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A vertical WSe₂–MoSe₂ p–n heterostructure with tunable gate rectification†

Hailing Liu,[†] Sajjad Hussain,[‡] Asif Ali,^{ab} Bilal Abbas Naqvi,^{ab} Dhanasekaran Vikraman,^c Woonyoung Jeong,^{ab} Wooseok Song,^d Ki-Seok An,^d and Jongwan Jung^{*ab}

Here, we report the synthesis of a vertical MoSe₂/WSe₂ p–n heterostructure using a sputtering-CVD method. Unlike the conventional CVD method, this method produced a continuous MoSe₂/WSe₂ p–n heterostructure. WSe₂ and MoSe₂ back-gated field effect transistors (FETs) exhibited good gate modulation behavior, and high hole and electron mobilities of ~ 2.2 and ~ 15.1 cm² V⁻¹ s⁻¹, respectively. The fabricated vertical MoSe₂/WSe₂ p–n diode showed rectifying *I*–*V* behavior with back-gate tunability. The rectification ratio of the diode was increased with increasing gate voltage, and was increased from ~ 18 to ~ 1600 as the gate bias increased from -40 V to $+40$ V. This is attributed to the fact that the barrier height between p-WSe₂ and n-MoSe₂ is modulated due to the back-gate bias. The rectification ratio is higher than the previously reported values for the TMDC p–n heterostructure grown by CVD.

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1. Introduction

The two-dimensional transition metal dichalcogenides (TMDCs), in the form of MX₂ (M = metal and X = S, Se or Te), have recently received much attention for the study of physics in 2D materials and in layered structures.^{1–3} In TMDCs, each M-atom (transition metal element) layer is enclosed within two X-atom (chalcogen element) layers and the atoms in the layers have hexagonally packed structures.^{1,3,4} Every X–M–X atom arrangement is held together by van der Waals interactions. And due to the weak van der Waals interactions of each layer, it is possible to tune the band structure of the X–M–X atoms from an indirect (~ 1.2 eV) to a direct band gap (~ 2.5 eV) through heterogeneous integration. TMDCs exhibit good electrical properties^{1,3,5,6} with high on/off ratios of $\sim 10^8$, and room-temperature mobility over 200 cm² V⁻¹ s⁻¹.^{7–11} Due to weak van der Waals forces between each stacking layer, 2D heterostructures can be easily produced by using mechanical transfer methods. Since p–n junctions are basic building blocks for electronic devices, and other optoelectronic devices,^{12–14} the implementation of homo or hetero p–n junctions

is a key interest among researchers. Mechanical exfoliation is an easy way to produce p–n junctions; however, it is not suitable for mass production. Recently, many efforts have been made to apply chemical vapor deposition (CVD) to 2D heterostructures such as MoS₂/graphene,¹⁵ WS₂/MoS₂,¹⁶ WS₂/h-BN,¹⁷ and n-MoS₂/p-WSe₂,¹⁸ MoSe₂–WSe₂.¹⁸ Nonetheless, the current rectification behavior of CVD-grown TMDC heterostructures is rarely reported and is poor.¹⁸ Our group has been focusing on the synthesis of TMDCs by a sputtering-CVD method.^{19,20} In this paper, we report a MoSe₂/WSe₂ p–n heterostructure. A W film was sputtered and then selenized to form WSe₂, and Mo was sputtered on the WSe₂ and selenized to form a vertical MoSe₂ (n)/WSe₂ (p) junction. Unlike the conventional CVD method, this method produces a continuous MoSe₂/WSe₂ film. The WSe₂ and MoSe₂ back-gate field effect transistors (FETs) exhibited good gate modulation behavior, and high hole and electron mobilities of ~ 2.2 and ~ 15.1 cm² V⁻¹ s⁻¹, respectively. The fabricated MoSe₂/WSe₂ p–n diodes showed rectifying *I*–*V* behavior, and the forward diode current increased with increasing back-gate bias. The p–n diode with back-gate tunability showed a high gate-tunable rectification ratio varying from ~ 18 to ~ 1600 at different back-gate biases. This can be attributed to the fact that the barrier height between p-WSe₂ and n-MoSe₂ is modulated due to the back-gate bias. The rectification ratio is much higher than the previously reported value for the TMDC p–n heterostructure (MoS₂/WSe₂) grown by CVD.¹⁸

2. Experimental details

2.1 Synthesis of MoSe₂/WSe₂

Fig. 1 illustrates the overall growth scheme for the vertical MoSe₂/WSe₂ heterostructure. The MoSe₂/WSe₂ films were

^aGraphene Research Institute, Sejong University, Seoul 143-747, Republic of Korea. E-mail: jwjung@sejong.ac.kr

^bInstitute of Nano and Advanced Materials Engineering, Sejong University, Seoul 143-747, Republic of Korea

^cDivision of Electronics and Electrical Engineering, Dongguk University-Seoul, Seoul 04620, Republic of Korea

^dThin Film Materials Research Center, Korea Research Institute of Chemical Technology, Daejeon 305-600, Korea

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‡ Authors contributed equally.



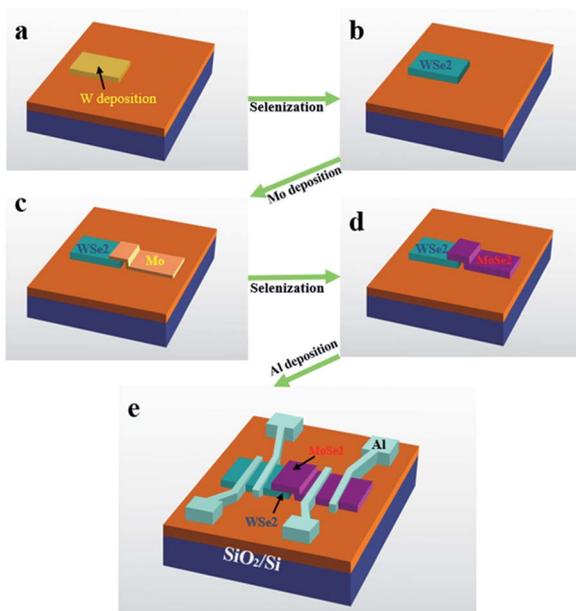


Fig. 1 Schematic of the MoSe₂/WSe₂ heterostructure. (a) W was deposited onto the SiO₂/Si substrate. (b) A WSe₂ film was formed *via* selenization. (c) Molybdenum (Mo) was deposited on the top of the WSe₂. (d) A MoSe₂/WSe₂ heterostructure was formed *via* selenization. (e) The MoSe₂/WSe₂ heterostructure with Al electrodes.

prepared by a RF magnetron sputtering system combined with a selenization process, using a W (99.9% pure) and a Mo (99.9% pure) target in an argon environment at room temperature. Initially a W thin film with a desired thickness was sputtered on a SiO₂/Si substrate through a metal shadow mask. Before sputtering, the chamber was evacuated by a turbomolecular pump to a vacuum at $\sim 2 \times 10^{-6}$ Torr. During the film deposition, the Ar gas was maintained at 10 sccm, and the power was fixed at 150 W with a deposition time of 1200 s. Subsequently, the as-deposited W film was further put in the center of a furnace for selenization at 650 °C for 30 min to form a WSe₂ film. The heating area for the selenium evaporation was fixed at 270 °C. The amount of selenium powder (0.5–0.8 g) used and the flow of Ar as a carrier gas were fixed for all the experiments. After the growth of the WSe₂, a Mo film was deposited on it. The sputtering conditions were the same for both films (W & Mo). The Mo/WSe₂ film was again placed in the tube furnace for selenization annealing to form the MoSe₂/WSe₂ heterojunction. The p–n junction area was defined by overlapped regions of two layers (Fig. 1). After the formation of the active area, Al (100 nm) was deposited on the top *via* e-beam evaporation.

2.2 Characterization techniques

All the samples were characterized using the latest analytical characterization techniques. WSe₂, MoSe₂ and MoSe₂/WSe₂ heterostructure films were analyzed by using a Renishaw inVia RE04, with a 514 nm Ar laser, a laser spot-size of 1 μm, laser power of 10 mW, and an exposure time of 30 s. A Si substrate with a Raman peak of 520 cm⁻¹ was used for calibration. X-ray photoelectron spectroscopy (XPS) (PHI 5000 Versa Probe, 25 W

Al Kα, 6.7×10^{-8} Pa) was used for binding energy and elemental composition analysis. The crystallinity of the film was examined using in-plan X-ray diffraction (XRD, Rigaku) with Cu-Kα radiation ($\lambda = 54.178$ Å) operated at 50 kV and 300 mA current. FE-SEM (HITACHI S-4700) was used to demonstrate the morphological nature of the WSe₂, MoSe₂ and MoSe₂/WSe₂ heterostructure films. The crystal structures of the resulting products were analysed using a JEOL-2010F TEM with the assistance of Gatan Digital Micrograph software (Gatan Microscopy Suite 2.0) for image acquisition and processing (FFT, R-FFT, *etc.*).

3. Results and discussion

Raman spectroscopy was used to characterize the formation of WSe₂, MoSe₂ and the MoSe₂/WSe₂ heterostructures. For the WSe₂ film, one main characteristic peak at 250.5 cm⁻¹, assigned to the E_{2g}¹ mode was observed.²¹ On the other hand, for the MoSe₂ film three characteristic phonon modes appeared in the Raman spectra: a sharp one at low wavenumber (~ 242.2 cm⁻¹) associated with the out-of-plane vibration of Se atoms, and two broad ones at higher wavenumber (~ 290.1 cm⁻¹), (~ 352.0 cm⁻¹) corresponding to the E_{2g}¹ and B_{2g}¹ modes associated with the in-plane vibration of Mo and Se atoms.^{22–24} In the Raman spectrum of the MoSe₂/WSe₂ heterostructure, peaks

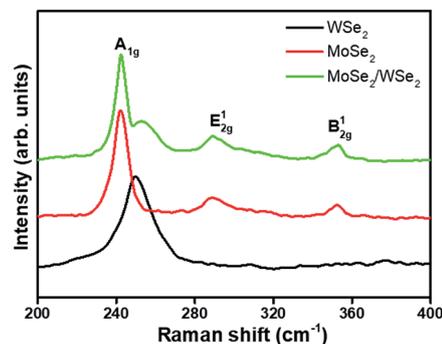


Fig. 2 Raman spectra of WSe₂, MoSe₂ and the MoSe₂/WSe₂ heterostructure films.

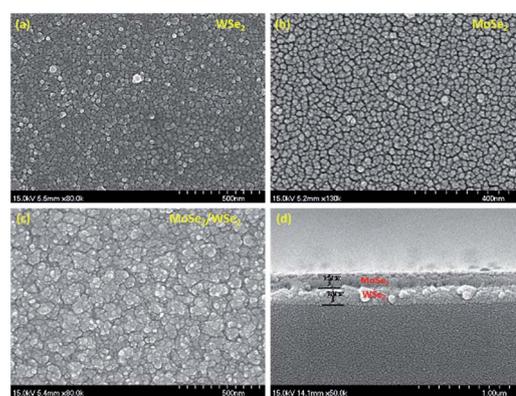


Fig. 3 Top-down and cross-sectional SEM images. Top-down images of (a) WSe₂, (b) MoSe₂ and (c) the MoSe₂/WSe₂ heterostructure (d) cross-sectional image.



corresponding to both WSe₂ and MoSe₂ films appeared. In addition, there was no significant shift of the representative peaks for WSe₂ and MoSe₂ in the heterostructure. This supports that there was no serious alloying process of the WSe₂ and MoSe₂ encountered in the synthetic procedure, since the alloying process would be accompanied by peak shifts (Fig. 2).¹⁸

Scanning electron microscope (SEM) images reveal the formation of homogeneous MoSe₂ and WSe₂ thin films (Fig. 3a and b). Further, SEM confirms the existence of a dense array of grains for the MoSe₂/WSe₂ heterostructure (Fig. 3c). The thicknesses of the MoSe₂ and WSe₂ films were ~160 nm and ~140 nm, respectively, estimated from the cross-sectional SEM image (Fig. 3d). The elemental mapping images of W, Mo and Se elements for the MoSe₂/WSe₂ heterostructure are provided in the ESI in Fig. S1.† Transmission electron microscopy (TEM) characterization was further performed to analyse the surface of the MoSe₂/WSe₂ heterostructure as shown in Fig. 4. The TEM images revealed that the film surface consisted of highly dense layers with a polycrystalline edge-exposed site structure.

X-ray photoelectron spectroscopy (XPS) was applied to examine the binding energies of WSe₂, MoSe₂ and the MoSe₂/WSe₂ heterostructure (Fig. 5a–d). The complete survey scans of WSe₂ and MoSe₂ are provided in Fig. S2.† From the WSe₂ film, the peaks at 32.2 and 34.4 eV were assigned to the doublet W 4f_{7/2}

and W 4f_{5/2} binding energies, respectively and the peak at 38 eV was assigned to W 5p_{3/2} binding energy. The Se peaks at 54.7 and 55.1 eV (Fig. 5a and b) were indexed to be Se 3d_{5/2} and Se 3d_{3/2} respectively.^{21,25} For the MoSe₂ film, Mo 3d_{3/2} and 3d_{5/2} core levels peaks were located at 231.1 and 228.0 eV, respectively. The peak of Se around 54.0 eV can be divided into Se 3d_{5/2} and Se 3d_{3/2} with peak positions at 54.6 and 55.2 eV, respectively^{26,27} (Fig. 5c and d). The XPS survey scan of the MoSe₂/WSe₂ heterostructure revealed the presence of W, Mo and Se elements (Fig. S3†).

XPS depth profile analysis was performed to investigate the typical WSe₂/MoSe₂ heterostructure. A 1 keV Ar ion beam was used for continuous etching of the WSe₂/MoSe₂ heterostructure in the direction from top to bottom. Fig. 6a–c show the XPS depth profile spectra for the W, Mo and Se binding energies. The Mo peak intensities were decreased and the W peak intensities were increased with etching time, whereas Se peak intensities were slightly varied due to the presence of Se in both structures. These findings confirm the heterostructure formation without diffusion or alloy formation. The Mo atomic concentration from the top-layer of MoSe₂ drastically decreased, although the W atomic concentration from the bottom-layer of WSe₂ linearly increased up to 120 s of etching time as shown in Fig. 6d. The cross sectional SEM image of the heterostructure is also evidence of our dual layered structure.

We characterized the electrical transport properties of WSe₂ and MoSe₂ back-gated field effect transistor (FET) devices (Fig. 7a and b). Transfer characteristics of source-drain current (*I*_{ds}) versus back-gate voltage (*V*_{gs}) were measured for WSe₂ and MoSe₂ FETs. The WSe₂ and MoSe₂ devices presented p-type and n-type behavior under back-gate biasing (constant bias, *V*_{ds} = 1 V), respectively, similar to the earlier reports by other research group.^{22,28} The field-effect mobility was extracted from the slope of $\Delta I_{ds}/\Delta V_{gs}$ fitted to the linear region of the transfer curves using the following equation

$$\mu = \frac{L}{WC_{ox} V_{ds}} \frac{\Delta I_{ds}}{\Delta V_{gs}} \quad (1)$$

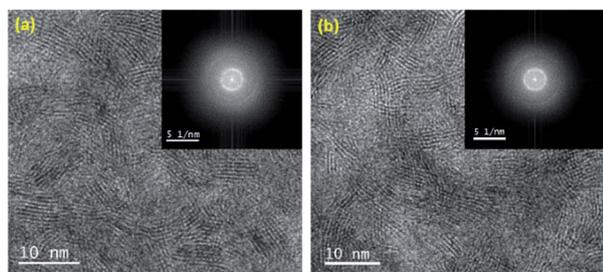


Fig. 4 (a and b) TEM images of the MoSe₂/WSe₂ heterostructure.

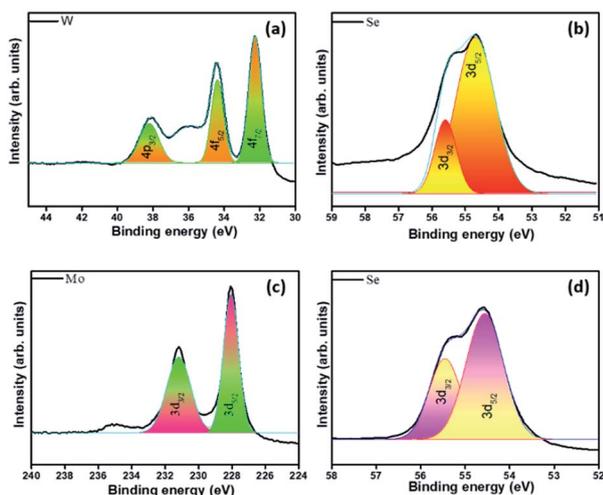


Fig. 5 XPS spectra: (a) W 4f and (b) Se 3d binding energies for WSe₂. (c) Mo 3d, 4f and (d) Se 3d binding energies for MoSe₂.

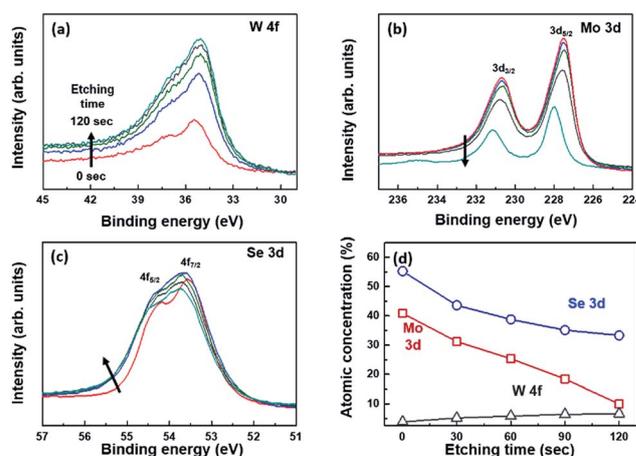


Fig. 6 XPS depth profile spectra of (a) W 4f, (b) Mo 3d, and (c) Se 3d binding energies and (d) their atomic concentration variations in terms of etching time for the MoSe₂/WSe₂ heterostructure.



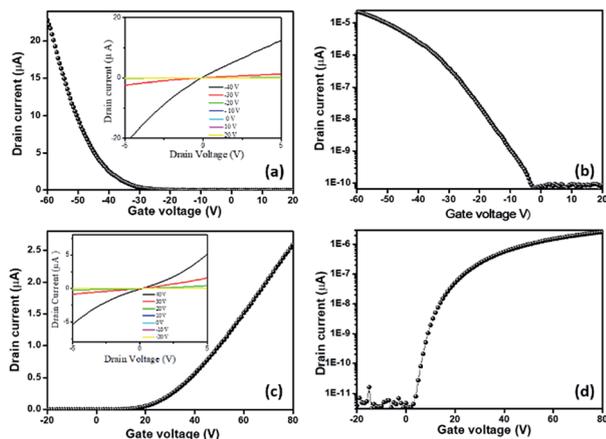


Fig. 7 Electrical output and transfer curves of the WSe₂ and MoSe₂ devices. (a and b) I_d - V_g of the WSe₂ FET at fixed $V_{gs} = 1$ V; I_{ds} - V_{ds} of the WSe₂ FET at V_{ds} : 20 V to -40 V (inset). (c and d) I_{ds} - V_{gs} of the MoSe₂ FET at $V_{gs} = 1$ V; I_{ds} - V_{ds} of the MoSe₂ FET at V_{ds} : 20 V to -40 V (inset).

where W is the width of the channel ($10 \mu\text{m}$), L is the length of the channel ($10 \mu\text{m}$), C_{ox} is the capacitance per unit area of the gate dielectric with 300 nm thickness ($1.15 \times 10^{-8} \text{ F cm}^{-1}$), V_{ds} is the applied drain voltage and $\Delta I_{ds}/\Delta V_{gs}$ is the slope of the linear part of the transfer plot (I_{ds} - V_{gs}) or the transconductance. The estimated field-effect mobility values of WSe₂ and MoSe₂ FETs are $\sim 2.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\sim 15.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively and on/off current ratios are ~ 3 - 6×10^5 . The linear I_{ds} - V_{ds} characteristics of both WSe₂ and MoSe₂ devices exhibited good ohmic contacts and there was an absence of significant charge injection barriers. Compared to the subthreshold characteristics, MoSe₂ had a better subthreshold swing than WSe₂. Electrical properties of the MoSe₂/WSe₂ heterostructure film were also measured. Voltages were applied to the metal pads of the p-type WSe₂ and the n-type MoSe₂ with changing back-gate bias. Fig. 8a shows the linear I - V curves of the stacked MoSe₂/WSe₂ p-n junction at various back-gate voltages. The drain voltage in

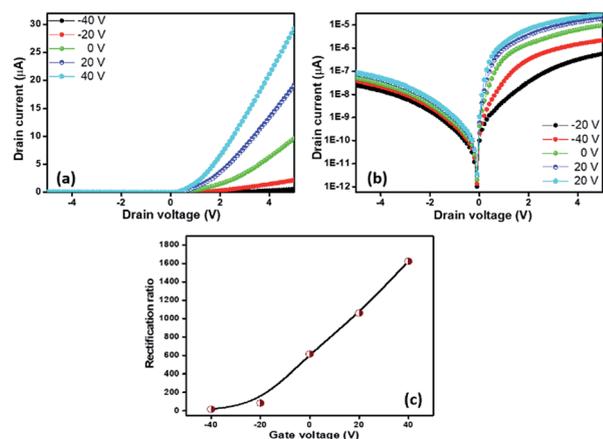


Fig. 8 Linear scale and log scale plots of I - V characteristics of the MoSe₂/WSe₂ heterojunction (a) linear scale plots of I - V . (b) Log scale I - V with different back-gate voltages V_{gs} (c) rectification ratio ($I_{ds}@V_{ds} = 1 \text{ V}/I_{ds}@V_{ds} = -1 \text{ V}$) as a function of back-gate voltage V_{gs} .

Fig. 8a is the voltage applied to p-WSe₂ with respect to n-MoSe₂. Rectifying I - V characteristics were observed from the p-n junction between n-type MoSe₂ and p-type WSe₂. The current in Schottky barrier diodes can be expressed as

$$I = I_0 \left(e^{\frac{qV}{kT}} - 1 \right) \quad (2)$$

where, I_0 is the saturation current, k is the Boltzmann constant, T is the absolute temperature, q is the elementary electric charge, and V is the applied voltage. The saturation current I_0 is expressed as

$$I_0 = AA^*T^2 e^{-\frac{q\Phi_b}{kT}} \quad (3)$$

where, A is the device area, A^* is the effective Richardson constant, and Φ_b is the barrier height. The ideality factor of the Schottky diode is extracted from the slope of the linear region of the $\ln I$ - V characteristic and is expressed as

$$n = \left[\frac{q}{kT} \right] \left[\frac{dV}{d(\ln I)} \right] \quad (4)$$

The ideality factor varies with back-gate bias, and is ~ 1.5 at a low bias range at $V_{gs} = 40$ V. The forward current is also increased upon increasing the back-gate voltage. The back-gate voltage controls the charge carrier densities of the electrons and holes in n-MoSe₂ and p-WSe₂. Since the bottom layer is p-type WSe₂ and the top layer is n-type MoSe₂, it is expected that hole concentration in WSe₂ decreases with increasing back-gate bias, while the top n-type MoSe₂ is less affected. Since the p-n junction is mainly composed of a vertical n-MoSe₂/p-WSe₂ junction and partly of a lateral side junction (the vertical junction area is much larger than the lateral side junction), the carrier concentration in the p-WSe₂ layer is readily modulated by the back-gate bias, while the electrons in the top MoSe₂ is less affected by screening due to the bottom WSe₂ layer. Therefore, upon increasing the back-gate bias, the barrier height between WSe₂ and MoSe₂ decreases, and in turn increases the forward current. Fig. 8b is a plot of logarithmic I versus linear V .

The reverse current also increases with increasing back-gate voltage. This is also due to the lowered barrier height between p-WSe₂ and n-MoSe₂. Fig. 8c shows the rectification ratios of the diode. The rectification ratio is defined as the forward current at 1 V anode bias (the p-WSe₂ voltage with respect to the n-MoSe₂ voltage) versus reverse current at -1 V anode bias. It is observed

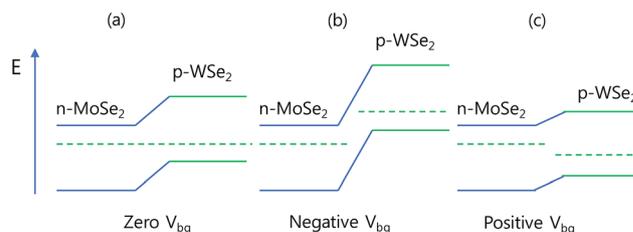


Fig. 9 Energy band diagram of n-MoSe₂ and p-WSe₂ at (a) 0, (b) negative and (c) positive back-gate voltage.



that the rectification is modulated by the back-gate voltage. The rectification ratio of the diode is increased from ~ 20 to ~ 1800 as the back-gate bias is varied from -40 V to $+40$ V as shown in Fig. 8c. This value is much higher than the reported value (~ 150) for the TMDC p-n heterostructure ($\text{MoS}_2/\text{WSe}_2$) grown by CVD.¹⁸

The energy band diagram (Fig. 9) reveals the formation of a built-in potential in the heterojunction p- WSe_2 /n- MoSe_2 , in which the conduction band (E_c) of WSe_2 lies above that of MoSe_2 . The built-in potential is produced due to the formation of a depletion region at the interface. This barrier height is increased at negative gate bias as energy levels in WSe_2 are shifted towards higher energy levels (Fig. 9b). Current is increased when the positive gate bias is applied (Fig. 9c). Positive gate bias leads to a decrease of the electron barrier and the energy levels in WSe_2 shift towards lower energy, which results in the reduction of the barrier between the p- and n-regions and increased the forward current.

4. Conclusions

We fabricated a $\text{MoSe}_2/\text{WSe}_2$ p-n heterostructure using a sputtering-CVD method. The WSe_2 and MoSe_2 back-gated field effect transistors (FETs) exhibited good gate modulation behavior, and high hole and electron mobilities of ~ 2.2 and ~ 15.1 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. The fabricated $\text{MoSe}_2/\text{WSe}_2$ p-n diodes exhibited gate-tunable rectifying I - V characteristics. The rectification ratio of the p-n diode is increased with an increase in the gate voltage, and it is increased from ~ 18 to ~ 1600 as the gate bias is increased from -40 V to $+40$ V. This is attributed to the fact that the barrier height between p- WSe_2 and n- MoSe_2 is lowered due to the back-gate bias. The rectification ratio is much higher than the previously reported value for the TMDC p-n heterostructure ($\text{MoS}_2/\text{WSe}_2$) grown by CVD.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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