A Van Der Waals Homojunction: Ideal p–n Diode Behavior in MoSe$_2$

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In conventional semiconductor technology, both p-type and n-type semiconductors are utilized for practical electronic and optoelectronic devices such as metal-oxide-semiconductor field-effect transistors (FETs), logic circuits, light-emitting diodes, and photovoltaics.[1–3] Recently emerged transition metal dichalcogenides (TMdCs) as atomically thin-layered semiconductors are one of strong contenders for leading next generation semiconductor technology, particularly in soft electronics, together with its counterparts of metallic graphene and insulating hexagonal-boron nitride, which are the basic components for active channel, electrode, and gate insulator for FETs.[4–7] As an important building block for practical device applications of TMdCs, van der Waals (vdW) p–n junctions have been intensively highlighted.[8–12] The homojunction p–n diode is an ideal platform compared to the heterojunction in terms of diode characteristics, e.g., more efficient current rectification and photovoltaic response, since the interface of the homojunction with continuous band alignments possess smaller carrier trap sites than that of the heterojunctions.[11,13] Nevertheless, only vertical vdW heterojunction devices have been realized so far, since explicitly converting the carrier type in the same material has not been realized in 2D TMdCs.

Engineering the carrier type is one of challenging issues in TMdCs, prior to the practical use of the materials. MoS$_2$, WS$_2$, and MoSe$_2$ show inherently n-type but WSe$_2$ and MoTe$_2$ show p-type in terms of semiconductor characteristics,[14] although the characteristics may vary slightly with the environment and contact metals.[15] To modulate the intrinsic carrier type of TMdCs, the surface functionalization method via chemical treatment has been widely studied, since it can be more effective in TMDC monolayers than bulk materials due to all the atoms accessible to the environment. However, this approach is available only for lateral devices and the stability cannot be guaranteed.[16,17] One fundamental question is whether the elemental doping, which has been successful for controlling carrier types in bulk material, works for 2D layered materials having weak vdW interaction. Historically well-known elemental doping method has been also adopted in bulk TMdCs.[18,19] For example, Nb (five valance electrons) or Re (seven valance electrons) has been used for a substitutional p-type or n-type dopant to replace the cation such as Mo or W with six valance electrons, where Nb has no miscibility gap for Mo alloys.[19] Recently, for 2D layered materials, this concept is expected by the theoretical calculation[20] and was also demonstrated for MoS$_2$.[21] By Nb-doping, the intrinsic MoS$_2$ semiconductors with n-type is converted to p-type degenerate semimetals.[21] Despite the successful type conversion for 2D layered materials, the applications are critically limited to Schottky diodes due to sacrifice of semiconducting properties. Therefore, it has not been possible to explicitly convert the carrier type in 2D materials with maintaining semiconducting properties by the elemental doping, so far. In our study, we synthesized semiconducting (nondegenerate) p-type MoSe$_2$ via Nb-elemental doping and demonstrated the vdW homojunction p–n diode having ideal diode characteristics via vertical stacking of the p-type and n-type semiconducting MoSe$_2$. Furthermore, we showed the usefulness of the synthesized p-MoSe$_2$ via demonstrating full device functionalities such as p-FETs and a complementary metal-oxide semiconductor (CMOS) inverter.

**Figure** 1a shows a schematic that Nb atoms can be p-type dopants by simply replacing Mo in undoped MoSe$_2$, where Nb has one less valence electron than Mo. The undoped MoSe$_2$ (n-MoSe$_2$) and Nb-doped MoSe$_2$ (p-MoSe$_2$) brought us to demonstrate vdW homojunction. We fabricated a vertically stacked p–n homojunction diode by physically overlapping the 3.2 nm-thick n-MoSe$_2$ on the already transferred 2.9 nm-thick p-MoSe$_2$ (the inset of Figure 1b, Experimental Section). The fabricated p–n diode reveals typical rectifying behavior at room temperature (300 K), as shown in Figure 1b. The forward current ($I_F$) at positive drain voltage ($V_D$) dramatically increases as a function of gate bias ($V_G$) owing to the enhanced tunneling current through the narrowed Schottky barrier width in the n-MoSe$_2$/metal junction, which will be discussed later in detail. Moreover, the on/off ratio of >10$^6$ does not change dramatically with $V_G$ modulation (Figure S1, Supporting Information).

In Figure 1c, the $I$–$V$ curve of p–n diode at $V_G = 0$ V consists of four regions: I) reverse bias region, II) ideal linear diode region, III) current injection region, and IV) series resistance-dominate region. To evaluate the rectifying performance, an ideality factor ($n$) was estimated at forward bias (the inset of Figure 1c) by fitting to the Shockley diode equation:[22]
\[
\begin{align*}
I_D &= I_S \left[ \exp \left( \frac{V_D}{nV_T} \right) - 1 \right] \\
\text{where } I_S \text{ and } V_T \text{ denote reverse bias saturation current and thermal voltage, respectively. Notably, the lowest } n \text{ value was estimated to } \approx 1.0 \text{ at region II, implying ideal diode behavior. This characteristic due to low charge trap density at the homo-junction interface is comparable to conventional Si p–n diode behavior (} \leq 12 n \leq 2) \text{[1,23]. In terms of the ideality factor, our homojunction diode is much better than not only heterojunction p–n diodes in bulk semiconductors (} n \gg 2) \text{[13] or TMDGs (} n = 6.5) \text{[24] but also homojunction p–n diodes in TMDGs via chemical (} n = 1.6) \text{[25] and gate doping (} n = 1.9). [26] At the region III, however, the Shockley diode equation is not applicable, since parasitic sheet and contact resistances (R_s) promote the voltage drop (I_D \cdot R_s) as typically observed in p–n diodes. [5] To take into account this series resistance effect in real devices, the ideality factor was also estimated by the extended diode equation with the Lambert-W function (Figure S2, Supporting Information). At } V_G = 0 \text{ V, the ideality factor from the extended diode equation, } n \approx 1.14, \text{ is } \approx 10 \% \text{ larger than that from the Shockley diode equation. The result qualitatively agrees with our conclusion of the ideal diode behavior.}
\end{align*}
\]

Figure 1d shows the formation of well-aligned bands with the same bandgap but different Fermi levels extracted from experiments. This will be discussed in detail in Figure 4. The homojunction reveals ideal diode characteristics over the heterojunction due to no potential discontinuities such as the cusp or notch between the conduction and valence bands, which could provoke carrier scattering and trap sites near the junction interface. [10,12] However, this ideal diode behavior is degraded as the Fermi level is upshifted at a positive } V_G. \text{ In Figure 1e, the } n \text{ values derived from the region II slightly increase when } V_G > 0 \text{ V, since the increased intraband recombination current is promoted by boosted electron diffusion at a positive } V_G. \text{[1] Here we assume that the Fermi levels for both n-MoSe}_2 \text{ and p-MoSe}_2 \text{ are upshifted with the same energy via the } V_G \text{ bias (the inset of Figure 1e), since the effective charge screening length is estimated to } \approx 53 \text{ nm by the equation: [5]}

\[
\lambda = \frac{1}{\sqrt{\varepsilon_s \varepsilon_0 t_s}} \left( \frac{1}{\varepsilon_{ox}} \right)
\]

which is much longer than the thickness of the vertically stacked p–n MoSe}_2 \text{ diode (=6 nm). Here, } \varepsilon_s \text{ and } \varepsilon_{ox} \text{ denote the permittivity of MoSe}_2 (=6.07) \text{[27] and gate oxide (=3.9), and } t_s \text{ and } t_{ox} \text{ are the thicknesses of channel material and gate oxide (=300 nm), respectively.}

The photoresponse of homojunction p–n diode was also explored by using various excitation powers at a fixed laser
wavelength ($\lambda = 405 \text{ nm}$), as shown in Figure 2a. Both open circuit voltage ($V_{OC}$) and short circuit current density ($J_{SC}$) increase as the laser power density ($P_{Laser}$) increment (inset). The similar behavior has been also observed in other TMdC heterojunction diodes. [8,9] We calculated the photoresponsivity ($R$) and the external quantum efficiency (EQE) of the p–n diode at $V_G = V_D = 0 \text{ V}$ via the equations:[16]

$$R = \frac{I_D}{P_{Laser}}$$

$$\text{EQE} = R \frac{hc}{e\lambda}$$

where $h$ and $c$ are Planck's constant and speed of light, respectively. In Figure 2b, as the laser power increases, EQE (or $R$) are enhanced at $V_D = 0$ and $-1 \text{ V}$, while the value slightly decreases at $V_D = 1 \text{ V}$. Although the maximum EQE value reaches $\approx 1049\%$ for $V_D = 1 \text{ V}$ at $P_{Laser} = 890 \text{ W m}^{-2}$, $I_D R_S$ voltage drop is rather dominated by increased photocarriers, as discussed in Figure 1. However, the EQE values at $V_D = 0$ and $-1 \text{ V}$ still increase as a function of $P_{Laser}$. Furthermore, the EQE values at $V_D = -1 \text{ V}$ are consistently higher than the values at $V_D = 0 \text{ V}$, since the generated electrons and holes are easily drifted to the electrode along stiffer band in the depletion region for reverse bias.

Notably, in the case of non-ideal diode ($n > 1$), Shockley–Read–Hall (SRH) recombination is promoted for reverse bias. When reverse bias is applied, the junction width of depletion region becomes thinner and interband tunneling probability increases. Here, existing SRH recombination sites at interface act as the bridge for tunneling, and thus the probability of SRH-assisted interband tunneling is enhanced for reverse bias.[8,13] Therefore, as photocarriers increase, $R$ for reverse bias will be degraded as similarly observed in vdW heterojunction diode.[10] In our homojunction diode, however, both $R$ and EQE increase for reverse bias with the laser power increment due to negligible SRH recombination sites at the homojunction interface. To rationalize advantages of homojunction, the results are compared to several heterojunction diodes reported previously. For example, EQE $\approx 34\%$ and $R \approx 120 \text{ mA W}^{-1}$ at 920 W cm$^{-2}$ were obtained with a focused 532 nm diode laser for multilayer MoS$_2$/WSe$_2$ heterojunction p–n diode at $V_G = 0 \text{ V}$.[8] Taking into account the power density, our homojunction diode outperforms the heterojunction diode.

Figure 2c shows the photoresponse ratio ($I_{Light}/I_{Dark}$), where $I_{Light}$ and $I_{Dark}$ denote the drain current with and without laser irradiation of $P_{Laser} \approx 890 \text{ W m}^{-2}$ (Figure S1, Supporting Information), which decreases with a $V_G$ increment. This is again attributed to the enhanced recombination current, as evidenced by the increased ideality factor as a function of $V_G$ (Figure 1e). The $I_{Light}/I_{Dark}$ decreases at reverse bias ($V_D < 0 \text{ V}$) due to enhanced band-to-band tunneling recombination of photoexcited carriers. This ratio is further reduced at forward bias ($V_D > 0 \text{ V}$) due to increased recombination current and $I_D R_S$ voltage drop effect (Figure 2d).
Such high diode performance and its photoresponse observed in our work require clear p-type and n-type characteristics of MoSe$_2$. We fabricated p-FET and n-FET with 4.2 nm-thick p-MoSe$_2$ and 3.5 nm-thick n-MoSe$_2$ on a 300 nm-thick SiO$_2$/Si substrate with Cr/Au (10/50 nm) electrodes. The n-FET shows Schottky contact behavior (Figure 3a), while the p-FET shows Ohmic contact behavior (Figure 3b) with various gate biases ($V_G$). Figure 3c shows the transfer characteristics of the p-FET and n-FETs. The p-FET shows a higher on/off current ratio of $\approx 10^7$ and a lower subthreshold swing (SS) of 7.2 mV nm$^{-1}$ dec$^{-1}$ than those of the n-FET (a on/off current ratio of $\approx 10^6$ and a SS of 8.7 mV nm$^{-1}$ dec$^{-1}$). From various of p-FETs and n-FETs, the field-effect mobilities are respectively calculated via the equation:

$$\mu = \frac{1}{C_i W} \frac{dI_D}{dV_G} \frac{1}{V_D}$$

where $C_i$, $L$, $W$, $I_D$, and $V_D$ denote the specific gate capacitance of 300 nm-thick SiO$_2$, channel length, channel width, drain current, and drain voltage, respectively.$^{[3]}$ Mobilities for p-MoSe$_2$ ($\mu_p$) are 3–10 cm$^2$ V$^{-1}$ s$^{-1}$ with on/off current ratio range of $10^8$–$10^9$, and mobilities for n-MoSe$_2$ ($\mu_n$) are 5–13 cm$^2$ V$^{-1}$ s$^{-1}$ with on/off current ratio range of $10^5$–$10^6$. The estimated mobility values for intrinsic n-MoSe$_2$ agree with the lower limit of the reported values in the range of 10–100 cm$^2$ V$^{-1}$ s$^{-1}$.\cite{28,29} To investigate electron and hole concentrations and confirm the carrier types of the p-MoSe$_2$ and n-MoSe$_2$, Hall measurements were conducted for Hall bar structures (Figure S3, Supporting Information). Hole and electron concentrations for the p-MoSe$_2$ and n-MoSe$_2$ are estimated as $4.3 \times 10^{11}$ and $4.8 \times 10^9$ cm$^{-2}$, respectively. From the p-FETs and n-FETs, hole and electron concentrations are estimated to $2.1 \times 10^{11}$ and $1 \times 10^{11}$ cm$^{-2}$, respectively.$^{[31]}$ While the hole concentrations for p-MoSe$_2$ agree with each other in the order of magnitude, the large deviation for n-MoSe$_2$ is attributed to asymmetric geometry effect of Hall bar structure. We attribute the low hole mobility to the high hole concentration with Nb doping resulting in the promoted charge scattering (impurities and carriers). By using our p-FETs and n-FETs, we demonstrated the p/n CMOS inverter revealing clear on/off behavior with the gain value of 0.5.

Figure 3. Electrical characteristics of p-MoSe$_2$ and n-MoSe$_2$ devices. a,b) $I_D$–$V_D$ characteristics of n-MoSe$_2$ (a) and p-MoSe$_2$ (b) as a function of $V_G$. Inset: Band diagram and optical micrograph for few-layered p-MoSe$_2$ and n-MoSe$_2$ FETs. c) Transfer characteristics at $V_D = 1$ V for p-MoSe$_2$ and n-MoSe$_2$ FETs. Inset: Log-scale transfer curves. d) CMOS inverter fabricated with p-MoSe$_2$ and n-MoSe$_2$ FETs having clear on/off behavior with the gain value of 0.5.

To elucidate the elemental doping effect in intrinsic material properties, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were conducted for p-MoSe$_2$ and n-MoSe$_2$. One obvious evidence of the p-type doping effect in p-MoSe$_2$ is the downshifted Fermi level of $0.5$ eV as seen by XPS (Figure 4a). The valence band maximum of p-MoSe$_2$ and n-MoSe$_2$, obtained by extrapolation of the linear region in the valence band, is located around 0.8 and 0.3 eV below the Fermi level, respectively. The total binding energy peaks of Mo 3d and Se 3d in p-MoSe$_2$ are also upshifted by 0.5 eV compared to those of n-MoSe$_2$ (Figure 4b).\cite{32} As for Nb-related peaks, the Nb 3d peak (Nb 3d$_{5/2}$)\cite{33} from NbSe$_2$ is clearly visible in p-MoSe$_2$. Furthermore, the Nb native oxide (NbO$_x$)-related peak\cite{34} is
also observed, which is attributed to the natively oxidized surface of bulk flakes. No Nb-related peak is observed in undoped n-MoSe₂. The elemental composition was extracted from the XPS data and the inductively coupled plasma mass spectrometry (ICP) measurements (Table S1a, Supporting Information). The nominal value of 1 at% Nb is similar to the results determined from ICP data, while Nb content is overestimated in XPS data compared to the nominal value. In Raman spectroscopy measurement for exfoliated samples with a few layers, several Raman modes for p-MoSe₂ and n-MoSe₂ were observed (Figure S4c, Supporting Information). They are almost identical, including the slightly blueshifted peak of the A₁₈g mode (out-of-plane) that occurs as the thickness increases, independent of the type of MoSe₂ (Figure 4c). The blueshifted A₁₈g mode of p-MoSe₂ compared to that of n-MoSe₂ is attributed to phonon hardening by hole doping.

To investigate crystal structure and optical properties, scanning transmission electron microscopy (STEM), X-ray diffraction (XRD), and optical absorbance were observed. In Figure 4d, STEM microscopy image of p-MoSe₂ shows a clear hexagonal lattice structure (2H phase), with a lattice parameter between Mo atoms of ~3.29 ± 0.05 Å. The fast Fourier transform (FFT) of the image in the inset of Figure 4d yields a triangular single-spot pattern, demonstrating that the single-crystal feature is still retained even after doping. Upon inspection of large areas, chances to form precipitation or segregation of Nb or other elements are very unlikely (Figure S5, Supporting Information).

The XRD patterns measured in a powder mode show similar peak positions for both types of MoSe₂, indicating that p-MoSe₂ maintains high crystallinity even after p-doping (Figure 4e). In addition, the XRD data were used to calculate the lattice parameters (Table S1b, Supporting Information). The lattice constant along the c axis is contracted from 12.954 to 12.895 Å with Nb-doping, while the change of the lattice constant a within the plane is negligible (from 3.292 to 3.289 Å). The slight volume contraction (c/a) indicates that Nb atoms take substitutional doping at Mo sites, not interstitial doping. The segregation-free state and contracted lattice constant for p-MoSe₂ also agree with the TEM results (Figure 4d). Figure 4f shows the absorbance spectra with absorption cut-off edges near 1.2 eV.

We successfully performed a carrier-type conversion from intrinsically n-type to p-type in MoSe₂ by the Nb-elemental doping. Our p-MoSe₂ FET maintained a high on/off ratio, which is quite different from previous report. For instance, Nb-elemental doping for MoS₂ had been tried before but the on/off ratio decreased significantly, provoking question of feasibility of elemental doping in 2D layered materials. Although the composition of Nb in the doped MoS₂ was low (0.5 at%) in the report, which is less than our value (1 at%), semi-metal...
(or highly degenerate semiconducting) behavior was observed. This difference could be originated from different formation energy of Nb with S in MoS\(_2\) and with Se in MoSe\(_2\), which also requires further study. To rationalize our approach for p-MoSe\(_2\), we characterized the device performances of the FET using the commercially available p-MoSe\(_2\) (unknown elemental dopant, 2D semiconductors Inc.) through the same fabrication procedure. However, the n-type dominant ambipolar FET was observed in this case (Figure S6, Supporting Information). Therefore, we conclude that our elemental doping method effectively replaces the cation in Mo alloy as expected in theory.\(^\text{[20]}\)

In addition, we investigated environmental effect on our p-FET. After annealing at 150 °C for 2 h in a vacuum, the p-FET maintained its p-type characteristics with the high on/off ratio, while the I–V characteristics were slightly degraded (Figure S7, Supporting Information). The chemical stability of our elemental doping approach is much greater than that of widely investigated chemically functionalized approaches.\(^\text{[16,17]}\) Therefore, our results shed light on providing a promising method to control the intrinsic carrier type of 2D TMdC semiconductors using conventional elemental doping approach.

**Experimental Section**

**Material Synthesis:** Single-crystalline p-type and n-type MoSe\(_2\) were synthesized using the chemical vapor transport (CVT) method. Mo, Se, and Nb powders were stoichiometrically mixed with an atomic ratio of Mo:Se:N= 32.3:66:7:1. This was then mixed with NaCl in 1:1 ratio. The powder mixture was sealed in a quartz tube under a vacuum at a pressure of 10\(^{-5}\) torr. After heat treatment in 1000 °C furnace for 48 h, the powder mixture in the quartz tube was cooled to room temperature at a rate of 0.5 °C h\(^{-1}\) to yield single-crystalline flakes.

**Characterization:** The crystal structures of n-MoSe\(_2\) and p-MoSe\(_2\) flakes were investigated using X-ray diffractometry (SmartLab, Rigaku) with Cu \(_{Kα}\) radiation (\(λ = 1.54059\) Å) and Bragg–Brentano geometry. XPS measurement was performed at the 8A1 beamline of the Pohang Accelerator Laboratory in Korea. The photon source was a U6.8 200 w undulator and the photon energy was set to 640 eV (photon energy 3057, Physical Electronics) was fixed at 54°. The defined energy window was from the incident light. This resolution:

\[ \alpha = \frac{\theta}{\sin \theta} \]

was 200 nm. The X-rays were incident in the vertical direction to the sample surface (0°) and an electron analyzer (PHI 3057, Physical Electronics) was fixed at 54° from the incident light. This geometry allowed collection of sensitive information about the sample surface using a shallow probing depth. The defined energy window was 0.75 eV. The quantities of each element of the p-MoSe\(_2\) and n-MoSe\(_2\) crystals were analyzed using ICP (Agilent 7500, Agilent Technologies). The absorbance of both types of MoSe\(_2\) samples, attached to the holder, was measured using a reflection mode of a UV–vis–NIR spectrometer (V-670, Jasco) without background signals.

Thin layers of n-MoSe\(_2\) and p-MoSe\(_2\) were prepared by a mechanical exfoliation of bulk materials on a SiO\(_2\) (300 nm)/Si substrate. The morphology of the exfoliated p-MoSe\(_2\) flakes was observed by optical microscopy (Axio Imager 2, Zeiss) and AFM (SPA-400, Seiko) in a tapping mode. Raman spectra of p-MoSe\(_2\) and n-MoSe\(_2\) were measured using a confocal Raman spectrometer (XperRamp 200, Nanobase) with a 5 s exposure time, a 532 nm wavelength laser, and a spectral resolution of 2400 g mm\(^{-1}\).

**Device Fabrication and Characterization:** FETs were fabricated with source and drain contacts by metal evaporation of Cr/Au (10/50 nm) after using e-beam lithography for patterning on 3.5 nm-thick (=5 layers) n-MoSe\(_2\) and 4.2 nm-thick (=6 layers) p-MoSe\(_2\). To fabricate the CMOS inverter, p-MoSe\(_2\) flake (1.7 nm) was transferred near n-MoSe\(_2\) (2.4 nm) by poly(methyl methacrylate) (PMMA) and the water-soluble layer (polyvinyl alcohol (PVA))-assisted transfer method.\(^\text{[40]}\) For the p–n diode, p-MoSe\(_2\) (2.9 nm) was transferred onto n-MoSe\(_2\) (3.2 nm) by the same transfer method. The electrical and optical characteristics of the devices were measured using an electrical characterization system (Keithley 4200-SCS, Keithley Instruments) and a laser diode (405 nm wavelength and beam diameter of ~1 mm). The Hall measurements were performed in the physical property measurement system (DynaCool, Quantum Design) with a lock-in amplifier (SRS 830, Stanford Research Systems).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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