Atomically Controlled Tunable Doping in High-Performance WSe\textsubscript{2} Devices

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2D transitional metal dichalcogenide (TMD) field-effect transistors are promising candidates for future electronic applications, owing to their potential for ultimate device scaling. However, it is acknowledged that substantial contact resistance associated with the contact-TMD interface has impeded device performance to a large extent. It has been discovered that O\textsubscript{2} plasma treatment can convert WSe\textsubscript{2} into WO\textsubscript{3}\textsubscript{−}\textsubscript{x} and substantially improve contact resistances of p-type WSe\textsubscript{2} devices by strong doping induced thinner depletion width. In this paper, temperature dependence of this conversion is studied, demonstrating an oxidation process with a precise monolayer control at room temperature and multilayer conversion at elevated temperatures. Furthermore, lateral oxidation of WSe\textsubscript{2} underneath contact revealed by high-resolution scanning transmission electron microscope leads to potential unpinning of the metal Fermi level and Schottky barrier lowering, resulting in lower contact resistances. The p-doping effect is attributed to the high electron affinity of the WO\textsubscript{3}\textsubscript{−}\textsubscript{x} layer on top of the remaining WSe\textsubscript{2} channel, and the doping level is dependent on the WO\textsubscript{3}\textsubscript{−}\textsubscript{x} thickness that is controlled by the temperature. Comprehensive materials and electrical characterizations are presented, with a low contact resistance of ≈528 \( \Omega \) \( \mu \)m and record high on-state current of 320 \( \mu \)A \( \mu \)m\textsuperscript{−1} at −1 V bias being reported.

1. Introduction

2D transitional metal dichalcogenides (TMDs) have attracted wide attention, owing to their excellent material properties and potential applications in post-CMOS,\textsuperscript{[1–8]} neuromorphic computing,\textsuperscript{[9–11]} as well as flexible electronics.\textsuperscript{[12–15]} Studying semiconducting TMDs (e.g., MoS\textsubscript{2}, WSe\textsubscript{2}) as the channel material for field-effect transistors (FETs) is one of the most vital research areas, due to their superior transport properties and ultrathin body thickness for ultimate device scaling.\textsuperscript{[16,17]} However, how to make good contacts remains a big challenge for TMD FETs, while it is widely acknowledged that minimizing contact resistance \( (R_{\text{c}}) \) is essential to obtain high-performance devices and reveal intrinsic TMD properties.\textsuperscript{[18–22]}

In general, there are two strategies to optimize current injection at a metal/semiconductor (MS) interface. One method is to select a metal contact with the preferred work function for electron or hole injection, given no strong Fermi level pinning at the contact interface, which is typically not the case for TMDs.\textsuperscript{[23–25]} The other method is to dope the semiconductor degenerately to reduce the depletion width of the MS junction.\textsuperscript{[26–30]} We will show in our paper that by controlling the temperature at which a multilayer WSe\textsubscript{2} FET device is exposed to direct O\textsubscript{2} plasma, the number of top WSe\textsubscript{2} layers gets converted into WO\textsubscript{3}\textsubscript{−}\textsubscript{x} \( (0 < x < 1) \) can be precisely controlled, which in turn determines the p-type doping level in the device. Moreover, this conversion is found to extend into the contact area by tens of nanometers, which can possibly unpin the Fermi level of the metal contact and dope a small segment of WSe\textsubscript{2} underneath the contact, resulting in reduced contact resistance of the device. The use of controlled oxidation at the interface of scandium contact and WSe\textsubscript{2} has also been recently reported to produce an optimized Schottky junction that can be controlled to exhibit n- or p-type transport.\textsuperscript{[31]}

In our unique O\textsubscript{2} plasma treatment, the top few WSe\textsubscript{2} layers are converted into WO\textsubscript{3}\textsubscript{−}\textsubscript{x} that behaves as a p-type doping layer for the underlying WSe\textsubscript{2} due to its high electron affinity. Different from the previously reported self-limiting oxidation of only the topmost WSe\textsubscript{2} layer in a remote plasma environment,\textsuperscript{[32]} a direct O\textsubscript{2} plasma is employed in our process.
Interestingly, we found that the doping level can be tuned from nondegenerate to degenerate by increasing the treatment temperature which directly controls the number of WSe₂ layers that get converted into WO_{3−x}. We further demonstrate low contact resistance of 528 Ω µm and a record high hole current in a scaled WSe₂ FET, shedding light on a promising path in the quest for high-performance electronics. In addition, the achieved p-type doping on WSe₂ has excellent air stability, precise doping level control, and is an industry compatible process.

2. Results and Discussions

Two types of Schottky barrier (SB) device structures (two- or four-probe) were implemented, as shown schematically in Figure 1a,b. A scanning electron microscope (SEM) of one of our four-probe devices is shown in Figure 1c with dimension being labeled. The critical fabrication processes are described in the Experimental Section. High-resolution scanning transmission electron microscope (HR-STEM) image and electron energy loss spectroscopy (EELS) line scan across a multilayer WSe₂ flake underneath of a Ti/Pd contact are shown in Figure 1d. Band diagrams and working principles of SB devices are illustrated in the insets of Figure 1e. It is known that the Fermi level of metal contact is pinned close to the mid-gap of WSe₂. Therefore, band movements modulated by scanning the back-gated voltage (V₆) lead to either hole injection from the source to the valence band at negative V₆ or electron injection from the drain to the conduction band at positive V₆. Consequently, transfer characteristics of a pristine WSe₂ device exhibit a typical ambipolar behavior, as shown in Figure 1e.

2.1. Material Analyses

Different samples were exposed to a direct O₂ plasma at various conditions. More detailed information regarding transferring process of chemical vapor deposition (CVD) flakes and plasma treatment can be found in the Experimental Section. Simply comparing color contrast of the samples before and after exposure under an optical microscope, it was rather clear that process temperature is more effective than plasma power or exposure time in controlling the WSe₂ oxidation process. Optical images and atomic force microscopy characterizations are presented in Section I (Supporting Information). Raman spectra of three pristine bi-layer and tri-layer CVD WSe₂ samples are presented in the top panels of Figure 2a. Consistent with previous reports, the 1B₂g Raman mode at 310 cm⁻¹ only appears in multilayers and bulk WSe₂ but does not show up in monolayers. In the bottom left panel of Figure 2a, the 1B₂g peak vanished after the room temperature (RT) O₂ plasma treatment on all three bi-layer samples, indicating that only the bottom WSe₂ layer was left while the top layer was oxidized. In contrast, the 310 cm⁻¹ peak remained in the spectra for all three
Figure 2. a) Comparison of Raman spectra between pristine bi-layer/tri-layer WSe$_2$ and after RT O$_2$ plasma treatment. b) W 4f and c) Se 3d core level spectra of pristine WSe$_2$ and after O$_2$ plasma treatment at RT, 90, 150, or 250 °C. d) Percentage of oxidized W atoms and Se to W ratio in the top few layers of pristine WSe$_2$ and after O$_2$ plasma treatment at various temperatures. e) The redshift of the binding energy calculated from (b) and (c) after O$_2$ plasma treatment at different temperatures. f) Raman spectra of WSe$_2$ before and after treatment at 250 °C. The blueshift of $E_{1g}/A_{1g}$ and 2LA(M) indicate p-doping effect in WSe$_2$. 
The surface chemistry alteration of exfoliated multilayer WSe₂ flakes (from commercially available synthetic crystal provided by HQ graphene) upon O₂ plasma exposure at different temperatures was investigated by X-ray photoelectron spectroscopy (XPS). Detailed information can be found in the Experimental Section. Figure 2b,c shows W 4f and Se 3d core level spectra of a pristine WSe₂ flake and following O₂ plasma exposure for 60 s at RT, 90, 150, and 250 °C. The dominant XPS signal originated from the substrate (SiO₂/Si) due to the lateral size and thickness of WSe₂ flakes is shown in Section III (Supporting Information). The XPS scan of pristine WSe₂ flake did not reveal any additional chemical states such as W–O or Se–O. In Figure 2b, after O₂ plasma exposure at RT, an additional chemical state corresponding to W–O chemical bond was detected at 36.2 eV in W 4f core level. No additional chemical states were detected in Se 3d core level, indicating that oxygen did not react with selenium. Similar to the O₂ plasma treatment at RT, the W–O chemical state was detected in W 4f chemical state following the treatment at 90, 150, and 250 °C with increasing red shift of binding energy. Noted that a more noisy and lower intensity spectrum for treatment at 150 °C was observed after the treatment at 250 °C. Therefore, we have confirmed that both atomically precise layer control and doping level modulation can be achieved through different treatment temperatures.

HR-STEM measurements were performed to directly quantify the number of WSe₂ layers being converted to oxide by the 250 °C O₂ plasma treatment. Detailed information of HR-STEM can be found in the Experimental Section. Figure 3a shows a cross-section view of a WSe₂ device with a channel length (Lc) of 65 nm. The observed bending curvature was caused by the carbon layer deposition induced stress during the TEM sample preparation using focused ion beam (FIB). From the magnified image of the channel region presented in Figure 3b, nearly three layers of WSe₂ were converted to WO₃₋ₓ by the 250 °C treatment, leaving two WSe₂ layers remaining underneath. Interestingly, it was observed that WO₃₋ₓ penetrated laterally into the contact at the scale of ≈12 nm, as revealed in Figure 3c. We believe this phenomenon contributes significantly to unpinning of the metal Fermi level and potentially lowering

Figure 3. a) Cross-section view of a WSe₂ device with Lc = 65 nm. b) The zoom-in observation of the channel region from (a), indicating approximately three layers of WSe₂ are converted into WO₃₋ₓ. c) The lateral penetration of WO₃₋ₓ underneath the edge of contact after the O₂-plasma treatment.
of the SB height for easier hole injection. Furthermore, WO$_{3-x}$ induced heavy doping in the remaining WSe$_2$ under the contact can effectively reduce the depletion width to produce a transparent barrier for carrier injection into the channel. Both mechanisms contribute to a very low contact resistance of 528 $\Omega$ $\mu$m and correspondingly record high on-state performance reported in the later paragraph. More detailed information regarding the EELS mapping can be found in Section IV (Supporting Information).

2.2. Electrical Characterizations

We now focus on electrical characterization of devices that have undergone O$_2$ plasma treatment at different temperatures, as shown in Figure 4a. One could immediately observe significant differences in the magnitude of the threshold voltage ($V_{TH}$) shift from the pristine (black) to after treatment (red) characteristics. It is clear that $V_{TH}$ shift, an indication of the doping level, increases with increasing temperature, consistent with the shift of binding energy shown in Figure 2e. We believe that the higher doping level achieved at higher temperature can be attributed to a larger number of WSe$_2$ layers being converted into a thicker WO$_{3-x}$ layer. Except for the device treated at 250 °C, $V_{TH}$ of the other two devices treated at RT and 150 °C is within the voltage window to reveal the off-state performance. The preserved on/off ratios of $\approx 10^7$ indicate that WO$_{3-x}$ serves as an effective doping layer rather than a conductive layer shunting between the source/drain (S/D) electrodes.[40] Based on the $V_{TH}$ shift extracted from the device characteristics, we can calculate the amount of charges induced by doping ($Q = C_{ox}V_{TH,shift}$, $C_{ox} \approx 38.5$ nF cm$^{-2}$) and estimate the dopant concentration to be $\approx 2.2 \times 10^{12}$ cm$^{-2}$ for devices undergone the RT treatment and $\approx 8.3 \times 10^{12}$ cm$^{-2}$ for those gone through the treatment at 150 °C. More devices data set can be found in Section V (Supporting Information).

In addition, device contact resistances ($R_C$) were significantly reduced after the plasma treatment. Four-probe configuration shown in Figure 1b was used to extract $R_C$. Figure 4b,c shows $R_C$ as a function of back-gate voltage for pristine devices and the same set of devices after the O$_2$ plasma treatment at 150 and 250 °C, respectively. Due to the positive $V_{TH}$ shift, $R_C$ is less
gate voltage dependent and reduced drastically. $R_C$ of a device gone through the 250 °C treatment was extracted to be as low as 528 Ω μm, at $V_{BG} = -50$ V. As explained earlier, we believe that the O$_2$ plasma treatment not only affects the channel doping but also lowers the SB height and barrier width at the contact interface to allow for higher current injection, which is now attributed to the lateral penetration of WO$_{3-x}$ as observed from our HR-STEM analysis. A table of extracted $R_C$ values from different devices with or without treatment can be found in Section VI (Supporting Information).

Utilizing the demonstrated doping and low $R_C$, we fabricated devices with scaled channel length ($L_C$) and achieved the outstanding on-state performance in WSe$_2$ FETs. 12 SB-devices with different $L_C$ ranging from ≈70 to ≈1050 nm were fabricated on exfoliated multilayer (5–10 layers) WSe$_2$, as shown in Section VII (Supporting Information) for several devices. 250 °C O$_2$ plasma treatment was performed to all devices. Total device resistance ($R_{total}$) and current density ($I_{DS}$) extracted at $V_B = -50$ V and $V_{DS} = -0.9$ V are shown in Figure 5a. Although these devices were not fabricated on the same flake to guarantee an accurate extraction of $R_C$ from the transmission line method (TLM), we still performed the extraction to get a rough estimate. $R_C = 1.1$ kΩ μm was extracted from the linear fitting of the $R_{total}$ versus $L_C$ plot, which agrees with the values obtained from the four-probe measurements, presented in Table S1 (Supporting Information). The output characteristics of our best performing device with $L_C = 70$ nm is shown in Figure 5b with $I_{DS} = 320$ μA μm$^{-1}$ being achieved at $V_{DS} = -1$ V. Finally, these O$_2$ plasma treated devices were placed in the laboratory ambient environment without any passivation layer for 7 days before remeasurements. Negligible changes in characteristics were observed as shown in Section VIII (Supporting Information), suggesting a robust p-doping scheme for high-performance WSe$_2$ devices.

Finally, we compare our result to other reported contact resistance for hole injection in WSe$_2$-based devices and summarize in Table 1. Our O$_2$-plasma treatment offers a comparable $R_C$ while requiring a simpler fabrication process compared to a 2D/2D contact.[22]

### Table 1. $R_C$ comparison for WSe$_2$ hole injection at room temperature.

| Layer number | $R_C$ [kΩ μm] | Special treatment |
|--------------|---------------|-------------------|
| 10L [22]     | 0.3           | 2D/2D contact     |
| 6L [22]      | 0.9           | MoO$_3$ passivation |
| 4L [23]      | 1.1           | Ozone treatment   |
| 10L [24]     | 1.3           | NO$_2$ treatment  |
| 2L [41]      | 4.0           | Transferred contact |
| 20L [42]     | 11.4          | W:Ta Co-sputtering |
| 13L [41]     | 12.5          | Transferred contact |
| 1L [41]      | 38.0          | NO$_2$ treatment  |
| 1L [41]      | 50.0          | Transferred contact |
| 7L [41]      | 100           | XeF$_2$ thinning  |
| ≈8L (this work) | 0.5         | O$_2$-plasma at 250 °C |

### 3. Conclusion

We have achieved tunable p-type doping on WSe$_2$ through O$_2$-plasma treatment at different temperatures, with supporting evidences from XPS, Raman, HR-STEM, and electrical characteristics. We conclude that the doping level is determined by how many WSe$_2$ layers being converted into WO$_{3-x}$ by the O$_2$-plasma treatment. Larger numbers of layers are converted at higher temperatures, resulting in thicker WO$_{3-x}$ for higher doping. The penetration of WO$_{3-x}$ into the contact region is believed to contribute to the unpinning of the Fermi level and thinning of the barrier width for higher current injection. Low $R_C = 528$ Ω μm was measured from four-probe measurements.

![Figure 5.](image_url)

Figure 5. a) Measured $R_{total}$ (black data) and current density (red data) at $V_B = -50$ V and $V_{DS} = -0.9$ V for 12 devices with $L_C$ ranging from ≈70 nm to ≈1050 nm. $R_C = 1.14$ kΩ μm is extracted from a linear fitting curve. b) Output characteristics of a device with record-high hole current density of 320 μA/μm at $V_{DS} = -1$ V after 250 °C O$_2$ plasma treatment.
after 250 °C O2 plasma treatment, leading to a record high hole current in WSe2 devices. This air-stable, efficient p-doping strategy can enable high-performance WSe2-based electronics or be applied to other material of interests for tunable doping effect by transferring WSe2 on top followed by self-limiting oxidation under specific temperature treatment.

### 4. Experimental Section

**Two-Probe and Four-Probe Device Fabrication:** Mono/bi-layer CVD WSe2 flakes were transferred or multilayer layers (5–10) WSe2 were exfoliated from a bulk crystal onto a 90 nm SiO2 capped Pt+ doped Si substrate as a global back-gated scheme. E-beam lithography was employed to define S/D regions (for two-probe devices) and two additional voltage probes (for four-probe devices) followed by e-beam evaporated Ti (1 nm) / Pd (30 nm) (at pressure =1E-6 torr) as electrodes and a polymethyl methacrylate lift-off process.

**CVD Flakes Transferring Process:** Mono/bi-tri-layer CVD WSe2 flakes were purchased from commercially available source (2D Layer, https://2dlayer.com/). The transferring process was performed in the cleanroom ambient in Purdue University. Polystyrene (PS) was used as the supporting film to peel off the WSe2 flakes from the growth substrate. 9 g of PS (molecular weight =192 000 g mol−1) was dispersed in 50 mL toluene. Then this solution was spin-coated on the growth substrate at a speed of 4000 rpm for 40 s, followed by baking at 90 °C for 5 min. In order to allow water to penetrate to the interface between the WSe2 film and the SiO2/Si substrate to detach the WSe2 flakes, a diamond scribe was used to make some scratches at the edges of the PS film. Next, the PS film attached to the WSe2 flakes was gradually peeled off from the growth substrate in water and transferred to the target substrate. Finally, the PS film was removed by soaking in toluene, acetone, and IPA.

**O2 Plasma Treatment Process:** The treatment was performed by AXIC plasma enhanced chemical vapor deposition (PECVD) system. The RF power was set 20 W with the sample placed at a distance of 3" away from the plasma source. The oxygen flow rate was set 100 sccm with the chamber pressure set to 100 mTorr during the process. The temperature was set depending on a desired treatment.

**Electrical Characterization:** The electrical measurements were performed by HP 4156B precision semiconductor parameter analyzer with Lake Shore probe station under vacuum at room temperature.

**X-Ray Photoelectron Spectroscopy:** XPS scans were carried out in an Ultra High Vacuum (UHV) cluster tool using an Omicron EA125 hemispherical seven channels analyzer with a monochromatic Al Kα source (hν = 1486.7 eV).[45] XPS peaks were deconvoluted and analyzed using Aanalyzer software.[46] Quantitative analysis of the elemental concentration of the samples was acquired based on integrated photoelectron intensity and sensitivity factor for a given core level.

Quantitative analysis of relative elemental concentration could be determined from XPS measurement. The number of photoelectrons per second for specific elemental core level ($j$) is directly proportional to the number of atoms of the elements per centimeter cubic of the sample surface ($n$), while it was indirectly proportional to atomic sensitivity factor ($S$). Atomic sensitivity factor ($S$) of the elements' core level was developed from a specific spectrometer. Thus, the elemental concentration ($C_j$) was described as:

$$C_j = \frac{n_j}{S_j} \times \frac{1}{\frac{1}{n_j}}$$

**Raman Spectroscopy:** Raman spectra were taken using a 532 nm laser focused through a 100X objective lens at room temperature and under ambient condition.

**TEM Analysis:** TEM analysis was carried out using an aberration-corrected (probe Cs-corrector) JEM-ARM200F (JEOL, USA, Inc.) electron microscope operated at 200 kV. The high angle annular dark field (HAADF) and annular bright field (ABF) images were performed to study the cross-sectional morphology of the device. The convergence semi-angle of the electron probe was set to 25 mrad, and the collection semi-angle was 70–250 mrad for HAADF and 12–24 mrad for ABF, respectively. The elemental characterization of the device was performed using the electron energy loss spectroscopy (EELS) line scan using a Gatan Enfina spectrometer with the collection semi-angle for EELS for 30 mrad.

### Supporting Information

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

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### Conflict of Interest

The authors declare no conflict of interest.

### Keywords

2D materials, atomically layered control, contact resistance, field-effect transistors, tunable doping

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