are inferred, offering to benefit designs of lateral TMDC devices. *Published by AIP Publishing*. https://doi.org/10.1063/1.5053144

Reducing dimensionality of bulk materials has unleashed great potential for functional properties available only in ultrathin or two dimensional (2D) forms. Following the huge success of graphene,^{1,2} a variety of 2D materials with exotic properties have been synthesized *via* different approaches.^{3–7} 1H monolayer transition metal dichalcogenides (TMDCs) MX_2 (M = W, Mo; X = S, Se), called inorganic analogues of graphene,⁸ attract much attention. Structural inversion asymmetry not only results in different optical selection rules for the interband transition at K and K' valleys but also leads the valley carriers to opposite directions in in-plane electric fields. Because of strong spin-orbit coupling of the metal elements, the K and K' valleys further possess opposite spin splitting.^{5,9} These semiconducting TMDC monolayers therefore play important roles in diverse fields such as electronics, optoelectronics, valleytronics, and spintronics.9-12

To improve functionality, vertical stacking of 2D materials including TMDC layers has been intensely investigated, leading to different types of p-n junctions and efficient optoelectronic units, based on designed band alignments and interlayer coupling.^{13–18} Moreover, it has been demonstrated that different TMDC monolayers can be stitched together forming lateral heterojunctions,^{19–21} in which carrier transport and exciton generation occur in seamless monolayers. As stacking methods influence physical properties in 2D layers in vertical devices, the stitched 1D interfaces may possess additional features due to dislocations or compositional differences between junction sides.^{22–24} Spatially resolving electronic structures of the 1D interfaces is thus important for the establishment of lateral heterojunction devices.

In this article, we present visualizations of narrow depletion regions in defect-rich areas at MoSe₂-WSe₂ boundaries deviating from the typical zigzag orientations. Using scanning tunneling microscopy (STM) and spectroscopy (STS), we imaged type-II band alignment across the $MoSe_2-WSe_2$ lateral heterojunction on HOPG. The depletion region width of a few nanometers can be explained by a high carrier concentration in the TMDCs on HOPG and gives rise to a high built-in electric field. In spite of abundant Mo substitution defects in WSe₂, the depletion region remains narrow and symmetric, indicating limited influences from extrinsic substitution defects on the band alignment.

High-crystalline-quality monolayer MoSe₂-WSe₂ lateral heterostructures were synthesized on sapphire by chemical vapor deposition (CVD) using the so-called one-step growth process in a horizontal hot-wall tube furnace with two heating zones. High-purity MoO₂ (99%, Aldrich) and WO₃ (99.995%, Aldrich) powders were placed in the same quartz boat located at the center heating zone and were heated to 880 °C during growth. The Se (99.5%, Alfa) powder was placed at the upstream heating zone and was maintained at 245 °C. Due to the different sublimation rates of MoO2 and WO₃ at different temperatures, MoO₂ evaporates more rapidly at lower temperatures and WO3 evaporates mostly at higher temperatures, leading to a sequential growth of MoSe₂ at the initial stage and then WSe₂ at the final stage when ramping up the temperature of the center heating zone to 880 °C. The MoSe₂-WSe₂ heterostructures were obtained by placing substrates at the downstream side using an Ar/H_2 (9% H₂) flowing gas (66 SCCM) at 5 Torr for 10 minutes.

After growth, the $MoSe_2$ -WSe₂ flakes on sapphire were dipped in BOE (HF:NH₄F = 1:6) solution for 2 hours to reduce TMDC-sapphire adhesion. By engaging clean polydimethylsiloxane (PDMS) stamps rinsed in acetone, glycol, and deionized water with the samples, TMDC flakes were peeled off and transferred onto an HOPG surface. Before STM measurements, the samples were annealed to $150 \,^{\circ}$ C in ultrahigh vacuum for 8 hours to remove adsorbates on the surface. STM and STS experiments were performed in *Omicron* multifunctional chambers in ultrahigh vacuum at room temperature, except the zoom-in image in Fig. 2(e), which was measured at 77.7 K. STM images were acquired in the constant current mode, and STS was performed with the help of lock-in techniques with a modulation of 15 mV and 1.5 kHz. The STM images and STS curves were processed using the WSxM software package.²⁵

During the CVD process, triangular $MoSe_2-WSe_2$ islands with the 1*H* structure grow as central $MoSe_2$ surrounded by WSe_2 [Fig. 1(a)]. Due to the nearly identical lattice constants of $MoSe_2$ and WSe_2 , the TMDCs are expected to be free from lateral strain and also effectively indistinguishable even in atomically resolved STM images. However, we are able to distinguish $MoSe_2$ from WSe_2 from bandgap positions extracted from STS curves, which represent the local density of states. The fact that WSe_2 is more a p-type semiconductor suggests a higher bandgap position compared to $MoSe_2$.^{26,27}

Figure 1(b) and the insets show averaged STS curves and TMDC domains from which the curves were acquired. The orange (brown) curve was acquired from the lower (higher) area in the topograph, taken at -2 V, as shown in the left-hand-side inset. Both curves were acquired at positions 7.5 nm away from the boundary to avoid boundary influences. The valence band maximum (VBM) and the conduction band minimum (CBM) positions extracted from turning points at the bandgap edges are (-1.49 eV, 0.67 eV) and (-1.12 eV, 0.93 eV) for the orange and brown curves, respectively. As a result, we suggest that the lower (higher) area in the left-hand-side inset in Fig. 1(b) is MoSe₂ (WSe₂) from the gap position.

While the unit cell height of monolayer WSe_2 is slightly higher than $MoSe_2$,²⁸ the apparent height difference is biasdependent and reversed at 1.5 V [right-hand-side inset in Fig. 1(b)]. The reason is that, based on the collection of tunneling electrons, STM images are influenced by the sample electronic structure. At 1.5 V, which is deep into the MoSe₂ conduction band, MoSe₂ yields a greater tunneling current than WSe₂ does and therefore appears higher in STM images. On the contrary, shown in the left inset, MoSe₂ appears lower at -2 V, at which point the WSe₂ valence band yields a larger current than the MoSe₂ one does.

Figure 2(a) shows a topography image of TMDC domains obtained at 0.6 V, with the atomic lattices enhanced with the aid of Fourier filtering. The continuous lattice structures across the boundary exhibit lateral epitaxial growth of WSe₂ following on from MoSe₂. The 1H TMDC surface can be described by a honeycomb lattice with a basis composed of chalcogen and metal atoms, and therefore, the zigzag and the armchair directions are indicated as dashed and solid lines in the schematics in Fig. 2(b). Comparing the zoomedin TMDC lattice structure in the inset in Fig. 2(a) with the schematics, we mark the zigzag and the armchair directions on the STM images. A corresponding contrast-enhanced dI/ dV map in Fig. 2(c) emphasizes the location of the curved MoSe₂-WSe₂ boundary, locally deviating from the typical zigzag directions.²⁹ More examples are shown in Fig. S1 in the supplementary material.

On the other hand, while the MoSe₂ surfaces are mostly flat and uniform, there always exist nano-size defects on the WSe₂ surface [circled in white in Fig. 2(d)]. The defect density decays with the distance from the boundary, over a length scale of tens of nanometers, which can be observed in Fig. S1 in the supplementary material. To better identify the defect type, a zoom-in image taken at 77.7 K with emphasized atomic structures is shown in Fig. 2(e). The defect outline is marked by a cyan triangle, and the center is represented by a smaller red triangle. The center locates at a hollow site of the observed hexagonal Se surface lattice, which corresponds to either an atom site or a vacancy site in



FIG. 1. (a) Schematics and the atomic structure of the MoSe₂-WSe₂ island. (b) STS curves taken from MoSe₂ and WSe₂ ($V_{bias} = 1.5$ V, set point: 10 nA). Energy positions of CBM and VBM are labeled in the plot. Inset: bias-dependent topography images with a scale bar of 8 nm. The left and right images were acquired at bias voltages of -2 and 1.5 V, respectively. Left-hand sides in both insets are MoSe₂ domains, and the right-hand sides are WSe₂ domains.



FIG. 2. (a) A lattice-enhanced STM image of the $MoSe_2$ -WSe₂ boundary at 0.6 V. Enhancement of lattice structures is done by overlapping original images several times with lattice structures extracted from fast Fourier transform. The zigzag (black dashed line) and the armchair (while solid line) directions are marked on the STM image and the top-view structure schematics in (b). (c) A corresponding dI/dV map of (a). The contrast is enhanced in order to emphasize the boundary position. (d) An STM image taken at 1.5 V. Red spots are Mo-substitution defects appearing in the WSe₂ region. One of the defects is circled by a white dashed line. (e) shows a lattice-enhanced zoom-in image at 77.7K. The defect is marked by a cyan triangle while the defect center is marked by a smaller red triangle, located at the hollow site of the hexagonal lattices.

the TMDC metal layer. The defect site and the decaying density from the boundary suggest that the observed defects are Mo substitutions in WSe₂, in agreement with previous investigations of CVD-grown $MoSe_2$ -WSe₂ heterojunctions *via* transmission electron microscopy.^{19,30}

To unveil detailed electronic structures at the heterointerface deviating from the zigzag directions and sided by rich Mo substitution defects, we performed STS measurements across the boundaries. A bandgap plot in Fig. 3 exhibits variation of bandgaps at the 1D MoSe₂-WSe₂ interface shown previously in Fig. 2(a). The VBM and CBM energy position marked by triangles reveal a smooth type-II N-n heterojunction. A corresponding topography line profile is shown at the bottom of Fig. 3. The brown dashed line is the middle point of the step, and the dark blue and black dashed lines are edges of the band transition region derived. The transition regions in the two TMDC domains are symmetric, and in total, the width is only 3.58 nm.

Compared with the distribution of the aforementioned Mo-substitution defects, the transition region is much shorter and symmetrically exists in both MoSe₂ and WSe₂ areas. The lack of correspondence implies limited compositional influences and points to electronic depletion regions in lateral TMDC heterojunctions, which is also evidenced by an increased width at 77.7 K shown in Fig. S2 in the supplementary material. Although substitution defects induced local band shifts,²⁴ the differences are smaller than the potential changes in the depletion region and thus do not have noticeable contribution to depletion regions resulting from free carrier motion. In addition, the region width is in the same order of magnitude with a more typical zigzag heterointerface in a similar system of MoS_2 -WS₂ on graphite.²⁴ The fact that depletion widths do not change drastically with boundary orientations is understandable, since edges or boundaries deviating from the zigzag directions are composed of zigzag segments^{17,19} and thus should possess similar local electronic structures.

Fitting the spatial variation of bandgap positions near the boundary with $\Delta V \propto e^{-d/\lambda_{TF}}$, we are able to extract



FIG. 3. A bandgap plot composed of STS curves at positions across the $MoSe_2$ -WSe_2 boundary in Fig. 1(b); $V_{bias} = 1.5$ V, set point: 10 nA. A total depletion width of 3.58 nm is observed. Compared with the simultaneously acquired topography line profile in the bottom, the depletion region is nearly symmetric to the topographic boundary marked by the brown dashed line. Inset: corresponding STM topography image.

information of the Thomas-Fermi screening length λ_{TF} of the TMDCs.³¹ Derived from CBM points in the range of 8 nm from the boundary, λ_{TF} is around 1.1 nm on both sides and slightly shorter than the 1.7 nm λ_{TF} acquired by Song *et al.* in WSe₂ on SiO₂. A possible reason is the different carrier densities induced by different substrates.³¹

On the other hand, the narrow and symmetric depletion region indicates equally high carrier concentration *N* at both the MoSe₂ and WSe₂ sides. λ_{TF} shorter than the depletion region width *d* implies a plausible use of an approximated formula for *d* in 2D layers^{32,33}

$$d = \frac{\pi \varepsilon_W \varepsilon_{Mo} V_{in}}{\ln\left(4\right) e(\varepsilon_W + \varepsilon_{Mo}) NT},\tag{1}$$

in which V_{in} and T are the built-in potential and layer thickness, respectively, and ε represents permittivity.²⁸ Substituting ε and an estimated V_{in} from the theoretical difference in work functions of the two TMDCs,³⁴ we acquire N around 2×10^{13} cm⁻², which is close to the reported values in highly doped TMDCs.^{35,36} A high carrier concentration and the change in WSe₂ from a p-type to an n-type semiconductor suggest strong electron doping in the TMDCs, which could originate from charge transfer from HOPG or the existence of defects such as Se vacancies. The narrow depletion region points to a large internal electric field at the heterointerface. A maximum internal electric field of around 70×10^6 V m⁻¹ at the boundary is derived by performing the derivative of the CBM built-in voltage with respect to the depletion width.

In conclusion, a smooth, narrow, and symmetric depletion region was unveiled at an irregular MoSe₂-WSe₂ heterointerface. Although ill-defined orientations and substitution defects may be practically unavoidable in TMDC heterointerfaces, high internal electric fields still exist on both sides of p-n junctions. Internal electric fields and smooth band alignment can efficiently separate excited electron-hole pairs into different junction sides and benefit performance of photovoltaics, in which field strength can be adjusted by controlling the carrier concentration, and selection of the constituent TMDC materials can adjust band alignment types at heterointerfaces. The 1D MoSe₂-WSe₂ heterointerfaces show potential in electronics and optoelectronics under nonperfect conditions and offer important clues for practical device designs.

See supplementary material for large-scale STM images of Fig. 2(d) and a band plot across the MoSe₂-WSe₂ boundary at 77.7 K.

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