Air Stable p-Doping of WSe₂ by Covalent Functionalization

Peida Zhao,‡ Daisuke Kiriya,‡ Angelica Azcatl,§ Chenxi Zhang,§ Mahmut Tosun,‡ Yi-Sheng Liu,§ Mark Hettick,‡ Jeong Seuk Kang,‡ Stephen McDonnell,§ Santosh KC,§ Jinghua Guo,§ Kyeongjae Cho,§ Robert M. Wallace,§ and Ali Javey*†

†Electrical Engineering and Computer Sciences, University of California, Berkeley, California 94720, United States, ‡Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States, §Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas 95080, United States, and ‡Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

ABSTRACT Covalent functionalization of transition metal dichalcogenides (TMDCs) is investigated for air-stable chemical doping. Specifically, p-doping of WSe₂ via NO₂ chemisorption at 150 °C is explored, with the hole concentration tuned by reaction time. Synchrotron based soft X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) depict the formation of various WSe₂₋ₓ₋ₓOₓNₓ species both on the surface and interface between layers upon chemisorption reaction. Ab initio simulations corroborate our spectroscopy results in identifying the energetically favorable complexes, and predicting WSe₂:NO at the Se vacancy sites as the predominant dopant species. A maximum hole concentration of ∼10¹⁹ cm⁻³ is obtained from XPS and electrical measurements, which is found to be independent of WSe₂ thickness. This degenerate doping level facilitates 5 orders of magnitude reduction in contact resistance between Pd, a common p-type contact metal, and WSe₂. More generally, the work presents a platform for manipulating the electrical properties and band structure of TMDCs using covalent functionalization.

KEYWORDS: layered materials - covalent binding - NO₂ - chemisorption - doping

Transition metal dichalcogenides (TMDCs) have garnered much attention in the recent years due to their unique material properties and potential applications in various electronic and optical devices.¹-² Possessing a layered structure with a monolayer thickness of down to 7 Å, TMDCs represent a viable electronic material system for future devices, especially as size scaling continues to the sub-10 nm regime. To facilitate TMDC integration into future electronic devices, doping becomes a vital stepping-stone. Indeed, many exploratory works have already reported both n- and p-doping utilizing surface charge transfer mechanisms aided by molecular physisorption.³-⁵ For instance, WSe₂ has been p-doped using physisorbed NO₂, while this doping scheme has achieved superb p-type field-effect transistors (FETs), the doping is unstable and decays almost completely within an hour.³ The instability is due to the physisorption process, which relies on weak van der Waals (vdW) interactions incapable of sustaining stable electron transfers at ambient conditions. Moving forward, an air stable doping scheme is needed as a fundamental enabler toward the integration of TMDCs into robust device fabrications.

In this work, we demonstrate air stable p-doping, up to the degenerate limit, by chemisorption of NO₂ on WSe₂ performed at a sample temperature of 150 °C. Synchrotron-based soft X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) depict formation of various WSe₂₋ₓ₋ₓOₓNₓ species upon NO₂ chemisorption on WSe₂. Formation of these species and their effects on the electronic properties of WSe₂ are also examined by ab initio simulations, which confirm the experimental observations. Notably, the chemisorption process retains WSe₂’s long-range crystal structure and optical properties. This doping process leads to a 5 orders of magnitude reduction in contact resistance (R_c) between WSe₂ and Pd metal, and results in a degenerate doping concentration of 1.6 × 10¹⁹ cm⁻³. From this study, we exhibit a
route toward an air stable p-doping method on WSe₂ that can be efficiently utilized for various device schemes in the future.

RESULTS AND DISCUSSION

A back-gated WSe₂ FET is fabricated via standard electron beam lithography or photolithography and exposed to NO₂ at 150 °C for a set reaction time of 4–12 h. Given the strong oxidizing nature of NO₂, we predict an induced NO₂ chemisorption process on WSe₂ due to the temperature and treatment time utilized. A defect-oriented model is proposed where NO₂ chemisorbs on WSe₂ surface and bulk defect sites (e.g., selenium vacancies), forming stable electron withdrawing WSe₂:O, WSe₂:NO₂, and WSe₂:NO species that lead to p-doping (Figure 1a,b). At the temperatures used here, NO₂ gas is partly decomposed to form O and NO, making various covalent functionalization schemes possible. Figure 1b depicts three most likely scenarios. Figure 1b (i) shows direct W oxidation resulting from the O of NO₂ occupying a Se vacancy followed by NO₂ thermal dissociation and desorption of NO. Figure 1b (ii) shows the alternative NO₂ adsorption configuration with N directly bonding to W at the presence of a Se vacancy. Figure 1b (iii) illustrates N of NO covalently bonded with W, where NO is created through NO₂ dissociation.

Transfer characteristics of doped devices are measured before and after NO₂ functionalization (Figure 1c). Here the thickness of WSe₂ flake is ~5 nm. Before NO₂ exposure, we observe a clear p-FET characteristic with an on/off ratio of ~1000 and a low I_on of ~10⁻⁸ A/µm due to severe contact resistance resulting from the Schottky barrier present between WSe₂ and Pd. After NO₂ chemisorption, we observe a drastic increase of I_on by about 10⁵, and gate’s inability to control the channel conduction. Gate control loss is due to hole doping by NO₂ chemisorption that moves the Fermi level (E_F) to close proximity of the valence band edge (E_V). The excessive states present in the vicinity of E_F then render gate modulation of E_F ineffective, reflecting a degenerate p-doping situation. The doping stability is studied by examining the changing transfer characteristics of the doped sample upon air exposure. As seen in Figures 1d and Supporting Information Figure S1, the device undergoes a gradual current drop for the first 2–3 h, and eventually stabilizes at a set current level. This initial current drop is attributed to desorption of weakly physisorbed NO₂. Inset: Drain current change is fitted to a time-dependent Langmuir isotherm desorption model vs air exposure time. Dash line represents fitted curve.
\( I(t) = \left( I_{\text{initial}} + \psi/(1 + \psi) \right) \left( 1 - e^{-t/\tau} \right) \)

where \( t \) is the air exposure time, \( I_{\text{initial}} \) is the initial current level right after chemisorption, \( \psi \) is a dimensionless parameter characterizing surface coverage, and \( \tau \) is the desorption time constant. We extract the desorption time constant \( \tau \sim 40 \text{ min} \) from NO\(_x\) physisorption, comparable to other physisorption-based gas sensors (such as ion-sensitive FET sensors) operating at room temperature.\(^8\) Notably, the doping effect is irreversible even after thermal annealing of the sample at 300°C in Ar, which further supports our proposed scheme of NO\(_x\) chemisorption leading to stable doping.

Given the stability of chemisorption, in-depth material characterization techniques in ultra-high vacuum (UHV) environments can be used to investigate the nature of chemisorbed species, in contrast with that of the unstable surface physisorbed molecules.\(^4,5\) First, the nitrogen K absorption edge was examined using XAS. A collection of both total electron yield (penetration depth of \( \sim 10 \text{ nm} \)) and total fluorescence yield (penetration depth of \( \sim 100 \text{ nm} \)) show similar emission trend, signifying various nitrogen containing species in both depth regimes. The results suggest that the chemisorption is occurring at both the surface and interface between the layers of WSe\(_2\). As a function of absorbed photon energy for N 1s electrons, a larger energy translates to a higher N oxidation state, as it becomes harder to remove electrons due to stronger electrostatic interactions. We observe 3 peaks at \( \sim 396, \sim 401, \) and \( \sim 406 \text{ eV} \) which we assign to N–W (from W-NO\(_x\) species), NO, and NO\(_2\) species, respectively, based on literature values.\(^9-14\) Therefore, XAS results substantiate all three predicted configurations shown in Figure 1b.

Core W levels were investigated via XPS. According to Figure 2b, six visible peaks were observed after doping compared to only two visible peaks before NO\(_x\) chemisorption. The six peaks correspond to three doublets (each doublet possessing a unique W 4f\(_{5/2}\) and W 4f\(_{7/2}\) peak value), each doublet indicating a different W containing species with W of different oxidation states. Doublet III at 35.81 eV is assigned to WO\(_x\) with an almost 6\(^+\) oxidation state.\(^15,16\) Doublets I and II (31.8 and 32.5 eV for W 4f\(_{7/2}\) values, respectively) are assigned to different stoichiometric ratio of WSe\(_2\)-x\(_y\)O\(_x\)N\(_y\) species (also observable at the Se 3d level in Figure 2c) and corresponds to W oxidation state between 0 and 4\(^+\) (ref 17). Note that the N stoichiometric ratio \( y \) is less than 0.003, corresponding to an atomic concentration of 0.1% and falling below the XPS detection limit. XAS, with a higher sensitivity due to Synchrotron excitation source, however, clearly identifies the N present and underlines the importance of using both XAS and XPS to probe the complete composition of the chemisorbed species present on WSe\(_2\).

The valence band edge of WSe\(_2\) was also examined by XPS. We observe a 0.8 eV shift of \( E_F \) (Figure 2d) upon

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**Figure 2.** (a) Total electron yield of Soft X-ray Absorption Spectroscopy (XAS) NO\(_2\) doped samples. Identifiable peaks N K-edge indicates N–W, NO, and NO\(_2\) species in host after NO\(_x\) chemisorption. (b) Tungsten core level via X-ray Photoelectron Spectroscopy (XPS) showing the formation of various WSe\(_{2-x-y}\)O\(_x\)N\(_y\) species. Labels I, II, and III indicate W doublets of different oxidation states. (c) Se 3d core level after NO\(_x\) chemisorption. Labels I and II indicate two different species of different Se oxidation states. (d) Valence band edge of WSe\(_2\) before and after NO\(_x\); a definitive \( \sim 0.8 \text{ eV} \) shift of the valence band edge is shown with respect to the Fermi level.
NO$_x$ chemisorption with $E_V - E_F \sim 50$ meV extracted via linear extrapolation of the valence band tail. This large $E_F$ shift is indicative of p-doping of WSe$_2$ and suggests a degenerate doping level ($E_V - E_F < 3kT$) by NO$_x$ functionalization. From $E_V - E_F$, we extract a hole concentration of $p \sim 1.3 \times 10^{19}$ cm$^{-3}$ by using the Joyce Dixon approximation$^{18}$ using an effective density of states$^{19}$ of $N_e$ at $2.54 \times 10^{19}$ cm$^{-3}$.

Subsequently, ab initio simulation (see Methods for details) was used to examine the thermodynamic stability of WSe$_2$ after NO$_x$ functionalization and the changing band structure of WSe$_2$ as a result. From density functional theory (DFT) calculations, we observe energetically favorable adsorption of O, NO and NO$_2$ at Se vacancies (Table 1), which is consistent with the experimental observations. Notably, on the basis of DFT calculations, adsorption was found to be unfavorable without the presence of Se vacancies.

Out of all adsorbates, only NO adsorption is predicted to contribute to p-doping of WSe$_2$ based on DFT simulations. Figure 3 shows the relaxed configuration of chemisorbed NO with N bonding to W, similar to Figure 1b (iii) configuration. By examining the band structure, we find that NO:WSe$_2$ configuration creates two defect bands close to the valence band edge shown in Figure 3b. The red dash line, overlapping with one of the NO adsorption induced defect bands, represents $E_F$. The other two chemisorbed species have minimal effects on the carrier concentration of WSe$_2$ based on the DFT simulations (Figure 3c).

Next we examine the effects of NO$_x$ functionalization on the crystal structure and luminescence properties of WSe$_2$. X-ray diffraction (XRD), Raman spectroscopy and photoluminescence (PL) were all performed on NO$_x$ functionalized WSe$_2$ samples. XRD data in Figure 4a demonstrates that the overall WSe$_2$ crystal structure remains intact as the two Miller index peaks 002 and 103 are preserved with similar intensities and no visible $\theta$ shifts. Figure 4b demonstrates the retention of the primary phonon modes $E_{2g}$ and $A_{1g}$ at 249 and 251 cm$^{-1}$, respectively, for a trilayer WSe$_2$ before and after doping, consistent with the literature.$^{20,21}$ PL spectra in Figure 4c shows the two peaks (1.47 and 1.6 eV) of a trilayer WSe$_2$ unaffected by NO$_x$ chemisorption.$^{22,23}$ From our XRD, Raman and PL characterizations, we conclude that doping functionalization does not compromise the unique properties of WSe$_2$ at the macroscopic level.

Electrical measurements of WSe$_2$ devices before and after NO$_x$ chemisorption were performed. Two studies were conducted, the first being a time dependent doping study at varying thicknesses. Figure 5a shows a representative transfer characteristic of 7.5 nm thick WSe$_2$ back-gated device as a function of NO$_x$ doping time. A progressively heavier p-doping can be observed, reflected by an increasing $I_{on}$ and diminishing gate control. The increasing $I_{on}$ displays a degree of doping tunability via doping time, with $I_{on}$ eventually saturating to degenerate behavior. Doping concentrations are explicitly extracted across three devices with different flake thicknesses of 0.7, 7.5, and 78 nm

<table>
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<th>adsorbates on Se vacancies</th>
<th>$\Delta E_{NO_2:WSe_2}$</th>
<th>$\Delta E_{NO:WSe_2}$</th>
<th>$\Delta E_{O:WSe_2}$</th>
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<tr>
<td>NO$_2$</td>
<td>-1.0 eV</td>
<td>-2.8 eV</td>
<td>-4.8 eV</td>
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$^*$The error for binding energy is within 0.1 eV.

Figure 3. Ab initio simulation results showing band structure and corresponding simulated model of (a) pristine WSe$_2$, (b) WSe$_2$ with NO adsorption in Se vacancy, and (c) WSe$_2$ with NO$_2$ adsorption in Se vacancy. The red dotted line indicates the Fermi level.
(monolayer thickness is determined by optical microscopy and the rest determined by AFM in Supporting Information Figure S2), respectively, versus doping time (Figure 5b). Assuming negligible $R_c$ due to the thinning Schottky barrier at higher doping concentrations and therefore higher tunneling current, we can estimate doping concentration by first finding the 2D sheet charge density $n_{2D} = (I_{DS}/L)/[qW(V_{GS} - V_D)]$ at $V_{GS} = 0$ where $V_{DS}$ is the drain voltage, $L$ and $W$ are the length and width of the channel, $q$ is the unit electron charge, and $\mu_p$ is the field effect hole mobility. From $n_{2D}$, we find volume doping concentration which saturates to $\sim 1 \times 10^{19} \text{cm}^{-3}$ across all three devices. The similar saturated doping level across all three devices demonstrates a uniform volume doping throughout the WSe$_2$ surface and body, supporting the XAS results discussed earlier. Notably, the electrically extracted saturation doping concentration is consistent with that extracted from XPS measurements.

Contact resistance, $R_c$ was extracted before and after NO$_x$ chemisorption using the transfer line method (TLM). Figure 6a shows the transfer characteristics of TLM devices with channel lengths of 500 nm, 1 $\mu$m, 1.5 $\mu$m, and 2 $\mu$m fabricated on a WSe$_2$ flake with a thickness of $\sim 7$ nm (Figure 6b inset). The observed low $I_{on}$ and ambipolar behavior prior to doping implies a large $R_c$ due to Schottky barrier height near the WSe$_2$ midgap. After doping, however, we see a significant increase in $I_{on}$ indicating a decrease in $R_c$. Using $R_{\text{total}} = 2R_{\text{contact}} + R_{\text{channel}}$, where $R_{\text{total}}$ and $R_{\text{channel}}$ are the unit-width normalized total resistance and channel resistance, $R_c$ is found to be 0.13 G$\Omega/$$\mu$m and 1.27
kΩ/μm before and after NO\textsubscript{2} chemisorption, respectively (Figure 6b,c). NO\textsubscript{2} doping is shown to reduce the $R_c$ by a remarkable 5 orders of magnitude. Finally, we revisit WSe\textsubscript{2} doping extraction including $R_c$, and find again consistent doping level $p \sim 1.6 \times 10^{19}$ cm\textsuperscript{-3}.

**CONCLUSION**

In summary, we have demonstrated air stable p-doping of WSe\textsubscript{2} via covalent functionalization by NO\textsubscript{2} at an elevated temperature of 150 °C. The stability of this covalent bonding scheme enables in-depth characterization via XAS and XPS, confirming WSe\textsubscript{2}--O\textsubscript{Nx} species formation due to NO\textsubscript{2} chemisorption on both the WSe\textsubscript{2} surface and body. From XPS, a shift of $\sim$0.8 eV of $E_T$ toward $E_F$ also conludes a degenerate doping situation. In addition, all observed WSe\textsubscript{2}--x--O\textsubscript{N}x species are shown to be energetically favorable from *ab initio* simulations, with NO:WSe\textsubscript{2} identified as the dominant configuration leading to p-doping. Our time dependent doping study also indicates doping tunability, and the TLM study further confirms the extracted doping concentration of $1.6 \times 10^{19}$ cm\textsuperscript{-3} while also showing a remarkable $\sim$5 orders of magnitude $R_c$ reduction via NO\textsubscript{2} functionalization. Controllable semiconductor doping is an important and fundamental enabler in the general field of electronic devices, and degenerate materials can be utilized anywhere from contact materials to junctions in tunneling devices. Therefore, our demonstration of air stable doping through covalent functionalization of WSe\textsubscript{2} presents another route for further enhancing and manipulating TMDC functionalities and applications.

**METHODS**

**Device Fabrication.** The device fabrication starts with mechanical exfoliation of WSe\textsubscript{2} (Nanosurf) on top of a SiO\textsubscript{2} (260 nm)/Si substrate. Source/drain contacts are patterned using photolithography, and e-beam evaporation of Pd/Au (10/30 nm) films and resist liftoff in acetone.

**NO\textsubscript{2} Doping.** The fabricated sample is placed inside an evacuated 250 mL Pyrex glass flask with ambient N\textsubscript{2} flow for gas exchange. Subsequently, a constant NO\textsubscript{2} gas flow (5000 ppm balanced in N\textsubscript{2}) is introduced through the flask and maintained throughout the entire doping procedure, exhausting to an external oil bath. Simultaneously, the flask is placed on a hot plate with the sample temperature maintained at 150 °C and doped for a set time. Finally, the sample is cooled first to $\sim$50 °C before purging the flask with N\textsubscript{2} and sample removal.

**XAS Characterizations.** X-ray absorption spectroscopy of NO\textsubscript{2} chemisorption in WSe\textsubscript{2} characterization was taken at Beamline 8.0.1 at Advanced Light Source, Lawrence Berkeley National Laboratory. N K-edge spectrum was calibrated carefully by measuring h-BN reference sample for energy calibration. The energy resolution at N K-edge region is about 0.1 eV and the vacuum of experiment chamber is lower than $5 \times 10^{-8}$ Torr. All XAS spectra were recorded in Total Electron Yield (TEY) and Total Fluorescence Yield (TFY) simultaneously.

**XPS Characterizations.** The XPS spectra were acquired using a monochromated Al K$\alpha$ source (hv = 1486.7 eV) connected to a UHV cluster system described elsewhere. An analyzer acceptance angle of $\pm$8°, a take-off angle of 45°, and pass energy of 15 eV were used for this study. The binding energy scale is calibrated using the ASTM procedure.

**Optical, Electrical, Raman, PL, and XRD Characterizations.** Optical images are taken with a Olympus BX51 microscope with an attached video camera. All electrical measurements are conducted on a HP 4155C analyzer with a corresponding probe station. Both Raman and PL are conducted using a commercially available HORIBA LabRAM HR8000 system with an external laser source with an excitation wavelength of 532 nm. The X-ray diffraction (XRD) was taken on a Bruker AXS D8 Discover GADDS XRD Diffractometer system.

**Ab initio Simulations.** First-principles calculations were utilized based on DFT\textsuperscript{27,28} with plane wave basis sets and Projector Augmented Wave (PAW) pseudopotentials\textsuperscript{29,29} implemented in the Vienna *Ab initio* Simulation Package (VASP).\textsuperscript{27,50,31} The electronic wave functions were represented by plane wave basis with a cutoff energy of 600 eV. The exchange and correlation interactions are incorporated as a functional of the Generalized Gradient Approximation (GGA).\textsuperscript{29,32,33} A $5 \times 5$ supercell of monolayer WSe\textsubscript{2} host was used for the simulations. Each model has $\sim$18 Å vacuum to avoid interaction between replica images as a result of the periodic boundary conditions. NO, NO\textsubscript{2} and O were separately placed near a singular Se vacancy of WSe\textsubscript{2} (or pristine WSe\textsubscript{2}) and allowed to relax energetically while the host cell size was kept fixed after optimization.

**REFERENCES AND NOTES**


**Conflict of Interest:** The authors declare no competing financial interest.

**Supporting Information Available:** Detailed device transfer characteristics after doping, and AFM of various flake thicknesses used. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

Air Stable $p$-Doping of WSe$_2$ by Covalent Functionalization

Peida Zhao$^{1,2}$, Daisuke Kiriya$^{1,2}$, Angelica Azcatl$^3$, Chenxi Zhang$^3$, Mahmut Tosun$^{1,2}$, Yi-Sheng Liu$^4$, Mark Hetrick$^{1,2}$, Jeong Seuk Kang$^{1,2}$, Stephen McDonnell$^3$, Santosh KC$^3$, Jinghua Guo$^4$, Kyeongjae Cho$^3$, Robert M. Wallace$^3$, and Ali Javey$^{1,2,*}$

1 Electrical Engineering and Computer Sciences, University of California, Berkeley, CA 94720
2 Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
3 Materials Science and Engineering, The University of Texas at Dallas, Richardson, TX 95080
4 Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

*E-mail: ajavey@berkeley.edu
**Figure S1.** Facsimile of Figure 1(d) represented in linear scale for drain current. A degenerate p-type trend is observed with small on/off ratio and slightly lower drain current at a more positive gate bias.

**Figure S2.** Optical microscopy (left) and atomic force microscopy (AFM, right) images of devices shown in Figure 5. WSe$_2$ layer thicknesses are (a) ~7.5nm and (b) ~78 nm. Scale bar is 3µm.