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Nanoscale Surface Photovoltage Mapping of 2D Materials and Heterostructures by Illuminated Kelvin Probe Force Microscopy

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ABSTRACT

Nanomaterials are interesting for a variety of applications, such as optoelectronics and photovoltaics. However, they often have spatial heterogeneity, i.e. composition change or physical change in the topography or structure, which can lead to varying properties that would influence their applications. New techniques must be developed to understand and correlate spatial heterogeneity with changes in electronic properties. Here we highlight the technique of surface photovoltage-Kelvin probe force microscopy (SPV-KFM), which is a modified version of non-contact atomic force microscopy capable of imaging not only the topography and surface potential, but also the surface photovoltage on the nanoscale. We demonstrate its utility in probing monolayer WSe₂-MoS₂ lateral heterostructures, which form an ultrathin p-n junction promising for photovoltaic and optoelectronic applications. We show surface photovoltage maps highlighting the different photoresponse of the two material regions as a result of the effective charge separation across this junction. Additionally, we study the variations between different

heterostructure flakes and emphasize the importance of controlling the synthesis and transfer of these materials to obtain consistent properties and measurements.

INTRODUCTION

Nanomaterials are interesting for solar energy conversion¹⁻³ and other optoelectronic applications⁴⁻⁸ for a variety of reasons: tunability of electronic properties based on size,⁹⁻¹¹ high surface area that allows for manipulation of properties via surface chemistry,¹²⁻¹⁴ and the ability to form unique heterojunctions due to minimization of lattice strain.¹⁵ However, many nanomaterials have spatial heterogeneity at the nanoscale that can lead to drastic variations in material properties. Spatial heterogeneity can involve both macroscopic properties, such as varying chemical composition and lack of uniformity in the size and shape as well as localized features, such as step edges, adsorbed atoms, and defects. The formation of heterostructures or doping of nanomaterials can also create spatially-varying properties based on changes in the chemical composition. All of these types of spatial heterogeneity can contribute to varying charge transfer properties, and it is critical to study how these changes influence the overall photoresponse of individual nanomaterials. Indeed, as new nanomaterials and heterostructures are synthesized, understanding charge transfer and dynamics within these materials is critically important,¹⁶ and high-resolution, high-throughput techniques with this capability are required.

Surface photovoltage (SPV) spectroscopy is a powerful technique for understanding the influence of surface electronic states on the photoresponse of materials,¹⁷⁻¹⁸ and has been used extensively to understand charge dynamics in a variety of semiconductor materials.¹⁹⁻²² This technique involves illuminating a semiconductor material and measuring the resulting surface

photovoltage, typically using a metal-insulator-semiconductor configuration. A limitation of this technique, however, is its inability to measure spatial variation, which makes it impractical for studying individual nanostructures. One method in particular can help fill this void — surface photovoltage-Kelvin probe force microscopy (SPV-KFM), also referred to as illuminated KFM or microscopic SPV. With this method, standard Kelvin probe force microscopy is used to measure the surface potential of the material both in the dark and under illumination, the net difference of which creates surface photovoltage maps. It has so far been demonstrated on a small number of materials such as silicon wafers,²³⁻²⁴ organic solar cells²⁵⁻²⁸ and inorganic thin films,²⁹⁻³⁰ but viable demonstrations on individual nanostructures have been limited.³¹⁻³³ Additionally, in a typical SPV-KFM setup, the sample is illuminated from below, thus requiring the use of a transparent conductive substrate, which is not always feasible or practical for device applications.

In this work, we have developed the SPV-KFM technique with illumination of the sample from above, and have demonstrated its efficacy on a monolayer lateral heterostructure of WSe₂-MoS₂. WSe₂ and MoS₂ are layered transition metal dichalcogenides (MX₂), which have received much research interest recently due to the ability to tune their properties based on the number³⁴⁻³⁵ and rotation³⁶⁻³⁷ of layers as well as their strong absorption at only a monolayer thickness.³⁸ Therefore, they have been demonstrated for a variety of electronic,³⁹⁻⁴⁰ optoelectronic,⁴¹⁻⁴² solar energy conversion² and catalysis applications.⁴³⁻⁴⁵ Additionally, these 2D materials can be synthesized as lateral heterostructures, allowing for the formation of covalently-bonded nanoscale p-n junctions that are promising for ultra-thin electronics.⁴⁶⁻⁵⁰ Extensive structural and electronic characterization of individual or heterojunction devices has been collected,⁴⁶⁻⁴⁸ but only rarely has there been information collected that combines charge transfer properties of these materials with spatial resolution.⁵¹⁻⁵⁴ In order to see the effects of both heterostructure formation as well as

variation among nanostructures, we have mapped the surface photovoltage of lateral WSe₂-MoS₂ heterostructures and revealed the heterogeneity in photoresponse between the two materials as a result of the charge transfer across the p-n junction that they form. We have also observed variations in the photoresponse of the WSe₂ nanoflakes that can be attributed to changes in the substrate interaction due to the material transfer process. This work demonstrates the ability of the SPV-KFM technique to help determine the changes in optoelectronic properties due to heterojunctions and spatial heterogeneity on the nanoscale, and demonstrates its capability to observe changes within a lateral monolayer heterostructure for the first time.

MATERIALS AND METHODS

Synthesis of the WSe₂-MoS₂ Heterostructures.

The heterostructures were synthesized using a two-step CVD process reported previously.⁴⁶ Briefly, during the first step for the growth of WSe₂, 0.6 g of WO₃ powder in a quartz boat was placed in the center of the furnace, and Se powder was placed in a boat at the upstream side of the furnace and held at a temperature of 260 °C during the reaction. The sapphire substrate was placed at the downstream side of the CVD tube, just past the WO₃ boat. The WO₃ was heated to 925 °C at a pressure of 20 Torr for 15 min before letting the reaction cool down naturally to room temperature. During the reaction, Ar and H₂ gas were flowed at 90 standard cubic centimeters per minute (sccm) and 6 sccm, respectively. The sample was then placed into a separate furnace for the MoS₂ growth. The setup of the boats for the MoS₂ growth was the same as for the WSe₂ synthesis, except now using MoO₃ and S powders in place of WO₃ and Se. The distance between the MoO₃ boat and the WSe₂ sample was about 9 cm. The hot zone of the furnace was set to 755 °C, while the S powder was held at 190 °C for 10 min and then naturally cooled to room

temperature. Only Ar was flowed at a flow rate of 70 sccm during this reaction, and the pressure was set to 40 Torr.

Transfer of WSe₂-MoS₂ Heterostructures.

The WSe₂-MoS₂ heterostructures were transferred from the sapphire growth substrate to native oxide coated degenerately-doped Si wafers via a standard poly(methylmethacrylate) (PMMA) transfer process (950 PMMA A4 MicroChem). PMMA was first spin-coated onto the surface of the sample, after which the entire sample was placed in 6 M HF solution to etch away the sapphire substrate. The remaining heterostructures covered in PMMA were removed from the HF, rinsed in DI water, and then transferred onto the Si substrate. The PMMA layer was then removed by placing the substrate into hot (60 °C) acetone for 30 min. After the removal, the heterostructures were annealed at 300 °C for approximately 2.5 h under vacuum (10⁻³ Torr).

Synthesis of the Individual WSe₂ and MoS₂ Monolayers.

The WSe₂ and MoS₂ monolayers were grown similarly to how they were grown for the heterostructure sample (see Synthesis of WSe₂-MoS₂ Heterostructures above).

Characterization of the WSe₂-MoS₂ Heterostructures.

The heterostructures were characterized using an optical microscope (Olympus BX51M), scanning electron microscope (LEO SUPRA 55 VP field-emission SEM) operated at 3 kV, and a Confocal Raman/Photoluminescence microscope/spectrometer (LabRAM Aramis). The Raman spectra and PL mapping measurements were collected using a 532 nm laser and a 100x microscope objective.

Surface Photovoltage-Kelvin Probe Force Microscopy (SPV-KFM) Measurements.

The SPV-KFM measurements were carried out on an Agilent 5500 Atomic Force Microscope.

The topography and the Kelvin probe measurements were collected simultaneously in single pass

non-contact amplitude modulation mode. The Kelvin probe measurements were conducted using

MikroMasch Pt coated Si tips (HQ:NSC18/Pt), which typically have a resonance frequency of 75

kHz, force constant of 2.8 N/m, and a tip radius of < 30 nm. In our setup, the DC offset bias was

applied to the tip, $V_{DC} = V_{tip}$. Therefore, $V_{tip} = -CPD$ and if $CPD = \Phi_{tip} - \Phi_{sample}$, then $V_{tip} = \Phi_{sample}$

$- \Phi_{tip}$.²⁶ In this configuration, changes to the surface potential are correlated directly to the sign

of the charge; i.e., a positive change in the surface potential corresponds to positive charging of

the surface. The surface photovoltage aspect of the technique was implemented by directing a laser

diode down onto the surface of the sample using a mirror. The laser diode for the WSe₂-MoS₂

experiments was from ThorLabs, Inc (LP405-SF10) and emits at 401.5 nm operated at ~4 mW. A

collimator (ThorLabs, Inc. F280FC-A) was attached to the laser diode to get a large beam size of

3.3 mm, which was then focused using a Newport lens with a focal length of 113 mm (KPX596-

C). The silicon test experiments were conducted using a laser diode that emits at 637.3 nm

(Thorlabs, Inc model LP635-SF8) with another collimator (Thorlabs Model F280FC-B).

RESULTS AND DISCUSSION

Design and implementation of the SPV-KFM technique. Figure 1 illustrates a simplified

schematic of the SPV-KFM setup. KFM involves the use of two lock-in amplifiers coupled with

feedback controllers that can simultaneously measure both the topography and the surface

potential of the sample relative to the tip by tracking the reflection of a laser off the cantilever onto

a photodiode. Because the tip and the sample will, in general, have different work functions, when

they are placed in electrical contact and brought close to each other a build-up of charge will occur as the Fermi levels equilibrate, known as the contact potential difference (CPD).⁵⁵ In typical KFM, a DC voltage is applied to offset this CPD, which is then mapped as the surface potential (SP) of the material relative to the tip.⁵⁵ The surface photovoltage (SPV) is defined as the change in local potential produced in response to optical excitation, which is measured experimentally by obtaining the CPD at each location in an image both in the absence of and in the presence of optical excitation from an external optical source; the difference between these images is a spatial map of the surface photovoltage.

$$\text{SPV} = \text{SP}(\text{light}) - \text{SP}(\text{dark})$$

Figure 1. Schematic of the SPV-KFM setup showing the implementation of an additional laser diode to illuminate the sample from above. The general formula for calculating the surface photovoltage (SPV) is shown as well.

To measure SPV-KFM images, we modified a commercial AFM (Agilent 5500) by adding another laser diode (Thor Labs, Inc. LP405-SF10, 401.5 nm, 4 mW) with a collimator and a focusing lens to illuminate the sample from above (e.g., from the same side as the AFM tip). A custom-built part from Agilent containing a pre-drilled hole with a mirror to reflect the laser light down onto the surface of the sample was used, as shown in Figure S1 in the Supporting Information (SI). The laser intensity could be modulated digitally with computer control, thereby allowing for measurements of the surface potential in the light as well as in the dark. While in principle the

optical illumination could be turned on and off at each point in an image, we found that better results were obtained by taking one AFM image with the laser on, and then re-scanning the same area with the laser off. From these two distinct images, the SPV maps can be calculated as the difference between these images.

To ensure that the SPV-KFM technique is working properly, we first measured the surface potential on n-type and p-type Si wafers of varying resistivities. Figure 2 shows the topography (Figure 2a) and the surface potential under illumination [SP (light)] (Figure 2b) of a native oxide coated n-type Si wafer of moderate resistivity ($\rho = 10 \Omega \bullet \text{cm}$). The surface potential measured in the dark [SP (dark)] on this sample is shown in the SI Figure S2. Figure 2c shows two line profiles of surface potential measured in the light (blue line) and dark (green line). The net SPV for this material is positive. In general, n-type semiconductors exhibit upward band bending at their surfaces due to the presence of mid-gap surface states.⁵⁶ When illuminated, the sub-surface electric field drives holes to the surface and shuttles electrons towards the bulk, such that the surface undergoes a shift toward more positive potentials. Thus, the positive SPV observed for n-type silicon is expected and has been reported previously.⁵⁷ We also performed this measurement on p-type Si wafers, which exhibit downward band bending. As expected, a negative SPV response was observed, shown in Figure S3 in the SI. Figure S3 also shows plots of the average SPV measured for Si wafers with a variety of resistivities. These plots show that at very low or very high resistivities there is little SPV response from the Si, and the maximum SPV is observed for Si with intermediate resistivities, which means that the Si is not too heavily doped (so that it is acting like a metal) or too lightly doped (so that it acts like an insulator). These results show that the surface potential and photopotentials that we measure experimentally with this SPV-KFM technique are in accordance with those expected when samples of known electronic structure are

tested. After this validation, we can apply this technique to understanding materials of interest.

Figure 2. SPV-KFM data of a control n-type Si wafer coated with native oxide with a resistivity (ρ) of $10 \Omega \cdot \text{cm}$. (a) Topography of the Si wafer. (b) Corresponding surface potential image of the Si under illumination with a 637.3 nm laser diode. (c) Line profiles of the surface potential with illumination [SP (light), blue line] and without illumination [SP (dark), green line]. There is a clear increase in surface potential under illumination vs. in the dark. Scale bars: 200 nm.

Characterization of the WSe₂-MoS₂ Heterostructures. The monolayer lateral heterostructures of WSe₂-MoS₂ are typically grown on insulating substrates such as c-plane sapphire⁴⁶ and must be transferred to other substrates for measurements requiring electrical contact. We synthesized WSe₂-MoS₂ heterostructures on sapphire substrates via chemical vapor deposition (CVD) and then transferred these heterostructures onto degenerately-doped n-type Si substrates (resistivity = $0.007\text{-}0.02 \Omega \cdot \text{cm}$) with native oxide coating using a method described previously⁴⁶ (see Materials and Methods for procedures). Degenerately-doped n-type Si was chosen as the substrate because it will not exhibit any measureable photoresponse. Additionally, the technique requires the use of a substrate that is not insulating to help facilitate the Fermi level equilibration required to get high-

resolution Kelvin probe surface potential images. Figure 3 shows the structural characterization of these WSe₂-MoS₂ heterostructures. Scanning electron microscopy (SEM) (Figure 3a) shows the heterostructures after transfer to the Si substrate. Many triangular features are clustered together and contain two distinct regions: a lighter inner triangle and a surrounding darker outer triangle. Figure 3b and 3c show photoluminescence (PL) spectra of the individual WSe₂ and MoS₂ regions, respectively. The peaks around 745 nm^{35, 58} for WSe₂ (Figure 3b) and 675 nm³⁴ for MoS₂ (Figure 3c) are at characteristic wavelengths for a monolayer of each material. Raman spectra (Figure S4 in SI) further confirm that both materials are one monolayer thick. For the MoS₂ monolayer, the distance between the A_{1g} and the E_{2g} peaks is approximately 18-19 cm⁻¹, which is in agreement with reported literature values and much smaller than those for a bilayer or thicker films, which are usually between 21-25 cm⁻¹.⁵⁹⁻⁶⁰ For the WSe₂ monolayer, there is no peak at 308 cm⁻¹, which only appears when WSe₂ becomes a bilayer or thicker.⁶¹⁻⁶² To illustrate which regions of the heterostructure shown in Figure 3a correspond to each material (WSe₂ vs MoS₂), Figure 3d and 3e show spatial maps of the photoluminescence intensity at emission wavelengths of 745 and 675 nm, respectively. Figure 3d shows that high fluorescence intensity is observed from triangular regions, while the spatial map at 675 nm in Figure 3e has a complementary appearance, with high fluorescence intensity in the regions between the triangles of Figure 3d. Based on the spatial distribution of fluorescence at each wavelength and the known emission spectra of MoS₂ and WSe₂, we conclude that the triangular regions are WSe₂ monolayers and the regions surrounding the triangles are MoS₂ monolayers.

Figure 3. Structural characterization of the lateral WSe₂-MoS₂ heterostructures. (a) SEM image of the WSe₂-MoS₂ heterostructures on Si. Scale bar: 20 μm . (b) and (c) Photoluminescence (PL) spectra of the WSe₂ region (black) at 745 nm and the MoS₂ region (purple) at 675 nm. (d) and (e) PL maps showing the emission corresponding to WSe₂ at 745 nm (d) and MoS₂ at 675 nm (e). These maps clearly show that the triangular flakes are WSe₂ and the surrounding regions are MoS₂. Scale bars: 2 μm .

SPV-KFM of the WSe₂-MoS₂ Heterostructures. Figure 4 displays the SPV-KFM data obtained from WSe₂-MoS₂ heterostructures that were grown on sapphire and then transferred onto n-type Si (resistivity 0.007-0.02 $\Omega\bullet\text{cm}$) as described above (see Materials and Methods for data collection details). Because of the high dopant concentration, such degenerately-doped Si substrate generates

little to no SPV, as confirmed in Figure S3 in the SI and by further control measurements on a bare region of the Si substrate (Figure S5 in the SI). Figure 4a shows the topography image of the heterostructures, revealing few distinguishing features between the two materials in the heterostructure; several small folds and/or wrinkles that arise from the transfer from sapphire to the Si substrate are observed. Figure 4b shows the surface potential map without illumination, revealing three brighter WSe₂ triangular flakes surrounded by the darker MoS₂. In this image, there is very strong contrast in the surface potential as a result of the chemical composition, which is not apparent in the topography image. The regions of WSe₂ and MoS₂ are labeled by correlating with the PL maps shown in Figure 3. Because of the already established connection between shape and composition, we can distinguish between the two materials in the KFM measurements.

Figure 4. SPV-KFM maps of the WSe₂-MoS₂ heterostructures on n-type Si of resistivity 0.007-0.02 $\Omega\cdot\text{cm}$. (a) Topography image of the WSe₂-MoS₂ heterostructures. (b) SP map taken with no illumination of the heterostructures. (c) SP map under illumination of the heterostructures. (d) Net SPV, calculated by subtracting the SP (dark) image from the SP (light) image. (e) Line

profiles of SP (light) in blue and SP (dark) in green corresponding to the traces in (b) and (c) marked with green and blue lines. Scale bars: 2 μm .

Work function values of these materials were not calculated, as KFM performed in ambient conditions generally does not provide accurate work function values, due to many factors such as surface adsorbates, tip conditions, etc. However, based on the convention adopted herein (see Materials and Methods), we can use the equation $V_{\text{tip}} = \Phi_{\text{sample}} - \Phi_{\text{tip}}$ to understand the work function differences between the two materials. The WSe_2 flakes have a larger surface potential than the surrounding MoS_2 , based on the color scale shown in Figure 4b. This indicates that the work function of WSe_2 is larger than that of MoS_2 . This work function difference would facilitate charge transfer between the materials, which will become more apparent under illumination.

Figure 4c shows the surface potential map under illumination with 401.5 nm light. In order to more easily see the differences in surface potential induced by illumination, Figure 4d shows the net SPV image, obtained by subtracting the SP (dark) image from the SP (light) image. The SPV image of Figure 4d has a color bar in which black has been set as zero SPV, with positive SPV appearing blue and negative SPV appearing red. To complement this image, Figure 4e shows the surface potential line profiles measured along the green line in Figure 4b and the blue line in Figure 4c. It is clear from this data that there is an average surface photovoltage of approximately -30 mV for the MoS_2 regions of the heterostructures, indicating an accumulation of negative charge when under illumination. This negative charge build-up could be a result of electron transfer across either the lateral p-n WSe_2 - MoS_2 junction or the MoS_2 -Si substrate interface. Different WSe_2 regions themselves exhibit some variability in the SPV signal, but the average SPV signal was close to 0 mV, indicating no measureable photoresponse. This result is similar to that seen in WSe_2 heterostructure field-effect transistor (FET) devices, where the WSe_2 has been demonstrated to have lower mobility than MoS_2 ⁶³ and is the limiting step of charge transport.⁶⁴ However, since

the surface potentials of WSe₂ and MoS₂ are different, there must be an electric field at the interface of these two materials. This electric field provides a lateral driving force for separation of electrons and holes that is induced by the surface potential difference of the two materials at the junction. These results show that the SPV-KFM technique provides a way to directly probe the spatially-varying charge transfer properties when the system is driven away from equilibrium by illumination.

We also observed that different WSe₂ flakes show variations in their SPV responses. For example, the bottom triangle shown in Figure 4d has strong negative SPV, while the other two WSe₂ triangles have nearly zero or slightly positive SPV. The lack of net photoresponse from these regions could be a result of offsetting processes, such as hole transfer across the WSe₂-MoS₂ junction in conjunction with electron transfer from the Si to the WSe₂, or a result of carriers with limited mobility in WSe₂ observed previously⁶³ that will recombine before being efficiently separated. Because the samples were transferred from the growth substrate (sapphire) to another substrate (Si), the 2D layers observed are not epitaxially bound or definitively oriented with respect to the underlying substrate. The different photoresponse from nominally identical WSe₂ triangles may arise from the variations of the interface between the structures and the underlying substrate. It is difficult to control the transfer to the Si substrate precisely, evident from the folds and wrinkles that are clearly present in the topography image in Figure 4a.

To further understand the SPV-KFM data, we have measured control samples of just WSe₂ and MoS₂ monolayers on the same degenerately-doped Si substrate. As shown in Figures S6 and S7 in the SI, these measurements show a large positive SPV for the WSe₂ monolayer, and a small negative SPV for the MoS₂ monolayer. The overall signs of the SPV remain the same, but the photoresponse appears to be suppressed for the WSe₂ and enhanced for the MoS₂ when in a

heterostructure as compared to the two materials when separate. These results further indicate that the photoresponse of the heterostructures is partially a result of the interaction between these two materials at the lateral junction.

We have further studied the SPV maps of a WSe₂-MoS₂ heterostructure that has been transferred to a p-type Si substrate that is not degenerately doped, as shown in Figure 5. A control scan taken on just the substrate, shown in Figure S8 in the SI, reveals the strong negative SPV exhibited by the substrate, typical for a p-type material of moderate resistivity (Figure S3 in the SI). Figure 5a shows the SP (dark) of one corner of a WSe₂ flake with MoS₂ surrounding it. The p-type Si substrate is also visible in this image beyond the boundary of the MoS₂. Figure 5b displays the SP (light) of the same area of the heterostructure, and the net SPV is shown in Figure 5c, illustrating the stark difference in photoresponse between the two materials and the substrate. To highlight this further, surface potential line profiles have been plotted in Figure 5d showing the change in SP in the dark (green) and under illumination (blue) for the WSe₂, MoS₂, and p-Si regions traced along the green and blue lines in Figure 5a, b. From this line profile, it is apparent that the SPV in the WSe₂ region is still approximately 0 mV, while the SPV in the MoS₂ region is now -110 mV. However, the p-Si substrate is generating an SPV of -70 mV. Therefore, we are likely measuring the SPV for both the MoS₂ and the underlying Si substrate in the MoS₂ region, resulting in the enhanced negative SPV signal compared to that shown in Figure 4e collected on the degenerately-doped n-type Si substrate. Interestingly, there is no corresponding change in the SPV for the WSe₂, which suggests different interactions with the Si substrate are occurring between the two materials; perhaps the electrons moving to the surface of the p-type Si are combining with holes in the WSe₂ generated when electrons move across the junction to the MoS₂. Regardless, this comparison between the SPV data collected on different Si substrates makes it

clear that the Si substrate itself does not dominate the photoresponse observed in Figure 4. The changes in the surface potential and the photoinduced changes in surface potential are driven by the differences in the intrinsic properties of these MX_2 materials. The substrate has some effect on the absolute sign of the surface potential, but the difference between two distinct MX_2 materials is largely independent of the nature of the substrate, particularly when the samples are transferred to the substrate.

Figure 5. SPV-KFM maps of a WSe_2 - MoS_2 heterostructure on p-type Si substrate with moderate resistivity. (a) SP of the WSe_2 - MoS_2 heterostructure in the dark. The regions of WSe_2 , MoS_2 , and substrate (p-Si) are labeled. (b) SP under illumination of the same area of the heterostructure as shown in a. (c) Net SPV of the heterostructure. (d) Line profiles of SP (light) in blue and SP (dark) in green corresponding to the traces in (a) and (b) marked with green and blue lines. Scale bars: 2 μm .

As mentioned earlier, the SPV-KFM signal can be affected by the interface between the substrate and the MX_2 material. For example, poor contact to the substrate could perhaps inhibit charge transfer between the two, which would influence the observed photoresponse. However,

we believe that the variations observed between samples due to poor contact would be a reflection of the substrate interaction with the MX_2 material, and could help to elucidate how the material would operate in an actual device, particularly when the sample must be transferred to a different substrate. To that end, there could be variation between samples that are a result of differences in the transfer process or interaction between substrate and material. However, three different samples that were prepared in a similar manner at different times all exhibited the same sign for the photoresponse for the individual MX_2 materials, indicating that some local variations will exist between samples, but generally the result is reproducible among different samples on different days.

CONCLUSION

Our results demonstrate SPV-KFM as a useful technique for correlating spatial heterogeneity and photoresponse of individual nanostructures and in heterojunctions, specifically of 2D materials. We have validated the technique using Si wafers with known doping type and resistivity and studied a complex structure, the monolayer lateral heterostructure of WSe_2 - MoS_2 . SPV-KFM has revealed that the two materials have quite distinct photoresponses, likely as a result of the p-n junction that can effectively separate charges between the two materials in the heterostructure. Interestingly, the photoresponse seems to be relatively uniform for MoS_2 at -30 mV but varies for WSe_2 . Differences in the photoresponse between neighboring WSe_2 flakes reveal the influence of varying substrate interaction as a result of transferring the as-grown samples to a conductive substrate. This SPV-KFM technique is useful for understanding charge transfer and accumulation in 2D materials and nanomaterials in general, and elucidating the effects of spatial heterogeneity

and sample transfer on the photoresponse. Understanding these influences on properties will lead to better design of nanostructures for optoelectronic and photovoltaic applications.

SUPPORTING INFORMATION

The supporting information is available free of charge at the ACS Publications website. It contains additional SPV-KFM data for silicon controls, Raman spectra of the heterostructures, SPV-KFM, Raman, and PL data for a WSe₂ monolayer and a MoS₂ monolayer.

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