A $WSe_2/MoSe_2$ heterostructure photovoltaic device

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We report on the photovoltaic effect in a $WSe_2/MoSe_2$ heterojunction, demonstrating gate tunable current rectification with on/off ratios of over 10^4. Spatially resolved photocurrent maps show the photovoltaic effect to originate from the entire overlap region. Compared to WSe_2/MoS_2 heterostructures, our devices perform better at long wavelengths and yield higher quantum efficiencies, in agreement with Shockley-Queisser theory. © *2015 AIP Publishing LLC*.
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Photovoltaic devices based on semiconductor p-n junctions require a judicious choice of materials that efficiently absorb solar radiation over a wide spectral range. Transition metal dichalcogenides (TMDCs) are a class of layered materials with band gaps in the range of 1–3 eV, making them ideal for optoelectronic applications including photovoltaics. Various optoelectronic devices like light emitting diodes (LEDs) and photodetectors have recently been demonstrated using TMDC-based p-n hetero- and homojunctions. For solar energy harvesting, the choice of TMDCs with different band gaps offers an unprecedented flexibility in designing the absorption profile of a p-n heterostructure to best match the solar spectrum. All existing TMDC-based p-n junction photovoltaic devices[1–4] use MoS_2 (direct band gap ~1.9 eV) as the n-type material, together with a p-type material like WSe_2 or WS_2. On the other hand, monolayer $MoSe_2$ has a relatively low direct band gap of 1.55 eV,[5,6] making it well-suited for absorbing in the near-infrared (IR) part of the spectrum (Figure 1). Although vertical $WSe_2/MoSe_2$ heterostructures have recently been demonstrated,[7] studies of electrical transport and the photovoltaic effect in such a device are still missing. In this letter, we report a $MoSe_2$-based photovoltaic device by fabricating a $WSe_2/MoSe_2$ vertical heterojunction. We show that the lower band gap of $MoSe_2$ makes the resulting device more efficient compared to a similar WSe_2/MoS_2 p-n junction.

We fabricate our devices on a transparent glass substrate instead of the standard Si/SiO_2 that is used in the vast majority of reported TMDC heterostructures. A transparent substrate allows us to perform optical measurements in transmission and optical characterization that is unobstructed by the substrate. On the other hand, it requires finding transparent substitutes for the back-gate and gate-dielectric. We choose ~10 nm thick multilayer graphene (MLG) and a ~25 nm h-BN flake as the gate electrode and gate dielectric, respectively. We start our device fabrication by stacking these two on top of a glass coverslip. Next, the vertical p-n junction is built by transferring few-layer $MoSe_2$ and WSe_2 (3 layer thick each) on top of the h-BN, forming an overlapping region of approximately ~10 μm^2 as depicted in Figure 2. This back-gated configuration allows us to electrostatically tune the doping in the semiconductors while retaining optical transparency.

For electrical characterization of the fabricated devices, we added metal contacts to both TMDC layers and to the MLG backgate by e-beam lithography (EBL), followed by evaporation of 20/40 nm of palladium (Pd) and gold (Au). The high work function metal Pd serves as a good hole injector into WSe_2 (Ref. 8) and should provide acceptable electron injection into $MoSe_2$ at the same time.

Both the MLG backgate and the TMDC layers are connected to a Keithley digital multimeter as seen in Figure 2(a). This allows us to apply a constant gate voltage (V_g) to the MLG and serves as a current source. In forward bias, electrons and holes are injected into the $MoSe_2$ (source) and WSe_2 (drain), respectively.

We first performed electrical measurements under different illumination intensities ($\lambda = 633$ nm, $I_{opt} = 65$, 130, 190, 250, and 320 W cm^{-2}). For studying the photocurrent $I_{ph} = I_{illuminated} - I_{dark}$, the backgate was kept at $V_g = 0$ V while sweeping over the drain-source voltage (V_{ds}). The resulting $I_{ph} - V_{ds}$ curves of our device are shown in Figure 3(a). Indeed, a clear photovoltaic response is observed that allows us to extract an open-circuit voltage of $V_{OC} \sim 0.46$ V and an illumination dependent short-circuit current of up to

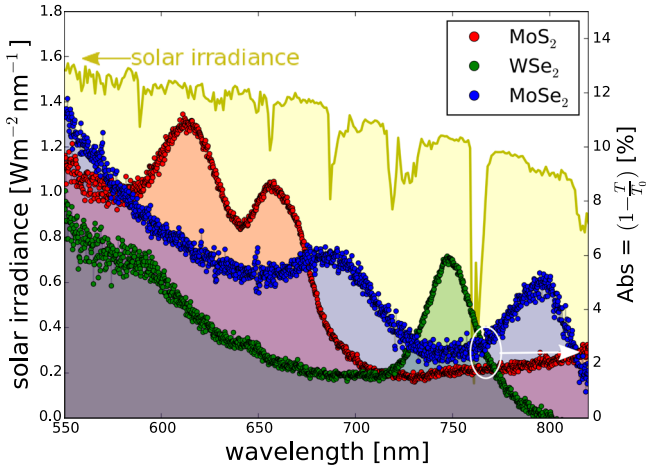

FIG. 1. Absorption in few-layer flakes of different TMDCs in comparison with the solar irradiance (AM1.5, yellow). The absorption is enhanced at the respective direct band gap energies. Of these three, $MoSe_2$ covers the broadest range in the absorption spectrum, starting at ~820 nm due to its small band gap, making it suitable for photovoltaic applications.

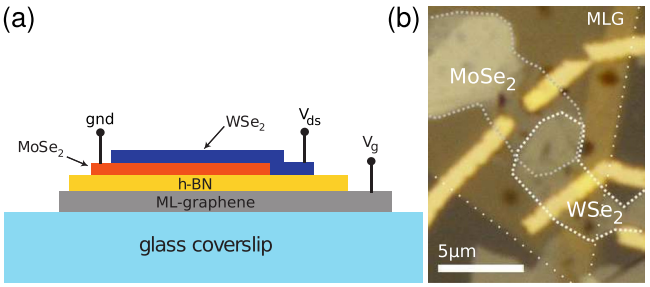

FIG. 2. (a) Schematic and (b) optical micrograph of the device showing the transparent glass substrate with a multilayer graphene and h-BN flake serving as the gate electrode and dielectric layer, respectively. On top of this stack, the $MoSe_2$ and WSe_2 flakes are transferred creating an overlapping junction. Metal contacts (Pd/Au) are added for electrical characterization.

$I_{SC} > 0.04\,nA$ for this device. The rather low fill factor, defined as the ratio of the product of the current and the voltage at the maximum power output and the product of I_{SC} and V_{OC}, could be a result of a large series resistance in our device, originating from the TMDC/metal contacts and the intrinsic TMDCs.[10]

To verify the origin of the photocurrent, a map was recorded at zero bias conditions ($V_g = V_{ds} = 0\,V$) by measuring I_{SC} while scanning the laser spot across the device. As illustrated in Figure 3(b), we observe a high photocurrent from the entire overlap region. This indicates the formation of a vertical junction with strong interlayer coupling, in addition to the PL spectra that show the existence of interlayer excitons (data not shown). We therefore conclude that the observed photocurrent is a result of charge separation at the junction from absorbed photons in the heterostructures.

Next, $I_{ds} - V_{ds}$ curves were repeated in the dark. For this experiment, the MLG served as a backgate to adjust the doping level in the TMDC layers. Figure 4(a) presents the drain-source current (I_{ds}) plotted against the drain-source voltage (V_{ds}) for different gate voltages V_g. A strong tunability of I_{ds} is observed showing excellent current rectification with on/off ratios of more than 10^4, limited only by the range of V_g, which we restrict ourselves to $-3\,V < V_g < +3\,V$ to avoid gate leakage currents.

The diode behavior becomes stronger for negative gate voltages ($V_g < 0\,V$), with a large current flowing under forward bias ($V_{ds} > 0\,V$) when WSe_2 is positively biased with respect to $MoSe_2$. Higher negative gate voltages increase the p-doping in the WSe_2 and hence result in an increased current. The observed IV characteristics are similar to those of reported p-WSe_2/n-MoS_2 devices.[1,2] Additional measurements were performed on a second device with two independent contacts on each flake. The observed ambipolar transport suggests that the rectifying behavior stems from an asymmetric p-p junction rather than from a true p-n junction.

In contrast to this rectifying behavior, a different regime is found for positive gate voltages ($V_g > 0\,V$). In this range, the magnitude of I_{ds} in forward bias is not as high as for $V_g < 0\,V$, which is consistent with a suppression of the p-type behavior in WSe_2 that limits the transport. Under strong reverse bias ($V_{ds} < 0\,V$), however, I_{ds} increases for $V_g > 0\,V$, as seen in Figure 4(b), displaying a "backward-diode" behavior. This sharp rise in I_{ds} suggests vertical band-to-band electron tunneling (BTBT) as a possible origin, as it was recently observed in other van der Waals heterostructures.[9]

In order to directly compare the optoelectronic properties of our $WSe_2/MoSe_2$ heterojunction with MoS_2 based devices reported recently,[1–4] we also fabricated a device by replacing $MoSe_2$ with MoS_2, keeping everything else the same. Transmission of the two devices was measured using a white light source (NKT SuperK Extreme). Reference spectra were taken by focusing the beam on an area with just the MLG gate and the h-BN layer, and these spectra were then used to normalize the transmission through the junctions. As expected, the absorption spectra of both the WSe_2/MoS_2 and $WSe_2/MoSe_2$ devices exhibit peaks at the corresponding exciton energies of their TMDC components (Figure 5). The indirect band gap does not play a significant role, despite the fact that the used TMDC layers are not monolayers. This is because the absorption cross-section at the indirect band gap is much smaller than at the direct band gap energy.

Because of their different TMDC compositions, the two different heterostructures absorb in partially different wavelength ranges. In particular, our $WSe_2/MoSe_2$ junction shows a high absorption in the range $675\,nm < \lambda < 725\,nm$ and $775\,nm < \lambda < 820\,nm$, regions where the WSe_2/MoS_2 junction is only able to collect a smaller fraction of the incident photons. Figure 5 also shows external quantum efficiency

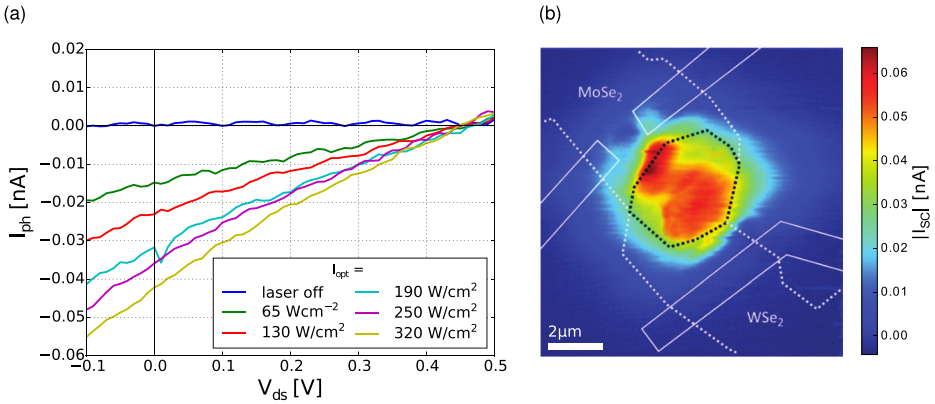

FIG. 3. Electrical characteristics of our $WSe_2/MoSe_2$ device under illumination. (a) $I_{ph} - V_{ds}$ curves taken at $V_g = 0\,V$ for different illumination intensities ($I_{opt} = 65$, 130, 190, 250, and $320\,W\,cm^{-2}$). A constant open circuit voltage of $V_{OC} \sim 0.46\,V$ can be extracted, whereas the short circuit current increases with illumination power up to $I_{SC} > 0.04\,nA$. (b) Photocurrent-map recorded at $V_g = V_{ds} = 0\,V$. A strong photocurrent is originating from the entire overlapping area indicating the formation of a vertical junction with high interface quality.

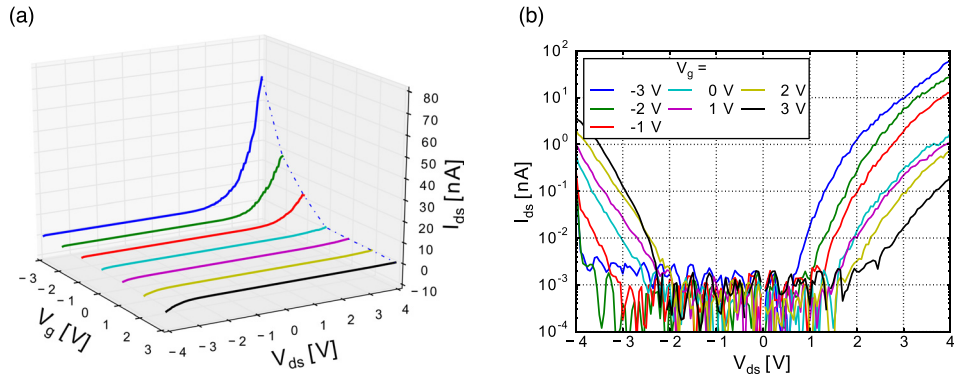

FIG. 4. Electrical characterization of a $WSe_2/MoSe_2$ heterojunction. (a) Several $I_{ds} - V_{ds}$ curves in the dark for different gate voltages. A strong rectification is visible at negative gate voltages $V_g < 0\,V$ in forward bias $V_{ds} > 0\,V$. (b) The same data as in (a), but plotted on a logarithmic scale. In forward bias for $V_g < 0\,V$, we see normal diode like behavior, whereas in reverse bias and for $V_g > 0\,V$, the device acts like a "backward-diode" with a sharp increase in I_{ds}.

(EQE) calculations from photocurrent measurements that were performed by selecting various wavelengths of the supercontinuum source (with optical intensities between $I_{opt} = 20$ and $430\,W\,cm^{-2}$). These measurements indicate that contributions to the photocurrent come from partly different spectral regions, in good agreement with the absorption spectra of the corresponding devices. Especially between $750\,nm < \lambda < 850\,nm$, a much higher EQE from the $WSe_2/MoSe_2$ device is observed than for the WSe_2/MoS_2 junction, highlighting the advantage of the smaller band gap of $MoSe_2$. Taking into account the solar spectrum, this leads to an overall enhancement of the EQE by a factor of ~5 for our $MoSe_2$ based device. Moreover, these observations clearly show the usefulness and advantages of a device that could be made combining three TMDCs in a single device to significantly broaden the absorption spectrum, and to hence enhance the current conversion efficiency.

In summary, we have fabricated and investigated the electrical characteristics of a vertical $WSe_2/MoSe_2$ heterostructure on a transparent glass substrate. We demonstrate good current rectification in forward bias and observe a "backward-diode" behavior in reverse bias, both of which can be tuned by an applied gate voltage. A photovoltaic response from the overlap region of the heterostructure is observed. Due to the transparency of our devices, we are able to measure the absorption spectrum as well as the photoresponse and provide a quantitative comparison with similar WSe_2/MoS_2 devices. The $MoSe_2$ device shows an enhancement of absorption and photocurrent generation over a reference WSe_2/MoS_2 device. We emphasize that the weak absorption and low EQE are the result of using $MoSe_2$ that is only three layers thick. To increase the absorption and the EQE near unity levels, the TMDC thicknesses need to be increased considerably. Our results show that the spectral behavior of photovoltaic devices can be tailored by a proper choice of TMDC materials and hence can be made to best suit given environmental conditions.

Note added: During the finalization of this manuscript we became aware of a related study.[11]

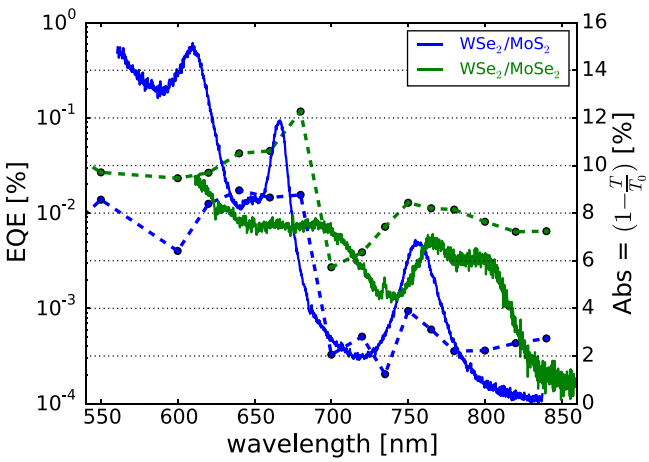

FIG. 5. Absorption (solid lines) and EQE measurements (dashed lines) for a WSe_2/MoS_2 and a $WSe_2/MoSe_2$ device. Both heterostructures show high absorption at the exciton energies at the band gaps of their corresponding TMDC compounds. Our $WSe_2/MoSe_2$ device shows a rather high absorption already starting at ~820 nm, as a result of the small band gap of $MoSe_2$. Additionally, EQE measurements were performed at different wavelengths that are in good agreement with the absorption spectra, attesting a higher photocurrent for higher wavelengths for our $WSe_2/MoSe_2$ junction compared to the WSe_2/MoS_2 junction.

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