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# Air-Stable n-Doping of WSe<sub>2</sub> by Anion Vacancy Formation with Mild Plasma Treatment

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**(5)** Supporting Information

**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  $H_2$ ) as an approach to reduce the contact resistance to WSe<sub>2</sub>. 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  $WSe_2$  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, WSe<sub>2</sub>, vacancy formation

ransition metal dichalcogenides (TMDCs) are a subset of two-dimensional layered materials that can be scaled down to a monolayer thickness. Since the interlayer bonding is based on van der Waals forces, TMDCs ideally have no surface dangling bonds, thus enabling low interface trap density at the semiconductor/dielectric or at the heterostructure interface. Therefore, TMDCs offer the ultimate level of scalability (6.5 Å) for semiconductor thickness, while preserving the integrity of the semiconductor in terms of electronic and material properties.<sup>1,2</sup> In addition to offering extreme thickness scalability, this material family, specifically  $WSe_2$ , possesses respectable mobility values for electrons<sup>3</sup> (110  $cm^2/V \cdot s$  and holes<sup>2</sup> (240  $cm^2/V \cdot s$ ). High effective mass<sup>4,5</sup> and the low dielectric constant<sup>6</sup> values in these materials as compared those in silicon and III-V systems also promise to reduce the direct source-drain tunneling and reduce the characteristic lengths<sup>7</sup> for aggressively scaled metal-oxidesemiconductor field-effect transistors. In addition, optical properties of monolayer TMDCs are intriguing given that they have direct band gaps.<sup>8,9</sup> While optoelectronic devices such as light-emitting diodes (LEDs) and lasers have been realized with monolayer TMDC semiconductors,<sup>10-12</sup> these proof-of-concept devices are realized through optical pumping<sup>10</sup> or their performances are limited due to large contact

resistances.<sup>11–13</sup> Therefore, developing optimized contacts to probe the intrinsic properties of the TMDC semiconductors and their performance limits is a fundamental problem in the study of TMDCs.<sup>13</sup> To overcome this challenge, many doping schemes and work function engineering studies have been performed.<sup>2,3,14–18</sup>

Defects in a semiconductor crystal lattice play a profound role in determining both the electronic and optical properties of the material. Therefore, defect engineering to either passivate or intentionally generate defects within the crystal can be utilized as a powerful tool to obtain the desired properties in a semiconductor. For the active regions of electronic and optoelectronic devices such as LEDs, laser diodes, photovoltaic cells, and transistors where electron—hole pair recombination/ generation or electron transport occurs, defect-free materials are desired. However, in all of the devices listed above, in order to have Ohmic contacts, heavy doping underneath the metal contacts induced by impurities or defects in the lattice is necessary.<sup>19</sup> In the conventional semiconductors, such as in silicon and III–V groups, substitutional doping by inserting a

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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.<sup>20,21</sup> Similarly, recent studies examining defects in  $MoS_2$  flakes have reported that sulfur-deficient and sulfur-rich regions on the surface are responsible for n-type or p-type doping, respectively.<sup>22,23</sup>

In this study, we investigate the use of a mild  $H_2$  plasma treatment to engineer defects in the WSe<sub>2</sub> lattice, as depicted in Figure 1. The effects of  $H_2$  plasma on the material properties of



Figure 1. (a) Schematic of an as-exfoliated WSe<sub>2</sub> flake. (b) Schematic of the WSe<sub>2</sub> flake after the H<sub>2</sub> plasma treatment, illustrating the creation of  $V_{Se}^{\bullet}$ .

WSe<sub>2</sub> 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  $WSe_2$  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<sub>2</sub> plasma on the material properties and chemical composition of the WSe2 lattice. WSe2 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 in situ XPS analysis was performed with an Omicron Dar400 achromatic Mg K $\alpha$  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<sub>2</sub> 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 ndoping. This core-level shift toward higher binding energy was also consistent with previous studies of n-doped WSe<sub>2</sub>.<sup>3</sup> 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<sub>2</sub> plasma time, indicating the loss of selenium atoms with increased exposure to hydrogen plasma.



Figure 2. (a) XPS spectra of core-level Se 3d binding energy peak with increasing H<sub>2</sub> plasma treatment time. (b) XPS spectra of core-level W  $4f_{5/2}$  and  $4f_{7/2}$  binding energy peak with increasing H<sub>2</sub> plasma treatment time. (c) Se/W ratio vs H<sub>2</sub> plasma treatment time extracted by calculating the areas under the peaks in (a,b). (d) Normalized valence band spectra with increasing H<sub>2</sub> plasma treatment time. (e)  $E_F - E_V$  values extracted by using (d). (f) Electron doping concentration vs increasing H<sub>2</sub> plasma treatment time calculated by using  $E_C - E_F$  extracted by the valence band spectra.



Figure 3. (a) Raman spectra measured before and after  $H_2$  plasma on the same WSe<sub>2</sub> flakes of monolayer, bilayer, and five-layer thickness. (b) PL spectra measured on the same WSe<sub>2</sub> monolayer flake before and after  $H_2$  plasma treatment at room temperature. (c) PL spectra performed on the same monolayer WSe<sub>2</sub> flake before and after  $H_2$  plasma treatment at 77 K. (d) Pump-power dependence of the free exciton and bound exciton luminescence for the WSe<sub>2</sub> monolayer flake measured at 77 K.

This shows that the observed Fermi level shift toward the conduction band was induced by creating Se vacancies  $(V_{Se}^{\bullet \bullet})$  in the WSe<sub>2</sub> lattice.

The XPS valence band spectra were used to evaluate the changes in the electron doping concentration as a function of H<sub>2</sub> plasma treatment time. Figure 2d shows the valence band spectra of WSe<sub>2</sub> with increasing H<sub>2</sub> plasma time, which were used to extract  $E_{\rm F} - E_{\rm V}$ , where  $E_{\rm F}$  and  $E_{\rm V}$  are the Fermi level and valence band edge energies, respectively. Linear extrapolation of the valence band edge tail was used to determine  $E_{\rm F}$  $-E_{\rm V}$ . As seen in Figure 2e,  $E_{\rm F} - E_{\rm V}$  increased from 0.73 eV to plateau around 1.19 eV. By assuming a band gap value of 1.2 eV for multilayer WSe<sub>2</sub>,<sup>2,24,25</sup> the conduction band edge ( $E_C$ ) was calculated with respect to the Fermi level. At the longest H<sub>2</sub> plasma treatment time of 12 s, the Fermi level was calculated to be 10 meV below  $E_{\rm C}$ . This corresponded to  $E_{\rm C} - E_{\rm F} < 3kT$  at room temperature and, thus, to a degenerate n-doping level. This analysis shows that this doping scheme can be used to controllably dope WSe2. After the position of the Fermi level relative to the conduction band edge was determinined, the electron doping concentration  $(N_{\rm D})$  was calculated. The 3-D effective density of states  $(N_{\rm C})$  for electrons was calculated using

$$N_{\rm C} = 2x \left[ \frac{2\pi m_n kT}{h^2} \right]^{3/2} \tag{1}$$

where  $m_n$  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  $m_n$  to be  $0.53m_0^{4,26} N_{\rm C}$  was calculated to be  $8.8 \times 10^{18}$  cm<sup>-3</sup>. Using the  $N_{\rm C}$  and  $E_{\rm C} - E_{\rm F}$  extracted *via* XPS valence band analysis,  $N_{\rm D}$  was calculated from

$$N_{\rm D} = N_{\rm C} \exp \frac{(E_{\rm F} - E_{\rm C})}{kT}$$
(2)

using the Boltzmann approximation and assuming nondegenerate doping for pristine, 3, and 6 s of H<sub>2</sub> plasma treatment. At the longest H<sub>2</sub> 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<sub>D</sub>. Therefore, if we assumed the boundary condition for degenerate doping  $(E_{\rm C} - E_{\rm F} = 3kT)$ , N<sub>D</sub> was calculated to be  $4 \times 10^{17}$  cm<sup>-3</sup> at room temperature. Given that 12 s of doping yields degenerate doping  $(E_{\rm C} - E_{\rm F} < 3kT)$ , N<sub>D</sub> was concluded to be greater than  $4 \times 10^{17}$  cm<sup>-3</sup> at room temperature. The results of the analysis are presented in Figure 2f, showing that N<sub>D</sub> increases monotonically with H<sub>2</sub> plasma treatment time.

To verify that the crystal structure of the WSe<sub>2</sub> remains intact after the mild H<sub>2</sub> plasma treatment, Raman spectroscopy was performed on the same flakes before and after H<sub>2</sub> 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<sub>2</sub> flakes before and after H<sub>2</sub> plasma treatment are presented in Figure 3a.<sup>27</sup> The samples show no significant change in the Raman peak positions or line widths, indicating that the lattices of WSe<sub>2</sub> flakes remained intact after H<sub>2</sub> 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.<sup>28,29</sup> 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



Figure 4. (a) Cross-sectional schematic of the WSe<sub>2</sub> flake with  $V_{se}^{se}$  on the doped (exposed) regions and pristine (masked) region by using PMMA as the mask. (b) AFM image of the WSe<sub>2</sub> flake after H<sub>2</sub> plasma treatment. (c) KPFM image showing the doped and undoped regions of the same WSe<sub>2</sub> flake. Line scan along the exposed-masked-exposed line shows a CPD of 200 mV.

signal with a 550 nm long-pass filter was removed. Figure 3b shows PL spectra of the same monolayer before and after H<sub>2</sub> plasma treatment, measured at an incident power of 5  $\mu$ W at room temperature. A significant full width at half-maximum broadening of the PL spectra from 62 to 98 meV was observed after H<sub>2</sub> plasma treatment and was expected for highly defective material due to the presence of a sub-band gap and trap states.<sup>30</sup> Finally, to understand the nature of the defects that are generated by H<sub>2</sub> 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  $(X_B)$  at 1.37 eV, present in the as-exfoliated monolayers. However, after  $H_2$  plasma treatment, the clear emergence of a second bound exciton peak, X<sub>0</sub>, 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, X<sub>B</sub>, saturated at high illumination intensities, whereas the free exciton, X<sub>0</sub>, showed linear dependence, which is consistent with previous reports.<sup>28</sup>

Kelvin probe force microscopy (KPFM) has been shown to be a useful characterization tool to determine the band alignments in the TMDC flakes.<sup>31</sup> Here, KPFM is used to demonstrate lithographically patternable doping within the same WSe<sub>2</sub> crystal. Figure 4a shows the schematic of the WSe<sub>2</sub> flake patterned using poly(methyl methacrylate) (PMMA), allowing local regions to be exposed to H<sub>2</sub> 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 H<sub>2</sub> plasma treatment. A mild H<sub>2</sub> 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 WSe<sub>2</sub> flake after  $H_2$  plasma treatment and after stripping the

resist in acetone. It is important to note that after  $H_2$  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 WSe<sub>2</sub> flake with  $H_2$  plasma treatment done on the unmasked regions. KPFM measured the contact potential difference (CPD) between the AFM tip and the sample given by

$$CPD = \frac{(\Phi_{tip} - \Phi_{sample})}{-e}$$
(3)

where  $\Phi_{tip}$  is the work function of the tip,  $\Phi_{sample}$  is the work function of the sample, and *e* is the electron charge.<sup>32,33</sup> 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 WSe<sub>2</sub> 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

$$\Delta CPD = CPD_{exposed} - CPD_{masked} = \frac{(\Phi_{masked} - \Phi_{exposed})}{-e}$$
$$= 200 \text{ mV}$$

This corresponds to a Fermi level shift of the  $H_2$ -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

$$\frac{N_{\rm D, exposed}}{N_{\rm D, masked}} = \exp \frac{(E_{\rm F, exposed} - E_{\rm F, masked})}{kT}$$
(4)

yielding a value of ~2200 at room temperature.

In order to investigate the effect of the  $H_2$  plasma treatment on the electrical performance of the WSe<sub>2</sub> FETs, two transistor structures were fabricated on the same WSe<sub>2</sub> flake (six layers



Figure 5. (a) Optical image of the control and H<sub>2</sub>-plasma-treated WSe<sub>2</sub> n-FETs fabricated on the same flake. (b) Transfer characteristics of the control (no plasma treatment) and H<sub>2</sub>-plasma-treated WSe<sub>2</sub> n-FETs at  $V_{DS} = 1$  V and  $1 \times 10^{-5}$  Torr. (c) Subthreshold swing vs  $I_{DS}$  of the control and H<sub>2</sub>-plasma-treated WSe<sub>2</sub> n-FETs. (d) Total resistance vs  $V_{GS}$  used to extract contact resistance values for the control device and device with H<sub>2</sub>-plasma-treated contacts.

thick). One was a control device where the metal contacts were deposited on intrinsic WSe<sub>2</sub>, and the other one was a device where H<sub>2</sub> plasma treatment was performed immediately prior to metal contact deposition, as seen in Figure S1a. Devices were fabricated on WSe<sub>2</sub> exfoliated on heavily doped silicon wafers with 50 nm thick SiO<sub>2</sub>, 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 H<sub>2</sub> plasma as explained in the Methods section. After the  $H_2$  plasma treatment, the fabrication was completed by metal (30 nm Ni) evaporation and liftoff in acetone. The control and the H<sub>2</sub>-plasma-treated devices were made on the same WSe<sub>2</sub> flake and have the same channel length  $(L = 1 \ \mu m)$  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 H<sub>2</sub>-plasma-treated device as 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 H<sub>2</sub>-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 H<sub>2</sub>-plasmatreated devices, respectively. The control device has a significant nonlinearity at low source-drain voltage  $(V_{DS})$ , 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  $I_{\rm DS}$  versus  $V_{\rm DS}$  dependence, indicating that the Schottky effects were reduced. Figure S2 shows the transfer characteristics of two WSe<sub>2</sub> 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 H<sub>2</sub>-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 H<sub>2</sub> plasma with the WSe<sub>2</sub> lattice but rather due to the formation of Se vacancies in the WSe<sub>2</sub> lattice as discussed previously.

The improvement in the electrical performance of the WSe<sub>2</sub> n-FETs with H<sub>2</sub>-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,  $W_{dep}$ , at the metal-semiconductor interface depends on the doping concentration  $(N_{\rm D})$  of the semiconductor and, based on the depletion approximation, is proportional to  $\sqrt{N_{\rm D}^{-1}}$ . Therefore, as the doping concentration in the contact regions of the WSe<sub>2</sub> flake was increased by H<sub>2</sub> plasma treatment,  $W_{dep}$  decreased. As a result, the probability of electron injection into the semiconductor by tunneling through the Schottky barrier increased, reducing the contact resistance.<sup>2,3,14</sup> 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.<sup>13</sup> However, the defects and dangling bonds created by the loss of Se atoms at the WSe<sub>2</sub> surface by

 $H_2$  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 WSe<sub>2</sub> flakes were transferred on local back gates with high-k dielectric  $ZrO_2$  (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 WSe<sub>2</sub> flake, as shown in Figure 5a. The devices were measured in high vacuum ( $\sim 1 \times 10^{-5}$  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 H2plasma-treated WSe2 n-FET was improved by 20×. At large negative gate bias  $(V_{GS})$ , the control WSe<sub>2</sub> n-FET showed ptype 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 WSe<sub>2</sub> n-FET with H<sub>2</sub>-plasma-treated contacts, the ambipolar p-type conduction was decreased by 2 orders of magnitude at large negative  $V_{GS}$  due to the fact that the Fermi level was closer to the conduction band edge, increasing the barrier for hole injection.<sup>18</sup> Another significant improvement observed in the H<sub>2</sub>-plasma-treated device was the subthreshold swing (SS), defined as the gate voltage,  $V_{GS}$ , that needs to be applied to raise the source-drain current  $(I_{DS})$  by 1 order of magnitude,  $SS = \left[\frac{d(\log I_{DS})}{d(V_{GS})}\right]^{-1}$ . 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  $\left(\frac{kT}{q}\ln 10\right)$ . As shown in Figure 5c, the control device showed a SS value of  $\sim$ 250 mV/dec, whereas the device with H<sub>2</sub>-plasma-treated contacts yielded 66 mV/dec. The nearly ideal SS value at room temperature was attributed to the improved contacts enabled by H<sub>2</sub> 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 WSe<sub>2</sub> n-FET. Contact resistances  $(R_{\rm C})$  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  $V_{\rm GS}$  is defined as  $2R_{\rm C}$ because the channel resistance becomes negligible compared to the contact resistances. The contact resistance for the H<sub>2</sub>plasma-treated device dropped by more than 2 orders of magnitude and was found to be 8 k $\Omega \cdot \mu$ m. This  $R_{\rm C}$  value is on the same order of magnitude as WSe<sub>2</sub> FETs fabricated using NO2 and K doping schemes. However, unlike the previous methods,  $H_2$  plasma treatment is air-stable and can be readily integrated into a fabrication process flow.<sup>34</sup> The field-effect mobility for electrons ( $\mu_{\rm FE}$ ) of the H<sub>2</sub>-plasma-treated WSe<sub>2</sub> n-FETs at a low  $V_{\rm DS}$  of 50 mV was calculated using  $\mu_{\rm FE} = g_m \times \frac{L}{WV_{\rm DS}C_{\rm OX}}$ , where L is the channel length, W is the channel width, C<sub>OX</sub> is the capacitance per unit area of the dielectric layer, and  $g_{\rm m}$  is the transconductance,  $g_{\rm m} = \left[\frac{d(I_{\rm DS})}{d(V_{\rm CS})}\right]$ Approximately 40 WSe<sub>2</sub> n-FETs were fabricated using the H<sub>2</sub> plasma treatment, and the field-effect mobility values were

found to range between 30 and 60 cm<sup>2</sup>/V·s. Figure 6a shows the transfer curves of  $WSe_2$  n-FETs with thicknesses ranging



Figure 6. (a) Transfer curves of control devices (*i.e.*, without plasma treatment of the contacts prior to metallization) and devices with H<sub>2</sub>-plasma-treated contacts with different layer thickness measured at  $V_{\rm DS} = 50$  mV. (b) Dependence of  $R_{\rm C}$  on WSe<sub>2</sub> layer thickness for both the control and the H<sub>2</sub>-plasma-treated devices.

from one layer to 10 layers. Control devices and devices with H<sub>2</sub>-plasma-treated contacts were fabricated on the same WSe<sub>2</sub> flakes as described earlier, using local back gates with high-*k* dielectric ZrO<sub>2</sub>. It is important to note that the mild H<sub>2</sub> 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  $R_{\rm C}$  reduction occurs in the monolayer device. Devices with thicker layers showed  $R_{\rm C}$  reduction between 5- and 10-fold. For a thick device with 10 layers,  $R_{\rm C}$  as low as 4.4 k $\Omega$ · $\mu$ m was achieved.

#### CONCLUSION

In conclusion, a defect engineering study was carried out using a mild  $H_2$  plasma treatment on WSe<sub>2</sub> 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. Lowtemperature 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 2200× due to H<sub>2</sub> plasma treatment. Finally, the H<sub>2</sub> plasma treatment method was optimized to treat only the contact regions of the WSe<sub>2</sub> n-FETs. Doping the contact regions provided significant improvements in the device metrics, such as 20× improvement in the ON current and 2 orders of magnitude reduction in the ambipolar p-branch, effectively reducing the OFF current. Moreover, a nearly ideal SS value of 66 mV/dec was achieved *via* H<sub>2</sub>-plasma-treated contacts. Moving forward, defect engineering at the TMDC contact regions, which has been explored for WSe<sub>2</sub> 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**

**H**<sub>2</sub> **Plasma Treatment.** H<sub>2</sub> 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 H<sub>2</sub> 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:

$$\frac{n_1}{n_2} = \frac{\left(\frac{I_1}{S_1}\right)}{\left(\frac{I_2}{S_2}\right)}$$

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 angleadjusted atomic sensitivity factor. For multilayer systems, overlayer thickness led to exponential attenuation of the photoelectron signal according to the Beer–Lambert law,  $I_S = I_o e^{-d/\lambda}$ , 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

$$\frac{n_{Se}}{n_{W}} = \frac{\frac{I_{Se_{1}}}{S_{Se}(1 - e^{-d_{Se}/\lambda_{Se}})} + \frac{I_{Se_{2}}}{S_{Se}(1 - e^{-d_{Se}/\lambda_{Se}})(e^{-d_{W}/\lambda_{W}})}}{\frac{2I_{W}}{S_{W}(1 - e^{-d_{W}/\lambda_{W}})(e^{-d_{Se}/\lambda_{Se}})}}$$

The peak areas for Se and W were quantified using regions of interest of 52.5 to 58.25 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 ( $\pm 0.5$  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

#### **S** 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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