

Spatiotemporal Imaging of Thickness-Induced Band-Bending Junctions

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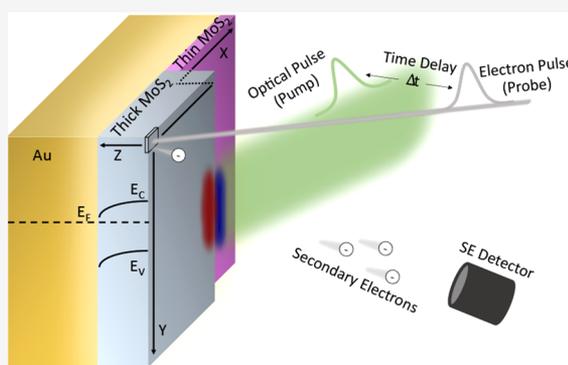
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ABSTRACT: van der Waals materials exhibit naturally passivated surfaces and an ability to form versatile heterostructures to enable an examination of carrier transport mechanisms not seen in traditional materials. Here, we report a new type of homojunction termed a “band-bending junction” whose potential landscape depends solely on the difference in thickness between the two sides of the junction. Using MoS₂ on Au as a prototypical example, we find that surface potential differences can arise from the degree of vertical band bending in thin and thick regions. Furthermore, by using scanning ultrafast electron microscopy, we examine the spatiotemporal dynamics of charge carriers generated at this junction and find that lateral carrier separation is enabled by differences in the band bending in the vertical direction, which we verify with simulations. Band-bending junctions may therefore enable new optoelectronic devices that rely solely on band bending arising from thickness variations to separate charge carriers.

KEYWORDS: band bending, two-dimensional, semiconductors, photovoltaics, ultrafast, spatiotemporal imaging



INTRODUCTION

Band bending in semiconductors is a fundamental consequence of the incomplete screening of external fields and is critical to the operation of nearly every electronic and optoelectronic device. Its existence was theoretically proposed by the works of Mott and Schottky,^{1,2} who argued that the electrostatic landscape must have electronic bands that “bend” to compensate for the difference in Fermi levels at an interface to minimize the overall free energy in the system. Mott also discovered that a characteristic length scale for the band bending in semiconductors is given by

$$L_D = \sqrt{\frac{\epsilon_S \epsilon_0 kT}{q^2 \rho_0}} \quad (1)$$

which is now commonly referred to as the Debye screening length, named after Peter Debye, who discovered the same length scale earlier in electrolytes.³ L_D usually ranges from tens of nanometers to a few micrometers, depending on the doping concentration ρ_0 and static dielectric constant ϵ_S . Here, ϵ_0 is the permittivity of free space, kT is the thermal energy, and q is the fundamental unit of charge. In most semiconductor systems, the region where band bending occurs is referred to as the depletion or accumulation region.

Layered van der Waals materials such as the semiconducting transition-metal dichalcogenides (TMDCs) are unique systems

for studying band-bending physics because of their highly passivated surfaces and the ability to form a wide assortment of heterostructures, which has enabled a variety of applications including transistors, solar cells, optical modulators, metasurfaces, and lasers.^{4–9} Furthermore, these materials can be easily cleaved to yield layers over a wide range of thicknesses, ranging from a single monolayer to hundreds of nanometers. The heterogeneity in sample thicknesses produced during mechanical exfoliation has led to novel “thickness” junctions (i.e., junctions formed from the difference in quantum confinement in few-layer-thick samples).^{10,11} Apparent thickness junctions have also been formed with materials whose thicknesses are greater than the quantum confinement regime;^{12,13} however, the mechanistic explanation for charge carrier separation for this regime of thicknesses remains unclear.

Furthermore, despite considerable research on layered materials in the atomically thin limit in recent years, there has been to our knowledge no direct observation of “vertical”

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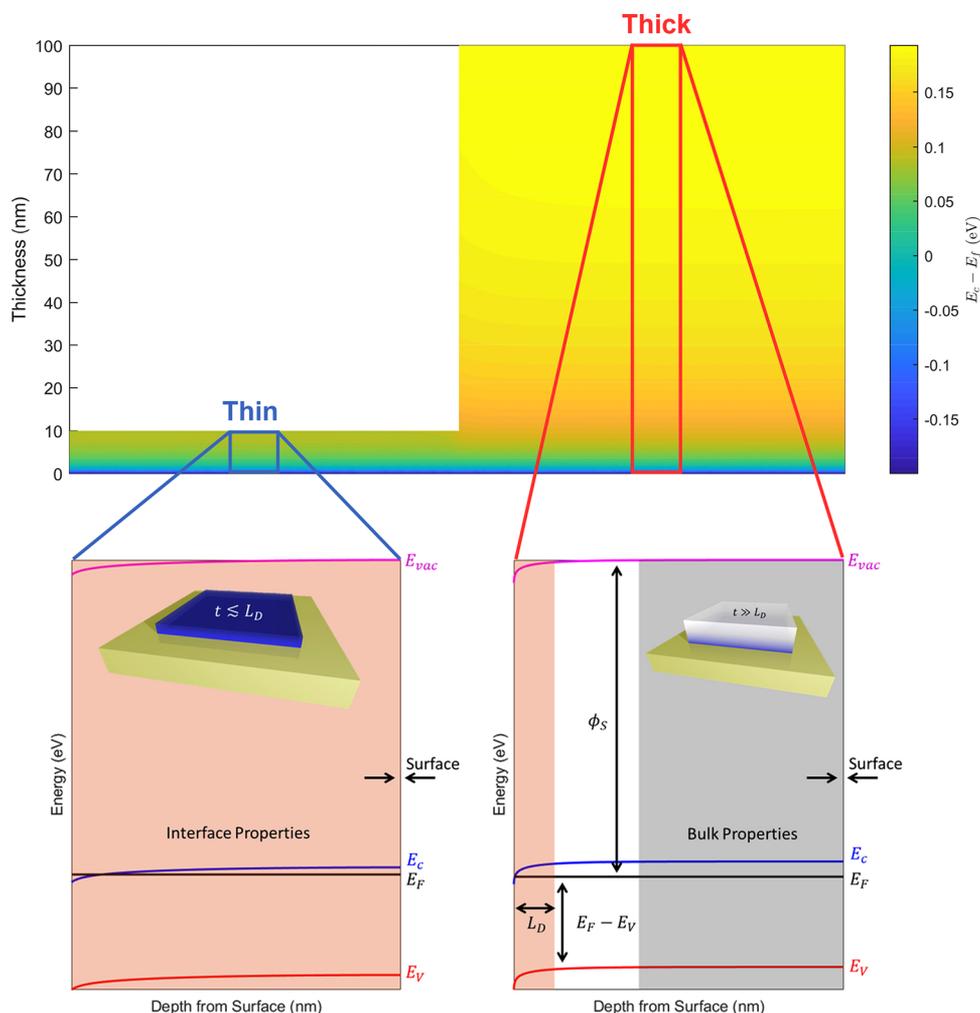


Figure 1. Thickness-dependent surface potentials due to vertical band bending: Calculated $E_c - E_f$ band diagram for 10- and 100-nm-thick flakes of MoS_2 on Au assuming strong electron transfer at the MoS_2/Au interface. Schematic band diagrams of a material dominated by its interface properties (bottom left) and bulk properties (bottom right), which depend on the thickness of the material relative to its electrostatic screening length (L_D). Insets correspond to a schematic of a semiconductor (e.g., MoS_2) on its substrate (e.g., Au), with the blue representing excess electron concentration relative to its bulk value. The surface of the material refers to the semiconductor–vacuum interface.

band bending (i.e., in the direction perpendicular to heterostructure interfaces). This is primarily due to the weak out-of-plane as opposed to in-plane transport in layered materials and the difficulty in probing buried interfaces. Meanwhile, direct observations of band bending can be used to estimate depletion widths and interface barrier heights and consequently can be used to deduce the electrostatic landscape and performance of the corresponding device.

In this letter, we show evidence for the first direct measurement of vertical band bending in a MoS_2 –Au interface. We directly observe correlations between the thickness and surface Fermi levels in samples with identical electronic band structures and preparation methods and find that the MoS_2 –Au interface results in a strong electron transfer to the MoS_2 layer. The direct observation of a surface potential difference between materials with differing thicknesses suggests that a new type of homojunction, arising solely from the differences in thickness and band bending, can be used to separate charge carriers. We directly observe this charge carrier separation spatiotemporally by utilizing scanning ultrafast electron microscopy and corroborate these observations with numerical simulations. The electrostatic landscape of materials

that are comparable to or thinner than their electrostatic screening length can therefore be carefully tailored by controlling their thicknesses, interfaces, and local geometry.

RESULTS

Correlation between Electronic Properties and Thickness in Ultrathin Semiconductors. To examine the interplay between interfaces, thicknesses, and band bending, we first consider theoretically a semiconductor on a metallic substrate surrounded by vacuum and solve Poisson's equation

$$\nabla^2 \phi = -\frac{\rho}{\epsilon} \quad (2)$$

to calculate the energy band diagrams for differing thicknesses, as depicted in Figure 1. As expected, we find the characteristic length scale to be the Debye screening length L_D , which we estimate to be approximately 40 nm for carrier concentrations corresponding to typical values for MoS_2 . Furthermore, our calculations suggest that layers that are thinner than their Debye screening length will have a surface potential that is directly related to their thickness. Importantly, this analysis requires the use of a material, such as MoS_2 , with an absence of

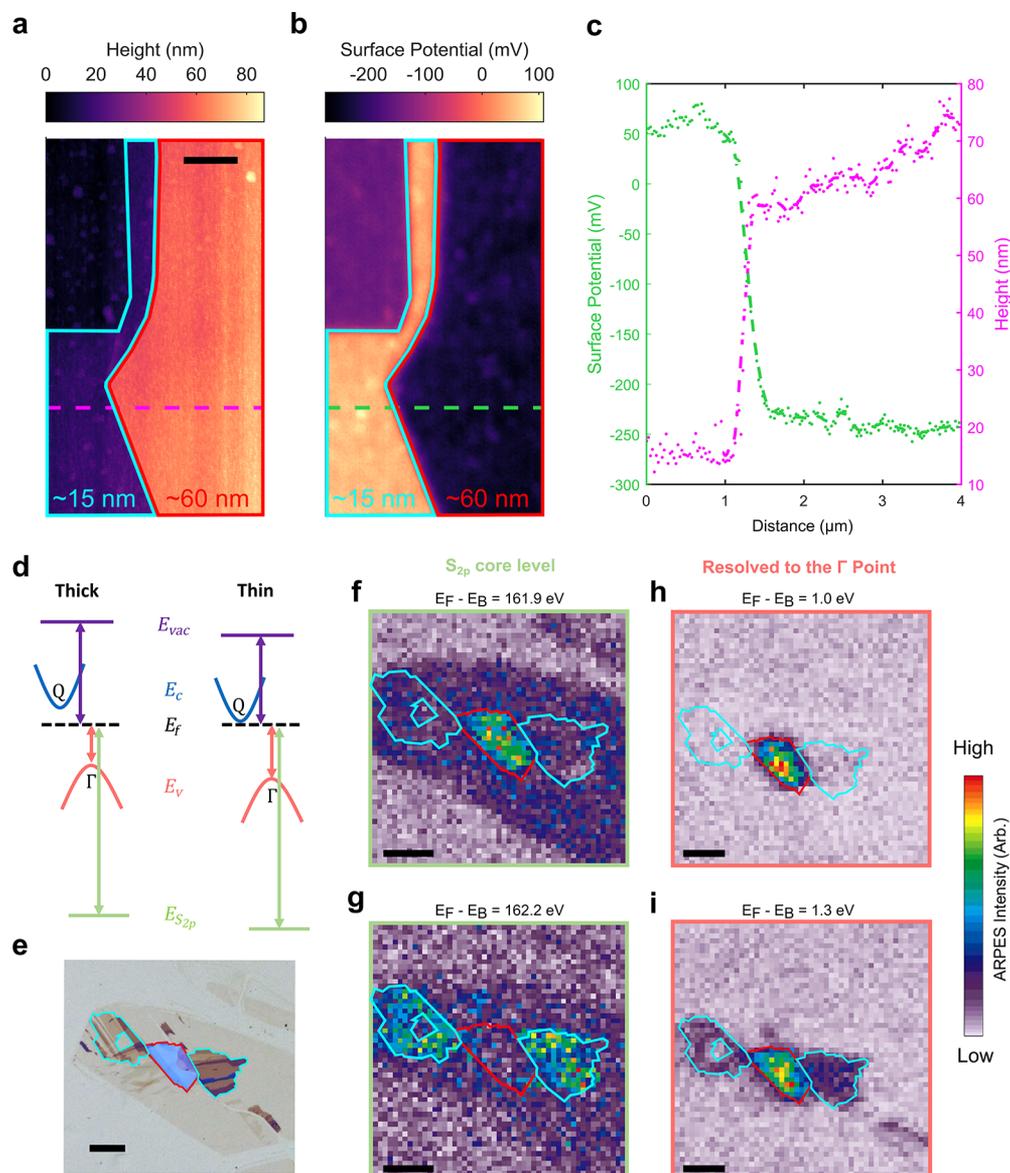


Figure 2. Experimental observation of thickness-dependent surface doping in MoS₂/Au. (a) Topographic image of MoS₂ exfoliated onto a gold substrate with the corresponding surface potential (b) mapped over the same area. The cyan and red outlines correspond to MoS₂ thicknesses of approximately 15 and 60 nm, respectively. The upper left region corresponds to monolayer MoS₂/Au. The scale bar is 1 μm. (c) Line cut of the topography and surface potential. The dashed lines are guides for the eye. (d) Proposed energy diagram at the surface for the thin and thick MoS₂. (e) Optical micrograph image of MoS₂ exfoliated onto a gold substrate. The thick (red outline) and thin (cyan outline) regions are ~30 and ~5 nm thick, respectively. Intensity map of photoemitted electrons at the sulfur 2p core level for binding energies of (f) 161.9 and (g) 162.2 eV. Intensity map of photoemitted electrons from the valence band of MoS₂ resolved to its Γ point for binding energies of (h) 1.0 and (i) 1.3 eV. The thin (cyan) and thick (red) flake outlines are superimposed. All scale bars in (e)–(i) are 50 μm.

surface states and other contaminants at the top (basal-plane) semiconductor–vacuum interface that is typical in most three-dimensional materials due to the formation of dangling bonds. van der Waals materials are therefore ideal for probing this thickness-dependent surface potential because of their naturally passivated surfaces.

To examine the effects of varying the semiconductor thickness on surface potential, we directly exfoliated MoS₂ on Au (details in Methods). These exfoliated samples produce a variety of thicknesses that can be determined with atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM), as shown in Figure 2a,b. These images clearly show a direct correlation between two different thicknesses of a MoS₂ flake (with thicknesses of about 15 and 60 nm), with

correspondingly different surface potentials (50 and –230 mV), as shown in Figure 2c. Importantly, these thicknesses are outside the realm where there are strong quantum confinement effects and therefore can be considered electronically to be “bulk” materials.¹⁴ Since these two flakes were fabricated under the same conditions, we therefore attribute the difference in observed surface potentials to vertical band bending at the MoS₂–Au interface. We further show this correlation between thickness and surface potential for a variety of thicknesses measured on other samples (Supporting Information Figure S1).

The relative surface potential difference between the 15 and 60 nm samples is about 280 mV, suggesting strong electron transfer from the gold substrate to the ultrathin MoS₂ (Figure

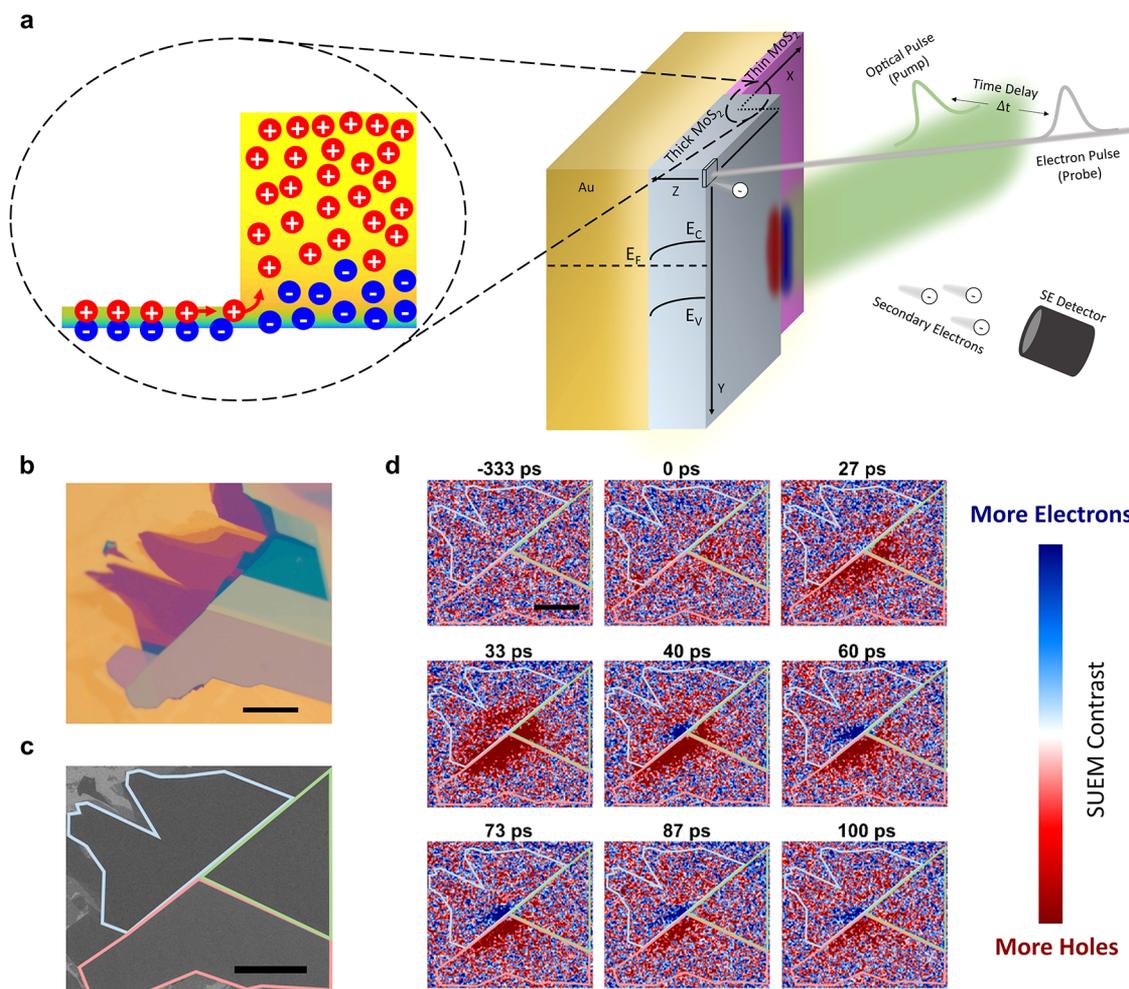


Figure 3. Scanning ultrafast electron microscopy imaging of a band-bending junction: (a) Conceptual depiction of the band-bending junction and its measurement via scanning ultrafast electron microscopy (SUEM). In a sample with different thicknesses of MoS₂, band bending induced by a gold substrate enables lateral carrier separation between electrons and holes. In SUEM, an optical pulse generates electron–hole pairs that subsequently evolve in space and time. An electron pulse is raster scanned across the surface of the sample for a given time delay Δt after the optical pulse. An image of the detected secondary electron (SE) intensity is formed. Contrast images are formed that correspond to the difference between the SE image at Δt relative to the SE image without an optical pulse. Contrast images are interpreted as images of the net charge density (i.e., increased (decreased) SE intensity corresponds to an increase in the local surface electron (hole) density). (b) Optical image of MoS₂ exfoliated onto a gold substrate. (c) Static scanning electron micrograph over the flake in (b), with highlighted regions of thick (pink border, ~ 100 nm), intermediate (light-green border, ~ 30 nm) and thin (light-blue border, ~ 10 nm) MoS₂ on one sample. (d) Contrast images over the same area as in (c) for different time delays, with the corresponding MoS₂ flake outline. Blue and red contrasts are interpreted as excess electrons and holes due to photoexcitation, respectively. All scale bars are $50 \mu\text{m}$.

2d). Strong electron transfer at the MoS₂–Au interface is contradictory to the well-known work function of Au (~ 5.1 eV), which instead would suggest hole doping of the neighboring MoS₂ layer. However, recent works have shown that the MoS₂–Au interface induces strong electron transfer,^{15,16} particularly if the interface remains pristine during the exfoliation process, which has also enabled large-area monolayer exfoliation of TMDCs and other 2D materials.^{16–20}

To further examine this correlation between thickness and electronic properties, we perform spatially resolved angle-resolved photoemission spectroscopy (ARPES) at beamline 7.0.2 at the Advanced Light Source (Methods) on another flake of MoS₂ on Au (Figure 2e). We find a direct correlation between the position of the sulfur 2p core levels and the thicknesses of the corresponding MoS₂ flakes (Figure 2f,g). The larger sulfur 2p binding energies for the thinner MoS₂ is suggestive of electron transfer at the MoS₂–Au interface. Finally, we examine electron binding energies and momenta

that correspond to the valence band edge, which occurs at the Γ point in the Brillouin zone in electronic bulk samples. We find that while the thicker sample has a Fermi level of about 1 eV above the valence band edge, the Fermi level at the surface of the thinner sample is about 1.3 eV above its valence band edge (Figure 2h,i). Assuming an electronic band gap of approximately 1.3 eV,²¹ we find direct evidence of strong electron transfer and vertical band bending at the MoS₂–Au interface, which corroborates the KPFM results shown earlier. Similar results are also observed on another MoS₂ sample (Supporting Information Figure S2). Given that the native doping of bulk MoS₂ is typically n-type, these results suggest that the MoS₂–Au interface would yield Ohmic n-type contacts by degenerately doping the neighboring MoS₂ region.²²

Spatiotemporal Imaging of Charge Carrier Separation Due to Thickness. To investigate the effects of the different vertical band-bending profiles on the charge carrier

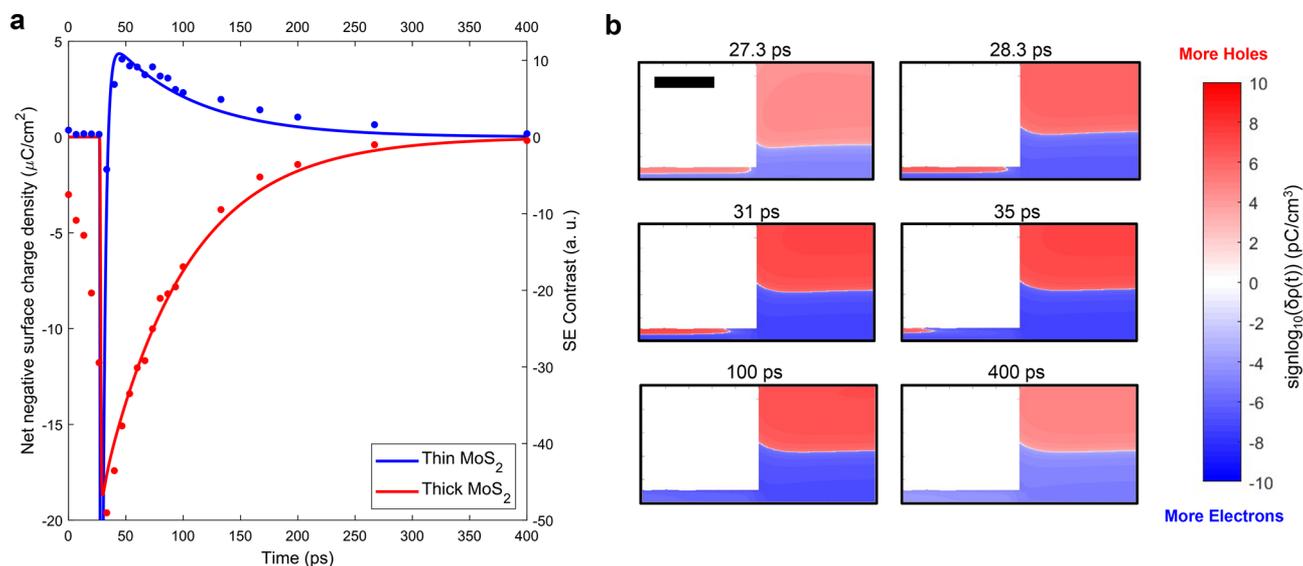


Figure 4. Simulation of carrier dynamics at a bend-bending junction. (a) Experimentally measured secondary electron contrast intensity (dots, right axis) on the thin (blue) and thick (red) MoS₂ as a function of different pump–probe delay times, along with the simulated net negative surface charge density as a function of time (solid lines, left axis). We assume that thin MoS₂ and thick MoS₂ are 10 and 100 nm thick, respectively, for the simulation. (b) Simulated cross-sectional maps of the net charge density at different time steps, plotted with a signed log function to examine the orders of magnitude change in carrier density more easily (scale bar = 50 nm). Red corresponds to net positive charge (i.e., holes), and blue corresponds to net negative charge (i.e., electrons).

dynamics, we perform scanning ultrafast electron microscopy (SUEM) on another sample of MoS₂/Au with thin–thick junctions of 10 and 100 nm, respectively (Figure 3b). Figure 3a shows a conceptual depiction of the SUEM measurement technique performed over this thin–thick junction. Briefly, SUEM is a pump–probe technique that uses an optical pump (~514 nm) and an electron pulse (~2 ps pulse width) that records the secondary electron emission in the presence of the optical pump as a function of the pump–probe time delay. Contrast images can be formed at different time delays by subtracting the static SEM image (Figure 3c) from a similar SEM image formed with the optical pump on at a specific time delay Δt . The contrast in the secondary electron emission as a result of the optical pump beam has been interpreted as direct images of electron (blue) and hole (red) carrier populations under ultrafast excitation, which has been previously used to image the carrier separation in pn junctions.²³ Similar methods to directly image ultrafast carrier dynamics have also been utilized in photoemission electron microscopy.^{24,25}

By examining the contrast images formed at different time delays via SUEM, we find direct evidence for carrier separation at a thin–thick junction (Figure 3d). First, the lack of carrier dynamics at negative time delays suggests appropriate background subtraction. At longer time delays, we initially find the appearance of excess holes (red contrast) on every thickness of MoS₂ for $\Delta t < 27$ ps. The oblong contrast profile is due to the beam shape of oblique excitation. At $\Delta t = 33$ ps, there is a simultaneous occurrence of both excess holes and electrons on the thin (10 nm) sample, with the excess electrons located near the thin–thick junction. At slightly longer time delays (40 ps $< \Delta t < 60$ ps), this population of excess electrons appears to increase and spread before monotonically decreasing with a time constant (single-exponential fit yields $\tau \approx 75$ ps) similar to that of the excess hole population on the thick MoS₂ ($\Delta t > 60$ ps). Interestingly, the intermediate thickness of MoS₂ (light-green outline, Figure 3d) yields little to no excess electrons, suggesting that the dominant path for

carrier transport is between the thin (10 nm) and thick (100 nm) layers of MoS₂. Further measurements on monolayer MoS₂ and bulk ($\gg 100$ nm thick) MoS₂ (Supporting Information Figures S3 and S4) yield little carrier dynamics and no appearance of excess electrons, as observed at this thin–thick junction.

We interpret the carrier dynamics in these contrast images as direct evidence of carrier separation at a thin–thick layer interface, which we refer to hereafter as a “band-bending junction”. The dynamics can be qualitatively explained as follows (schematic in Supporting Information Figure S5): (1) Optical excitation results in the generation of electron–hole pairs, which rapidly separate vertically due to vertical band bending and thicknesses in the semiconductor that are small compared to carrier diffusion lengths. The strong electron transfer at the MoS₂–Au interface results in a band profile schematically depicted in Figure 1, which causes holes (electrons) to move toward the MoS₂–vacuum (MoS₂–Au) interface for both thicknesses. Thus, the time scale for the initial contrast is primarily due to the vertical carrier drift velocity and thickness of the sample. (2) After the carriers are separated, both carriers can travel on average over one diffusion length laterally within their lifetime. Therefore, if the holes on the thin side are within a diffusion length of the thin–thick junction, then they can travel laterally and then vertically to separate from the remaining electrons on the thin side. Electrons can also travel within their own diffusion length but will remain near the MoS₂–Au interface due to the band profile. The lateral transport that results in carrier separation and the eventual contrast flip therefore follows the time scales of carrier diffusion. (3) Once some holes move across the thin–thick interface, remaining holes follow along due to the gradient in the quasi-Fermi level in the holes. (4) After the electrons and holes have completely separated, they recombine primarily monomolecularly through Shockley–Read–Hall recombination kinetics via trap states within the bulk of

MoS₂. These trap states are naturally available due to defects in the crystalline lattice (e.g., sulfur vacancies).^{26,27}

To model the lateral carrier separation dynamics of this band-bending junction, we turn to time-dependent drift-diffusion equations (Methods). To simplify the numerical modeling substantially, we make the following assumptions: (1) The MoS₂–Au interface results in strong electron transfer to MoS₂. (2) The dynamics can be qualitatively modeled by semiconductor drift-diffusion equations. Ab initio calculations combined with the Boltzmann transport equations may yield more accurate results while considering the unique band structures of these systems. (3) The carrier dynamics can be effectively modeled in two dimensions due to the prominent dynamics at the thin (10 nm)–thick (100 nm) interface. (4) The anisotropic mobilities in the vertical vs horizontal directions are effectively compensated for by scaling the horizontal dimension by the ratio of the square root of the mobilities. (5) While the carrier dynamics in other semiconductor materials at these time scales has been shown to exhibit superdiffusion and therefore a time-dependent mobility,^{28,29} we fix our mobility to a single value which effectively represents a time-averaged and spatially averaged quantity. (6) Since we are interested in primarily the lateral carrier dynamics, we assume carrier excitation occurs at 27 ps in the simulation. (7) Secondary electron contrast is primarily due to the net charge density near the surface of the MoS₂ layer, with the secondary electron emission decaying exponentially from the surface of the semiconductor with a length scale of λ_{SE} .

With these simulation assumptions in mind, we find excellent agreement between the experimental secondary electron emission contrast and the calculated time-dependent net negative surface charge density (Figure 4a). Snapshots of the charge density at specific times are also shown in Figure 4b, showing lateral carrier separation at the thin–thick interface shortly after excitation. The agreement has been achieved from a variety of simplifications in the theoretical modeling, which suggests that the extracted material parameters used to achieve this matching (specifically, the electron and hole mobility of MoS₂) should not be taken to be necessarily physical. Improved modeling that explicitly includes (1) the anisotropic mobility, (2) the large aspect ratio between the lateral and vertical directions, and (3) a time-dependent mobility due to hot carrier dynamics would substantially enhance the accuracy of a material parameter fit. However, we find that the qualitative picture of the band-bending junction is robust (Supporting Information Figure S6) for a variety of material constants (i.e., lateral carrier separation is achieved independently of the specific choice of material parameters), suggesting that this junction should be observable in other van der Waals materials as well. Our calculations also suggest that the current density at the thin–thick interface is dominated by the hole current (Supporting Information Figure S7), which is expected since it acts as a minority carrier in this electron-doped system. Finally, we emphasize that the carrier separation demonstrated here is present in the absence of quasiparticle band gap or exciton binding energy differences, which has previously led to novel junctions.^{10,11,30} Here, the carrier separation is enabled by the unique interplay between thickness and band bending.

CONCLUSIONS

Our results suggest that the interplay between thickness and band bending for materials thinner than their screening length

can result in the formation of a new type of homojunction, which we refer to as a band-bending junction. These band-bending junctions are formed by combining the highly passivated surfaces of van der Waals materials with vertical band bending in materials whose thicknesses are comparable to or less than the characteristic electrostatic screening length. Thus, while these results were obtained with the MoS₂/Au system, they are likely generalizable to other van der Waals heterostructures and perhaps also 3D bonded semiconductors if one can generate chemically passivated yet electronically active surfaces in the ultrathin thickness (<100 nm) limit. Furthermore, these band-bending junctions may find use as new photodetector geometries or could be useful for sensing applications. From the fundamental perspective, they may enable the formation of two-dimensional electron/hole gases or enable a wide variety of surface-sensitive measurement techniques to indirectly examine vertical carrier transport in layered van der Waals materials. More generally, the observation of charge carrier transport at these band-bending junctions should be considered while modeling and interpreting ultrathin optoelectronic devices that are geometrically inhomogeneous.

METHODS

Sample Preparation. Large-area ultrathin flakes of MoS₂ were fabricated by utilizing the strength of the Au–S bonds, which has been known to yield large-area samples.^{16–18} To summarize our procedure, we first created atomically smooth Au substrates using template stripping techniques which routinely yield <3 Å RMS.^{5,31} Then, bulk crystals of MoS₂ (HQgraphene) were cleaved from the native crystal using thermal release tape (Semiconductor Equipment Corp., no. 319SMS) and were directly pressed onto the template-stripped Au substrate. With the tape and bulk MoS₂ directly pressed onto the Au substrate, the entire stack was then heated to ~120 °C on a hot plate for ~2 min to release the bulk crystal from the tape and to promote adhesion between MoS₂ and the Au substrate. The MoS₂/Au sample was then sonicated in acetone for ~5 s to release the bulk crystal from the ultrathin layer of MoS₂ that would remain adhered to the Au substrate. The sample was finally rinsed with isopropanol and blown dry with N₂. We found that it was necessary to template strip the Au substrate immediately before pressing with the MoS₂ bulk crystal to yield large-area flakes, similar to what has been observed previously.¹⁶

Kelvin Probe Force Microscopy Measurements.

Scanning probe microscopy was performed on an Omega-Scope-R SPM (AIST-NT, now-Horiba Scientific). HQ NSC-14-Cr/Au probes (Mikromasch) were used for characterization. Kelvin probe imaging was performed in frequency modulation mode, which allowed improved spatial resolution of the distribution of the contact potential difference (which reflects the distribution of the surface potential on the sample). The value of the surface potential of the probes was not calibrated, so it was the contrast in the contact potential difference images, not the absolute value of the surface potential, which bore the physical meaning in the contact potential difference images.

Photoemission Spectroscopy Measurements. Photoemission spectroscopy measurements were performed at beamline 7.0.2 (MAESTRO) at the Advanced Light Source. Samples were characterized at the microARPES UHV end station, with synchrotron beam spot sizes of approximately 10

μm . Incident photon energies were 145 and 330 eV for the valence band and core-level measurements, respectively. Measurements were performed at ~ 72 K, and multiple frames were averaged to achieve sufficient signal-to-noise ratios.

Scanning Ultrafast Electron Microscopy Measurements. Scanning ultrafast electron microscopy is a newly developed technique that can directly image the dynamics of photoexcited carriers in both space and time with subpicosecond temporal resolution and nanometer spatial resolution. Details of the setup can be found elsewhere^{32,33} and are briefly summarized here (also illustrated in Figure 3a). Compared to optical pump–probe spectroscopy, SUEM is a photon–pump–electron–probe technique, with subpicosecond electron pulses generated by illuminating a photocathode (ZrO-coated tungsten tip) with an ultrafast ultraviolet (UV) laser beam (wavelength 257 nm, pulse duration 300 fs, repetition rate 5 MHz, fluence $300 \mu\text{J}/\text{cm}^2$). A typical probing electron pulse consists of tens to hundreds of electrons, estimated by measuring the beam current through a Faraday cup, and is accelerated to 30 keV before impacting the sample. The probing electron pulses arrive at the sample after the optical pump pulses (wavelength 515 nm, fluence $80 \mu\text{J}/\text{cm}^2$) by a given time controlled by a mechanical delay stage (-700 ps to 3.6 ns with 1 ps resolution). The probing electron pulses induce the emission of secondary electrons from the sample, which are subsequently collected by an Everhart–Thornley detector. To form an image, the probing electron pulses are scanned across the sample surface and the secondary electrons emitted from each location are counted. Because the yield of secondary electrons depends on the local average electron energy, more/fewer secondary electrons are emitted from regions of the sample surface where there is a net accumulation of electrons/holes. Typically, a reference SEM image is taken long before the pump optical pulse arrives and is then subtracted from images taken at other delay times to remove the background. In the resulting contrast images, blue/red contrasts are observed at places with a net accumulation of electrons/holes due to higher/lower yields of secondary electrons. In this fashion, the dynamics of electrons and holes after excitation by the optical pump pulse can be monitored in real space and time.

Electromagnetic and Transport Simulations. The coupled drift-diffusion and Poisson equations were solved using the CHARGE solver in Lumerical DEVICE, which uses finite-element meshing to solve the coupled differential equations iteratively. Due to the anisotropic mobility known for these materials,^{34,35} solving the multidimensional coupled differential equations is computationally costly. Instead, we argue that since we are interested in a qualitative picture of the carrier transport and because the lateral extent of the junction is dominated by the in-plane diffusion length, a proper rescaling of the in-plane dimensions by a factor of $\frac{L_{\parallel}}{L_{\perp}} = \sqrt{\frac{\mu_{\parallel}}{\mu_{\perp}}} \approx \sqrt{1000}$ allows us to treat the problem with an approximate isotropic, spatially, and temporally averaged mobility ($\mu = 2000 \text{ cm}^2/(\text{V s})$). Since the experimentally observed in-plane junction width is $\sim 10 \mu\text{m}$, the rescaled in-plane width should be about 300 nm. In our simulations, our total lateral span is 500 nm. Band bending was captured by assuming an ohmic contact at the Au–MoS₂ interface with a metal work function of 3.8 eV and a semiconductor electron affinity of 4.0 eV. Fermi–Dirac statistics were included due to the high level of modulation doping. Furthermore, we used a

band gap value of 1.3 eV,²¹ a hole effective mass of $0.785m_0$,³⁶ an electron effective mass of 0.686 m_0 (for the electron effective mass, we took the geometric mean of the effective masses in the transverse and longitudinal directions at the Q point³⁶), a dielectric constant of 7,³⁷ and a Shockley–Read–Hall recombination lifetime of 75 ps. Exciton dynamics were deemed not relevant since the majority of the transport should occur at the lowest-energy conduction band and highest-energy valence band, with exciton binding energies of $\ll kT$.³⁸ Native doping of MoS₂ was assumed to be n-type with a doping level of 10^{16} cm^{-3} , similar to that quoted from the supplier. Optical generation values were calculated by assuming that the system is optically one-dimensional over a specific thickness (either 10 or 100 nm); therefore, 1D transfer matrix calculations were applicable for each region. These generation rates were then directly imported into Lumerical DEVICE. Calculated volumetric charge densities ρ were exponentially weighted from the surface with a characteristic length scale of $\lambda_{\text{SE}} = 4 \text{ nm}$ to yield surface charge densities ρ_s . The SUEM signal is expected to be proportional to the net negative surface charge density $I_{\text{SUEM}} \propto -\delta\rho_s = -q(\delta p_s - \delta n_s)$, where the positive/negative SUEM signal scales with the net electron/hole population.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.1c01481>.

Additional KPFM, ARPES, and SUEM measurements; additional simulations and analysis of band-bending junction charge carrier transport dynamics (PDF)

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J.W., A.D., D.J., and H.A.A. developed the main ideas. J.W., A.D., and D.J. fabricated the samples. B.L. performed SUEM measurements, developed in the laboratory of A.H.Z. A.K. and K.J. performed the Kelvin probe measurements. J.W. performed ARPES measurements with support from D.J., E.R., A.B., and C.M.J. J.W. performed both the time-domain and steady-state simulations with assistance from A.D. H.A.A. supervised all of the data analysis. All authors contributed to the discussion and interpretation of results as well as the presentation and preparation of the manuscript.

Notes

The authors declare no competing financial interest.

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