ABSTRACT: Transition metal dichalcogenides (TMDCs) have been extensively explored for applications in electronic and optoelectronic devices due to their unique material properties. However, the presence of large contact resistances is still a fundamental challenge in the field. In this work, we study defect engineering by using a mild plasma treatment (He or H2) as an approach to reduce the contact resistance to WSe2. Material characterization by X-ray photoelectron spectroscopy, photoluminescence, and Kelvin probe force microscopy confirm defect-induced n-doping, up to degenerate level, which is attributed to the creation of anion (Se) vacancies. The plasma treatment is adopted in the fabrication process flow of WSe2, n-type metal-oxide–semiconductor field-effect transistors to selectively create anion vacancies at the metal contact regions. Due to lowering the metal contact resistance, improvements in the device performance metrics such as a 20× improvement in ON current and a nearly ideal subthreshold swing value of 66 mV/dec are observed. This work demonstrates that defect engineering at the contact regions can be utilized as a reliable scheme to realize high-performance electronic and optoelectronic TMDC devices.

KEYWORDS: transition metal dichalcogenides, defect engineering, air stable doping, WSe2 vacancy formation
foreign atom (impurity) in the crystal lattice is typically used to increase the free electron or hole concentration. In compound semiconductors, another doping mechanism can be induced by formation of anion or cation vacancies. Anion vacancies act as donor sites and result in n-doping, whereas cation vacancies act as acceptor sites and result in p-doping.\textsuperscript{20,21} Similarly, recent studies examining defects in MoS\textsubscript{2} flakes have reported that sulfur-deficient and sulfur-rich regions on the surface are responsible for n-type or p-type doping, respectively.\textsuperscript{22,23}

In this study, we investigate the use of a mild H\textsubscript{2} plasma treatment to engineer defects in the WSe\textsubscript{2} lattice, as depicted in Figure 1. The effects of H\textsubscript{2} plasma on the material properties of WSe\textsubscript{2} crystals and flakes are investigated extensively with X-ray photoelectron spectroscopy, Raman spectroscopy, photoluminescence spectroscopy, and Kelvin probe force microscopy. The results point to the formation of Se vacancies. Similar results are obtained employing a He plasma, suggesting that the formation of vacancies is not due to a chemical reaction such as protonation. We then demonstrate WSe\textsubscript{2} n-type field-effect transistors (FETs) with plasma-treated contact regions that exhibit contact resistance significantly lower than that of devices made without plasma treatment of the contacts. This paper shows that a mild plasma treatment at the contact regions can yield self-aligned and air-stable doping via generation of anion vacancies.

**RESULTS AND DISCUSSION**

X-ray photoelectron spectroscopy (XPS) was used to investigate the effect of H\textsubscript{2} plasma on the material properties and chemical composition of the WSe\textsubscript{2} lattice. WSe\textsubscript{2} crystals (purchased from HQ Graphene) were exposed to an inductively coupled, downstream hydrogen plasma (13.56 MHz, at 200 mTorr) and were transferred through a gate valve to the XPS chamber. The \textit{in situ} XPS analysis was performed with an Omicron Dar400 achromatic Mg K\textalpha\ X-ray source and an Omicron EA 125 hemispherical analyzer operated at constant 50 eV pass energy. Figure 2a,b shows the Se 3d and W 4f peaks, respectively, prior to exposure and after 3, 6, and 12 s of exposure to H\textsubscript{2} plasma. With increasing exposure times, the binding energies increased. The upshift by 0.5 eV after 12 s of treatment indicated a Fermi level shift toward the conduction band edge, which can be attributed to n-doping. This core-level shift toward higher binding energy was also consistent with previous studies of n-doped WSe\textsubscript{2}.\textsuperscript{3} Figure 2c shows the ratio of the areas under the Se 3d and W 4f peaks. The areas were quantified after Shirley background subtraction and corrected with sensitivity factors and attenuation according to the Beer–Lambert law (see the Methods section). The Se/W ratio decreased with H\textsubscript{2} plasma time, indicating the loss of selenium atoms with increased exposure to hydrogen plasma.
Article

This shows that the observed Fermi level shift toward the conduction band was induced by creating Se vacancies ($V_{\text{Se}}^+$) in the WSe$_2$ lattice.

The XPS valence band spectra were used to evaluate the changes in the electron doping concentration as a function of H$_2$ plasma treatment time. Figure 2d shows the valence band spectra of WSe$_2$ with increasing H$_2$ plasma time, which were used to extract $E_F - E_C$, where $E_F$ and $E_C$ are the Fermi level and valence band edge energies, respectively. Linear extrapolation of the valence band edge tail was used to determine $E_F - E_C$. As seen in Figure 2e, $E_F - E_C$ increased from 0.73 eV to plateau around 1.19 eV. By assuming a band gap value of 1.2 eV for multilayer WSe$_2$, the conduction band edge ($E_C$) was calculated with respect to the Fermi level. At the longest H$_2$ plasma treatment time of 12 s, the Fermi level was calculated to be 10 meV below $E_C$. This corresponded to $E_F - E_C < 3kT$ at room temperature and, thus, to a degenerate n-doping level. This analysis shows that this doping scheme can be used to controllably dope WSe$_2$. After the position of the Fermi level relative to the conduction band edge was determined, the electron doping concentration ($N_D$) was calculated. The 3-D effective density of states ($N_C$) for electrons was calculated using

$$N_C = \frac{2\pi m_e kT}{h^2} \left[ \frac{2m_e kT}{\pi} \right]^{3/2}$$

(1)

where $m_e$ is the effective mass for electrons, $T$ is the temperature, $k$ is the Boltzmann constant, and $h$ is Planck's constant. At room temperature, by assuming $m_e$ to be 0.53$m_0$, $N_C$ was calculated to be $8.8 \times 10^{19}$ cm$^{-3}$. Using the $N_C$ and $E_C - E_F$ extracted via XPS valence band analysis, $N_D$ was calculated from

$$N_D = N_C \exp \left( \frac{E_F - E_C}{kT} \right)$$

(2)

using the Boltzmann approximation and assuming non-degenerate doping for pristine, 3, and 6 s of H$_2$ plasma treatment. At the longest H$_2$ plasma treatment time, for 12 s, because of degenerate doping, the Boltzmann approximation cannot be used and eq 2 is not valid to calculate $N_D$. Therefore, if we assumed the boundary condition for degenerate doping ($E_F - E_C = 3kT$), $N_D$ was calculated to be $4 \times 10^{17}$ cm$^{-3}$ at room temperature. Given that 12 s of doping yields degenerate doping ($E_F - E_C < 3kT$), $N_D$ was concluded to be greater than $4 \times 10^{17}$ cm$^{-3}$ at room temperature. The results of the analysis are presented in Figure 2f, showing that $N_D$ increases monotonically with H$_2$ plasma treatment time.

To verify that the crystal structure of the WSe$_2$ remains intact after the mild H$_2$ plasma treatment, Raman spectroscopy was performed on the same flakes before and after H$_2$ plasma treatment. The samples were excited by the 514.5 nm line of an Ar ion laser (20 $\mu$W incident power), and the spectra were measured with a triple spectrometer configured in subtractive mode with a 2400 g/mm grating in the final stage. Raman spectra of one-, two-, and five-layer thick WSe$_2$ flakes before and after H$_2$ plasma treatment are presented in Figure 3a. The samples show no significant change in the Raman peak positions or line widths, indicating that the lattices of WSe$_2$ flakes remained intact after H$_2$ plasma treatment while point defects were created. A more sensitive probe of the defects generated in the material was provided by photoluminescence (PL) measurements on direct band gap monolayer WSe$_2$ both at room temperature and at 77 K. These measurements were taken using the 514.5 nm line of an Ar ion laser for excitation, and the PL spectra were dispersed by a 150 groove/mm grating in a $f = 340$ mm spectrometer after the excitation...
signal with a 550 nm long-pass filter was removed. Figure 3b shows PL spectra of the same monolayer before and after H2 plasma treatment, measured at an incident power of 5 μW at room temperature. A significant full width at half-maximum broadening of the PL spectra from 62 to 98 meV was observed after H2 plasma treatment and was expected for highly defective material due to the presence of a sub-band gap and trap states.30 Finally, to understand the nature of the defects that are generated by H2 plasma, PL measurements were performed at 77 K in a flow microcryostat, as shown in Figure 3c. Measurements taken on pristine samples indicated that there was a deep level trap, manifested as a bound exciton (XB) at 1.37 eV, present in the as-exfoliated monolayers. However, after H2 plasma treatment, the clear emergence of a second bound exciton peak, X0, at 1.52 eV was observed. It can be confirmed by pump-power-dependent measurements that both peaks originated from defects, as shown in Figure 3d. The bound exciton peak, XB, saturated at high illumination intensities, whereas the free exciton, X0, showed linear dependence, which is consistent with previous reports.28

Kelvin probe force microscopy (KPFM) has been shown to be a useful characterization tool to determine the band alignments in the TMDC flakes.31 Here, KPFM is used to demonstrate lithographically patternable doping within the same WSe2 crystal. Figure 4a shows the schematic of the WSe2 flake patterned using poly(methyl methacrylate) (PMMA), allowing local regions to be exposed to H2 plasma, resulting in defect-induced doping, while leaving the PMMA-coated region intrinsic (undoped). In order to realize the structure shown in Figure 4a, e-beam lithography was used to define a mask with PMMA on the channel region. After the exposed regions were developed, PMMA remained protecting the region underneath from the H2 plasma treatment. A mild H2 plasma treatment was then performed, only affecting the unmasked regions. Finally the PMMA was stripped in acetone, and KPFM was performed. Figure 4b shows the atomic force microscopy (AFM) image of the WSe2 flake after H2 plasma treatment and after stripping the resist in acetone. It is important to note that after H2 plasma treatment, the flake still had a uniform thickness, as can be seen in the corresponding line scan. Figure 4c shows the KPFM image of the WSe2 flake with H2 plasma treatment done on the unmasked regions. KPFM measured the contact potential difference (CPD) between the AFM tip and the sample given by

\[ \text{CPD} = \frac{(\Phi_{\text{tip}} - \Phi_{\text{sample}})}{-e} \]  

where \( \Phi_{\text{tip}} \) is the work function of the tip, \( \Phi_{\text{sample}} \) is the work function of the sample, and \( e \) is the electron charge.32,33 When the change in the CPD between the masked and the exposed regions was measured, the work function difference was extracted and the band alignment was determined. When KPFM was performed on the WSe2 flake, the masked region showed a CPD value lower than that of the exposed regions by 200 mV; in other words, the change in the CPD along the line scan yields

\[ \Delta \text{CPD} = \text{CPD}_{\text{exposed}} - \text{CPD}_{\text{masked}} = \frac{(\Phi_{\text{masked}} - \Phi_{\text{exposed}})}{-e} \]

\[ = 200 \text{ mV} \]

This corresponds to a Fermi level shift of the H2-plasma-treated regions by 200 meV toward the conduction band, relative to the masked region. Using the difference in the Fermi levels, the electron doping concentration ratio between the exposed and the masked region was calculated using

\[ N_{D,\text{exposed}} = \exp \left( \frac{E_{F,\text{exposed}} - E_{F,\text{masked}}}{kT} \right) \]

\[ N_{D,\text{masked}} \]

yielding a value of ~2200 at room temperature.

In order to investigate the effect of the H2 plasma treatment on the electrical performance of the WSe2 FETs, two transistor structures were fabricated on the same WSe2 flake (six layers...
Figure 5. (a) Optical image of the control and H2-plasma-treated WSe2 n-FETs fabricated on the same flake. (b) Transfer characteristics of the control (no plasma treatment) and H2-plasma-treated WSe2 n-FETs at VDS = 1 V and 1 × 10−5 Torr. (c) Subthreshold swing vs. IDSS of the control and H2-plasma-treated WSe2 n-FETs. (d) Total resistance vs. VGS used to extract contact resistance values for the control device and device with H2-plasma-treated contacts.

One was a control device where the metal contacts were deposited on intrinsic WSe2, and the other one was a device where H2 plasma treatment was performed immediately prior to metal contact deposition, as seen in Figure S1a. Devices were fabricated on WSe2 exfoliated on heavily doped silicon wafers with 50 nm thick SiO2, which was utilized as a global back gate. First, the control device was fabricated by defining the contact regions with e-beam lithography followed by metal (30 nm Ni) deposition and liftoff using acetone. Then a second e-beam lithography step was carried out to make the device with the H2-plasma-treated contacts. After the contact regions in the second e-beam lithography step were defined and the exposed regions were developed, the contact regions were treated with a mild H2 plasma as explained in the Methods section. After the H2 plasma treatment, the fabrication was completed by metal (30 nm Ni) evaporation and liftoff in acetone. The control and the H2-plasma-treated devices were made on the same WSe2 flake and have the same channel length (L = 1 μm) and the contact metal width such that the electrical performance can be compared directly. Figure S1b shows the comparison of the transfer characteristics of the two devices in ambient air and at room temperature. The ON current for the n-branch improves by 2 orders of magnitude for the H2-plasma-treated device compared to the control device. For the large negative gate bias, the ambipolar p-type conduction observed in the control device was suppressed by 2 orders of magnitude in the device with the H2-plasma-treated contacts. Reducing the ambipolar p-type conduction was advantageous to decrease the power consumption in the OFF state for the n-FETs. Figure S1c,d shows the output characteristics of the control and the H2-plasma-treated devices, respectively. The control device has a significant nonlinearity at low source–drain voltage (VDS), which is a strong indication that electron injection to the channel was dominated by Schottky contacts. In contrast, the output characteristics of the H2-plasma-treated device show linear IDSS versus VDS dependence, indicating that the Schottky effects were reduced. Figure S2 shows the transfer characteristics of two WSe2 n-FETs fabricated on the same flake, one without He plasma treatment and one with He plasma treatment done on the contact regions. The ON current in the He-plasma-treated device improves by 3 orders of magnitude similar to the results seen for the devices with H2-plasma-treated contact regions. The fact that He plasma also shows n-type doping in the electrical characterization results indicated that the mechanism of doping was not due to a chemical reaction of H2 plasma with the WSe2 lattice but rather due to the formation of Se vacancies in the WSe2 lattice as discussed previously.

The improvement in the electrical performance of the WSe2 n-FETs with H2-plasma-treated contacts can be attributed to several effects. At the metal–semiconductor interface, electrons can be injected from the metal to the semiconductor either by thermionic emission over the Schottky barrier or by tunneling through the Schottky barrier width. The Schottky barrier width, also called depletion width, Wdep, at the metal—semiconductor interface depends on the doping concentration (N0) of the semiconductor and, based on the depletion approximation, is proportional to \( \sqrt{N_0} \). Therefore, as the doping concentration in the contact regions of the WSe2 flake was increased by H2 plasma treatment, Wdep decreased. As a result, the probability of electron injection into the semiconductor by tunneling through the Schottky barrier increased, reducing the contact resistance.15,16 In addition, the ideal TMDC surfaces possess no dangling bonds, which prevents the formation of strong covalent bonding at the metal–TMDC interfaces. As opposed to a strongly bonded interface, a van der Waals gap exists between the metal–TMDC interface. This inherent physical gap acts as an additional tunneling barrier to the depletion width discussed above.13 However, the defects and dangling bonds created by the loss of Se atoms at the WSe2 surface by...
H₂ plasma may improve bonding between the metal and the TMDC surface, removing the intrinsic van der Waals gap and, thus, reducing the tunneling barrier thickness.

To further investigate the effect of H₂-plasma-treated contacts on the device performance parameters of WSe₂ n-FETs, few-layer WSe₂ flakes were transferred on local back gates with high-k dielectric ZrO₂ (12 nm thick). Using the fabrication flow described previously, transistors with no treatment (as control) and H₂-plasma-treated contacts were fabricated on the same WSe₂ flake, as shown in Figure 5a. The devices were measured in high vacuum (~1 × 10⁻⁵ Torr) in order to reduce the effects of hysteresis. Figure 5b shows the comparison of the transfer curves of the two transistors fabricated on four-layer thick WSe₂. The ON current of the H₂-plasma-treated WSe₂ n-FET was improved by 20x. At large negative gate bias (VGS), the control WSe₂ n-FET showed p-type conduction because the Fermi level of the control device at the contact regions is near midgap, allowing for the injection of both holes and electrons. On the other hand, in the WSe₂ n-FET with H₂-plasma-treated contacts, the ambipolar p-type conduction was decreased by 2 orders of magnitude at large negative VGS due to the fact that the Fermi level was closer to the conduction band edge, increasing the barrier for hole injection.

Another significant improvement observed in the H₂-plasma-treated device was the subthreshold swing (SS), defined as the gate voltage, VGS, that needs to be applied to raise the source–drain current (IDS) by 1 order of magnitude, SS = \[ \frac{d\log(\text{IDS})}{d(V_{GS})} \]. The subthreshold swing is a critical parameter to evaluate the power consumption of the transistors because it determines the operating voltages required to run the transistors with an acceptable ON/OFF ratio. In MOSFETs, the SS value is fundamentally limited to ~60 mV/dec at room temperature, given by \[ \frac{kT}{q} \ln(10) \]. As shown in Figure 5c, the control device showed a SS value of ~250 mV/dec, whereas the device with H₂-plasma-treated contacts yielded 66 mV/dec. The nearly ideal SS value at room temperature was attributed to the improved contacts enabled by H₂ plasma treatment. Figure 5c shows that the near-ideal SS value of 66 mV/dec persisted for nearly 3 orders of magnitude in the subthreshold regime of the WSe₂ n-FET. Contact resistances (Rc) for the control and the H₂-plasma-treated devices were calculated by fitting the total resistance of the channel and the contacts to an exponentially decaying fitting function, as shown in Figure 5d. The asymptote to the y-axis at infinite VGS is defined as 2Rc because the channel resistance becomes negligible compared to the contact resistances. The contact resistance for the H₂-plasma-treated device dropped by more than 2 orders of magnitude and was found to be 8 kΩ·μm. This Rc value is on the same order of magnitude as WSe₂ FETs fabricated using NO₂ and K doping schemes. However, unlike the previous methods, H₂ plasma treatment is air-stable and can be readily integrated into a fabrication process flow. ³⁴ The field-effect mobility for electrons (μFE) of the H₂-plasma-treated WSe₂ n-FETs at a low VGS of 50 mV was calculated using μFE = \[ \frac{g_m \times l}{W_{\text{OX}} C_{\text{OX}}} \], where L is the channel length, W is the channel width, C_{OX} is the capacitance per unit area of the dielectric layer, and g_m is the transconductance, g_m = \[ \frac{\partial(\text{IDS})}{\partial(V_{\text{GS}})} \]. Approximately 40 WSe₂ n-FETs were fabricated using the H₂ plasma treatment, and the field-effect mobility values were found to range between 30 and 60 cm²/V·s. Figure 6a shows the transfer curves of WSe₂ n-FETs with thicknesses ranging from one layer to 10 layers. Control devices and devices with H₂-plasma-treated contacts were fabricated on the same WSe₂ flakes as described earlier, using local back gates with high-k dielectric ZrO₂. It is important to note that the mild H₂ plasma treatment was able to reduce the contact resistance in monolayer and bilayer devices, which are typically significantly higher than those observed in thicker flakes. The monolayer device showed ON current improvement of over 2 orders of magnitude and an SS reduction from 270 to 90 mV/dec. Figure 6b shows the contact resistances of the devices presented in Figure 6a as a function of layer thickness. The most dramatic Rc reduction occurs in the monolayer device. Devices with thicker layers showed Rc reduction between 5- and 10-fold. For a thick device with 10 layers, Rc as low as 4.4 kΩ·μm was achieved.

CONCLUSION

In conclusion, a defect engineering study was carried out using a mild H₂ plasma treatment on WSe₂ flakes. Material characterization performed by XPS showed a binding energy shift to higher values and a decrease in Se/W ratio, indicative of n-doping caused by Se vacancies in the crystal. Low-temperature PL measurements provided additional evidence of defect-induced doping. KPFM measurements on the treated and untreated regions of the same flake showed a Fermi level shift toward the conduction band by 200 meV that corresponded to an electron doping concentration increase by 2200x due to H₂ plasma treatment. Finally, the H₂ plasma treatment method was optimized to treat only the contact regions of the WSe₂ n-FETs. Doping the contact regions provided significant improvements in the device metrics, such
as 20x improvement in the ON current and 2 orders of magnitude reduction in the ambipolar p-channel, effectively reducing the OFF current. Moreover, a nearly ideal SS value of 66 mV/dec was achieved via H₂-plasma-treated contacts. Moving forward, defect engineering at the TMDC contact regions, which has been explored for WSe₂ using plasma treatment, can be utilized as an air-stable and viable method to achieve high-performance electronic and optoelectronic devices, without introducing processing complexities.

METHODS

H₂ Plasma Treatment. H₂ plasma treatments were performed using a commercially available plasma system (The Plasma-Therm PK-12 RIE). The optimized plasma conditions were found to be 140 mTorr at a 100 sccm H₂ flow rate with a power of 5 W for 5 s. This treatment was used for the fabrication of all devices shown in Figures S1 and 3–6.

XPS Characterization. For a homogeneous sample, elemental ratios could be calculated by a simple relation between peak areas:

\[
\frac{n_i}{n_2} = \frac{I_i}{I_2} = \frac{\frac{1}{S_i}}{\frac{1}{S_2}}
\]

where \(n_i\) is the number of atoms of element \(i\), \(I_i\) is the peak intensity (i.e., peak area) after background subtraction, and \(S_i\) is the angle-adjusted atomic sensitivity factor. For multilayer systems, overlayer thickness led to exponential attenuation of the photoelectron signal according to the Beer–Lambert law, \(I_d = I_o e^{-d/\lambda}\), where \(d\) is the overlayer depth and \(\lambda\) is the mean free path of an electron through the material.

In the case of multiple layers of stacked Se–W–Se, the final elemental ratio of Se/W was given by

\[
\frac{n_{Se}}{n_W} = \frac{I_{Se}}{I_W} = \frac{\frac{1}{S_{Se}}(1-e^{-d_{Se}/\lambda_{Se}})}{\frac{1}{S_W}(1-e^{-d_{W}/\lambda_{W}})(e^{-d_{Se}/\lambda_{Se}})/(e^{-d_{W}/\lambda_{W}})} \frac{1}{S_{Se}}(1-e^{-d_{Se}/\lambda_{Se}})
\]

The peak areas for Se and W were quantified using regions of interest of 5.25 to 8.25 eV and 30.2 to 40.2 eV, respectively. Thicknesses \(d\) were calculated based on material parameters, and \(\lambda\) values were taken from predictive models from the NIST electron inelastic-mean-free-path database.

The final ratios were sensitive to the background subtraction parameters, particularly the region of interest in which background subtraction was carried out. Alternative choices of a constant Se region width (≥0.5 eV) can translate into a uniform shift of the curve in Figure 2c of up to 5% but does not affect the relative ratio decrease as a function of plasma exposure time. Different sources for the mean free path values can also introduce systematic error, but this similarly has a negligible effect on the overall trend.

KPFM Characterization. PeakForce KPFM mode using PFQNE-AL probe on Dimension Icon AFM (Bruker Nano, Santa Barbara, CA) was used to obtain the KPFM data. Lift height of 25 nm and ac bias voltage of 4 V were used during the measurement.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b02521.

Figures S1 and S2 (PDF)

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Notes

The authors declare no competing financial interest.

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