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Band Structure Engineering of Layered WSe₂ via One-Step Chemical Functionalization

Jun Hong Park,^{†,‡,¶}[®] Amritesh Rai,^{∥,¶}[®] Jeongwoon Hwang,^{#,∇} Chenxi Zhang,[#] Iljo Kwak,[‡] Steven F. Wolf,[‡] Suresh Vishwanath,[⊥] Xinyu Liu, [◆] Malgorzata Dobrowolska, [◆] Jacek Furdyna, [◆] Huili Grace Xing,^{⊥,○} Kyeongjae Cho,[#] Sanjay K. Banerjee,[∥] and Andrew C. Kummel^{*,‡,§}[®]

[†]School of Materials Science and Engineering, Gyeongsang National University, Jinju 52828, Republic of Korea

[‡]Materials Science and Engineering Program, University of California, San Diego, La Jolla, California 92093, United States [§]Departments of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, United States ^{II}Microelectronics Research Center, Department of Electrical and Computer Engineering, The University of Texas at Austin, Austin, Texas 78758, United States

[#]Department of Materials Science and Engineering, The University of Texas at Dallas, Dallas, Texas 75080, United States $^
abla$ Department of Physics Education, Chonnam National University, Gwangju 61186, Republic of Korea

¹School of Electrical and Computer Engineering, Cornell University, Ithaca, New York 14853, United States

^ODepartment of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, United States

Physics Department, University of Notre Dame, Notre Dame, Indiana 46556, United States

Supporting Information

ABSTRACT: Chemical functionalization is demonstrated to enhance the p-type electrical performance of twodimensional (2D) layered tungsten diselenide (WSe₂) fieldeffect transistors (FETs) using a one-step dipping process in an aqueous solution of ammonium sulfide $[(NH_4)_2S_2]$ (aq)]. Molecularly resolved scanning tunneling microscopy and spectroscopy reveal that molecular adsorption on a monolayer WSe₂ surface induces a reduction of the electronic band gap from 2.1 to 1.1 eV and a Fermi level shift toward the WSe₂ valence band edge (VBE), consistent with an increase in the density of positive charge carriers. The mechanism of electronic transformation of WSe₂ by



 $(NH_4)_2S(aq)$ chemical treatment is elucidated using density functional theory calculations which reveal that molecular "SH" adsorption on the WSe₂ surface introduces additional in-gap states near the VBE, thereby, inducing a Fermi level shift toward the VBE along with a reduction in the electronic band gap. As a result of the $(NH_4)_2S(aq)$ chemical treatment, the p-branch ON-currents (I_{ON}) of back-gated few-layer ambipolar WSe₂ FETs are enhanced by about 2 orders of magnitude, and a $\sim 6 \times$ increase in the hole field-effect mobility is observed, the latter primarily resulting from the pdoping-induced narrowing of the Schottky barrier width leading to an enhanced hole injection at the WSe₂/contact metal interface. This $(NH_4)_2S(aq)$ chemical functionalization technique can serve as a model method to control the electronic band structure and enhance the performance of devices based on 2D layered transition-metal dichalcogenides.

KEYWORDS: transition-metal dichalcogenides, tungsten diselenide, $(NH_4)_{2}(aq)$ chemical treatment, scanning tunneling microscopy/spectroscopy, band structure, field-effect transistors

emiconducting two-dimensional (2D) transition-metal dichalcogenides (TMDs) have been demonstrated as a potential material platform for digital logic, radio frequency (RF), and optoelectronic device applications¹⁻⁴ because of several promising attributes such as atomically thin bodies with finite band gaps,⁵⁻⁷ thickness-dependent indirectto-direct band gap transition, and the absence of undesired dangling bonds at their surfaces.⁸ Typically, a monolayer (ML) TMD consists of a mono-atomic layer of transition-metal atoms 'M' (e.g., Mo or W) sandwiched in between two layers of chalcogen atoms 'X' (e.g., S or Se) in the form of an X-M-X (MX₂) triple-atomic layer structure. By combination of

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Figure 1. Investigation of bare ML WSe₂ grown by molecular beam epitaxy (MBE). (a) Schematic diagrams of the ML WSe₂ atomic structure with top and cross-sectional views. (b) Filled state STM image of bare ML WSe₂ ($V_S = -2 V$, $I_T = 20$ pA). A small triangular BL WSe₂ region is also observed within the scanned image. (c) Atomically resolved STM image of ML WSe₂ ($V_S = -0.8 V$, $I_T = 320$ pA). It is noted that the STM image is slightly distorted due to thermal drifting during STM imaging. Inset shows the Fourier transform of the STM image. (d) Empty state STM image of the bare ML WSe₂ scanned over the same area as in (b) ($V_S = 2 V$, $I_T = 20$ pA). (e) Enlarged empty state STM image showing defects (bright protrusion marked by a red cross) and defect-free areas (marked by white cross) ($V_S = -1 V$, $I_T = 50$ pA). (f) LDOS probed using STS at the defect sites (red curves) and defect-free areas (black curves) corresponding to the red and white cross '×' marks, respectively, as shown in (e).

different M and X atoms, the band structure of TMDs can be altered to achieve band gaps in the range of $\sim 1-2$ eV,^{6,7} resulting in different electrical or optical characteristics in TMD-based devices. Since the electronic structure of TMDs is the most important determinant of the electrical performance as well as the intrinsic limitation of TMD-based field-effect transistors (FETs),^{9,10} engineering the band structure of TMDs is critical.

The band structure of TMDs originates from the orbital overlap of d orbitals of transition metals and p orbitals of chalcogens in the mirror symmetry crystal structure,¹ therefore, the band structure of TMDs can be tuned by perturbing the overlapped orbital configuration of their constituent atoms.¹²⁻¹⁶ Moreover, if molecular adsorption is intentionally introduced in TMDs (typically via surface doping), both the band gap and the carrier concentration can be controlled.^{17–19} Typically, high-density molecular adsorption on the channel of TMD FETs can act as scattering or trapping centers for charge carriers.¹⁹⁻²³ However, if the molecular dopant adsorption sites are spatially confined to the desired regions in a FET, for example, source/drain (S/D) contact and access regions, they can boost the FET performance by decreasing the resistance at the contact metal/TMD interface resulting in enhancement of ION and field-effect mobilities due to a more efficient charge carrier injection into the FET channel.^{17,18,24-34}

In the present report, band structure engineering is demonstrated to enhance the electrical performance of layered tungsten diselenide (WSe₂) FETs using a one-step dipping process in $(NH_4)_2S(aq)$ solution. Although various aqueous chemical treatment methods have been demonstrated to enhance the electronic performance of TMDs, their underlying mechanisms have not been fully understood at the molecular level in previous studies.^{35–39} WSe₂ is chosen as the representative TMD in this study since it is simple to achieve both n-type⁴⁰ and p-type⁴¹ transport in WSe₂-based devices, thereby, making it attractive for complementary-metal-oxide-

semiconductor (CMOS) applications.^{42,43} $(NH_4)_2S(aq)$ solution, on the other hand, has been widely employed in semiconductor research for the passivation of semiconductor surfaces.⁴⁴ Thus, it can be expected that the chemical treatment of WSe₂ with $(NH_4)_2S(aq)$ solution can be easily integrated into existing CMOS fabrication processes. Moreover, previous reports have revealed that the $(NH_4)_2S(aq)$ chemical treatment of 2D molybdenum disulfide (MoS_2) leads to an enhanced electrical performance, and sulfur and its related compounds have been considered possible candidates for functionalization of 2D materials.^{45,46}

 $(NH_4)_2S(aq)$ chemical treatment of WSe₂ is investigated at the molecular level using scanning tunneling microscopy (STM) and spectroscopy (STS) to elucidate the mechanism of the electronic transition in WSe₂. The $(NH_4)_2S(aq)$ chemical treatment of ML WSe2 induces an electronic band gap reduction to almost half of the value of bare ML WSe2 and increases the density of positive charge carriers or holes. This Fermi level shift toward the WSe₂ valence band edge (VBE) is confirmed by density functional theory (DFT) calculations which reveal that this shift is induced due to the adsorption of molecular "SH" species on the bare WSe2 surface. As a consequence of this $(NH_4)_2S(aq)$ chemical treatment, I_{ON} at the p-branch increases more than an order of magnitude in back-gated few-layer (FL) WSe2 FETs. This electrical enhancement in WSe2 FETs can be achieved by a simple and facile one-step dipping method without employing any additional complicated processes or specialized equipment, thereby, enabling easy integration of this $(NH_4)_2S(aq)$ chemical treatment technique into the conventional TMD transistor fabrication process.

RESULTS AND DISCUSSION

The bare surface of ML WSe_2 grown *via* molecular beam epitaxy (MBE) was probed using STM and STS (see the Methods section for details of the MBE and STM/STS methods and Section 1 of the Supporting Information for



Figure 2. $(NH_4)_2S(aq)$ chemical treatment of ML WSe₂ using diluted $(NH_4)_2S$ in H₂O. (a) Schematic diagram illustrating the one-step chemical treatment process of ML WSe₂ using 20% $(NH_4)_2S(aq)$ solution. (b) Large area empty state STM image of chemically treated MBE-grown ML WSe₂ ($V_s = 2.5 V$, $I_T = 10 pA$). It is noted that there is an imaging noise induced by weak interactions between the adsorbates and the STM tip. From the line trace, the expected step height of 6–7 Å was determined for the WSe₂ ML. (c) Raman spectra of mechanically exfoliated ML WSe₂ before (black curve) and after (red curve) $(NH_4)_2S(aq)$ chemical treatment, showing negligible change in its characteristic Raman modes.

additional discussion on STM/STS of MBE-grown WSe₂). Schematic diagrams in Figure 1a represent the side and top views of WSe₂. As shown in Figure 1b, a WSe₂ ML (lateral size ~100 nm) grown on a highly oriented pyrolytic graphite (HOPG) surface was observed via STM, and a triangular island of bilayer (BL) WSe2 was identified within the scanned area of the STM image along with the ML WSe₂ region. Note that the applied sample bias and the measured tunneling current during STM/STS measurements are denoted by $V_{\rm S}$ and $I_{\rm T}$, respectively, in the figure captions. Atomically resolved STM imaging was performed on the ML WSe₂; as shown in Figure 1c, a honeycomb array of Se atoms in ML WSe₂ was observed through a hexagonal moiré pattern, consistent with the hexagonal pattern observed in the Fourier transform image as shown in the inset.^{47,48} It is noted that the periodic brightness pattern observed in the Se atom array is consistent with the presence of different local density of states (LDOS). This variation of LDOS can result from different orbital overlapping with the underlying HOPG, consistent with the moiré pattern. The interatomic spacing in the dotted white triangle drawn in Figure 1c was determined to be about 0.33 \pm 0.01 nm, in good agreement with previously reported results.^{48,49}

The defects in the basal plane of ML WSe₂ were probed by applying a variable sample bias during STM imaging. It is noted that the density of defects has flake-to-flake variation. As shown in Figure 1b, a flat and smooth terrace was only observed under the "filled state" imaging with a -2 V sample bias. However, when the imaging mode was switched to "empty states" using a +2 V sample bias, bright protrusions were observed on the terrace along with bright brims of step edges as shown in Figure 1d. The asymmetrically enhanced brightness of defects indicates that the defects have a different electronic structure from the defect-free terrace in ML WSe₂. To elucidate the nature of the asymmetric bias dependence of defects, LDOS was probed using STS. As shown in Figure 1e, STS was recorded with the STM tip at the defects (red ' \times ') and far away from the defects (white ' \times '). The measured LDOS from STS of defects and defect-free regions are compared as shown in Figure 1f. The black curves, corresponding to the defect-free areas, have an apparent gap centered at the Fermi level (0 V) and states at both conduction band (CB) and valence band (VB) edges. However, as the STM tip was moved to the defect site, the acquired STS curves (shown in red) reveal a larger LDOS at both CB and VB edges than the black curve. Furthermore, the Fermi level is pinned closer to the VBE indicating a large density of positive charge carriers or holes.

The effect of chemical treatment on ML WSe₂ was probed after dipping the as-prepared ML WSe₂ sample in a 20% (NH₄)₂S(aq) solution (source: Sigma-Aldrich; 98% purity).^{35,36} As shown in Figure 2a, the dissociation of (NH₄)₂S in H₂O solution is expected to result in the generation of SH and H₂S species as per the following chemical reactions:^{50,51}

$$(\mathrm{NH}_{4})_{2}\mathrm{S}(\mathrm{aq}) \rightarrow 2\mathrm{NH}_{3}(\mathrm{aq}) + \mathrm{H}^{+}(\mathrm{aq}) + \mathrm{HS}^{-}(\mathrm{aq}),$$

$$\leftrightarrow 2\mathrm{NH}_{3}(\mathrm{aq}) + \mathrm{H}_{2}\mathrm{S}(\mathrm{aq}) \qquad (1)$$

As shown in previous reports, the $(NH_4)_2S$ molecules are readily dissociated into molecular species such as NH_3 , SH, and H_2S in H_2O solution. Thus, these dissociated molecular species, including NH_3 , SH, H_2S , *etc.*, can readily adsorb on the bare WSe_2 surface when the WSe_2 samples are dipped in $(NH_4)_2S(aq)$ solution. The $(NH_4)_2S(aq)$ chemical treatments were performed at 300 K followed by a gentle spray of



Figure 3. Tuned band structure of WSe₂ via formation of new electronic states after $(NH_4)_2S(aq)$ chemical treatment. (a) A chemically treated WSe₂ surface with filled state STM imaging ($V_S = -1$ V, $I_T = 40$ pA). (b) Defects in chemically treated WSe₂ revealed with empty state STM imaging ($V_S = 1$ V, $I_T = 20$ pA). Note that (b) is imaged on the same surface area as (a). (c) High-resolution zoomed-in filled state STM image of the chemically treated WSe₂ surface acquired from the dashed square region marked in (b). The dashed purple circle marks the location of the CTI defects, whereas black 'X' denotes the defect-free lower terrace ($V_S = -0.8$ V, $I_T = 100$ pA). (d) STS plots obtained after $(NH_4)_2S(aq)$ chemical treatment from the lower defect-free terrace point X (black curve) and defect points inside the dashed purple circle (red and blue curves) as shown in (c). (e) Averaged STS curves of ML WSe₂ before (black curve) and after (red curve) $(NH_4)_2S(aq)$ chemical treatment. Each STS curve was averaged over 5–7 different STS curves measured on the WSe₂ surface distant from the step edges and domain boundaries.

isopropyl alcohol (IPA) to remove unintentional contaminants such as hydrocarbons, following which the samples were airdried.

The large area empty state STM image shown in Figure 2b reveals the surface of chemically treated MBE-grown ML WSe₂ with interspersed BL WSe₂ islands; noticeable surface changes were not clearly observed in the large area empty state STM imaging in this case, possibly due to imaging noise induced by weak interactions between the adsorbates and the STM tip. It is noted that the surface topographies of ML WSe₂ were also probed using atomic force microscopy (AFM) both before and after $(NH_4)_2S(aq)$ chemical treatment as described in detail in Section 2 of the Supporting Information. Moreover, as shown in Figure 2c, Raman spectra acquired on a mechanically exfoliated ML WSe2 surface before (black curve) and after (red curve) $(NH_4)_2S(aq)$ chemical treatment shows a negligible change in the characteristic Raman modes, that is, the A_{1g} and 2LM(M) modes, suggesting no change in the structural integrity of ML WSe₂ post-chemical treatment. It is noted that there is no clear evidence for the intercalation of SH molecules in the van der Waals (vdW) gap between adjacent WSe₂ layers. If a large number of SH molecules were indeed intercalated between adjacent WSe₂ layers, then the top WSe₂ layers should get delaminated. However, the Raman plots shown in Figure 2c, and later in Figure 5b, indicate that there is no noticeable change in the peak positions and peak widths (i.e., fwhm) of the WSe₂ Raman modes after chemical treatment. This implies that the structural integrity of WSe₂ is maintained even after chemical treatment. Therefore, it is hypothesized that SH molecules mostly adsorb on the top surface of WSe2 rather than intercalating between adjacent WSe2 layers. The chemical analysis of bulk WSe₂ before and after (NH₄)₂S(aq) chemical treatment using X-ray photoelectron spectroscopy (XPS), shown in Supporting Information Section 3, also reveals that the $(NH_4)_2S(aq)$ chemical treatment does not induce any chemical oxidation or decomposition of WSe₂.

After the chemical treatment of ML WSe₂ using 20% $(NH_4)_2S(aq)$ solution, a large density of electronic states was indeed observed by STM on the WSe₂ surface under optimized imaging conditions. As shown in Figure 3a, the chemically treated ML WSe₂ showed filled state STM imaging (-1 V bias) similar to that of a bare ML WSe₂ surface, as shown in Figure 1(b), that is, the step edges are electrically enhanced, while defects are not clearly observed on the terraces. However, switching the imaging mode to empty states with a +1 V sample bias in Figure 3b, a high density of adsorbate-like features was observed on the terraces as well as step edges which can be denoted as chemical treatment-induced (CTI) defects.

To elucidate the nature of these CTI defects, the LDOS on the surface of chemically treated ML WSe2 was probed using STS. Figure 3c shows the high-resolution zoomed-in filled state STM image of the CTI defects, acquired from the dashed square region marked in Figure 3b, by precisely positioning the STM tip at their locations. STS curves were measured at the defect-free lower terrace (marked by \times) and at the location of the CTI defects (inside the dashed purple circle). As shown in the STS spectra in Figure 3d, three different STS curves were observed, as depicted by the red, blue, and black curves, within the voltage range of -1 V to +1 V. In comparison to the black curve acquired at the defect-free lower terrace, both the red and blue STS curves acquired on the adsorbed CTI defects reveal that the band edge states expand across the Fermi level position (0 V) and have larger LDOS near the WSe₂ VBE (*i.e.*, below the Fermi level), thereby, confirming that the Fermi level at the CTI defect sites is positioned closer to the ML WSe₂ VBE after $(NH_4)_2S(aq)$ chemical treatment. It is noted that probing the sample surface using STM tips relies on the feedback of tunneling current between metal tips and sample surfaces, while maintaining only a few angstrom (Å) distance. Thus, if mobile molecules or atoms are placed between the metal tip and sample surfaces, the interaction of metal tip with



Figure 4. Electronic band structures of bare and chemically treated ML WSe₂ calculated *via* DFT. (a) Calculated band structure of ML WSe₂, with and without adsorbed species, *versus* energy. Only the adsorption of chemically generated "SH" molecules on the WSe₂ surface introduces in-gap states and shifts the Fermi level toward the WSe₂ valence band edge (red curves). Adsorption of other molecular species $(S, H_2S, and NH_3)$ has a negligible effect on the ML WSe₂ band structure. Total DOS for (b) bare ML WSe₂, (c) ML WSe₂ with a single SH molecule adsorbed, and (d) ML WSe₂ with two SH molecules adsorbed. In the latter two cases, the increase in the DOS right below the VBE is indicated by black arrows. The modeled atomic structure corresponding to each of these cases is shown on the right. A free-standing ML WSe₂ layer is considered in all cases. Note that for the localized defect-induced states, the partial occupancy of both spin up and spin down states is energetically unfavorable due to the strong repulsive interaction between localized electrons (see Supporting Information Figure S4).

molecules induces STM imaging noise (horizontal lines) as shown in Figures 2b and 3a-c.^{52,53}

Based on the observation of STS measurements on adsorbed CTI defects, it can be hypothesized that if the density of CTI defects increases on ML WSe₂, then the overall charge carrier density increases. Moreover, since both the blue and red STS curves corresponding to CTI adsorption sites reveal a larger density of electronic states near the WSe₂ VBE, it can be hypothesized that the population of positive charge carriers (holes) should be larger than the population of negative charge carriers (electrons), resulting in an enhanced p-type behavior. This CTI electronic transition in ML WSe₂ is further confirmed by the large range STS spectra shown in Figure 3e. It is noted that in Figure 3e, during STS measurements on the surface of $(NH_4)_2S(aq)$ -treated WSe₂, the STM tip mostly approaches the adsorbed molecules on WSe₂ (physical distance <1-3 nm to molecules). Each STS curve was averaged over 5-7 curves with each curve recorded from random positions on multiple ML WSe₂ samples while intentionally avoiding domain boundaries and step edges, but not the defects. Although some of the recorded STS data may

have been on defects, the final STS curves should represent a random sampling of terrace sites. As shown in the LDOS of bare ML WSe_2 (black curve), an electronic band gap of ${\sim}2.1$ eV can be observed consistent with previously reported values. $^{54-56}$ However, $(\mathrm{NH}_4)_2\mathrm{S}(\mathrm{aq})$ chemical treatment of ML WSe₂ for 15 min at 300 K induces a reduction of this electronic band gap to ~1.1 eV and pins the Fermi level closer to the edge of the valence band, as shown by the red STS curve in Figure 3e. Therefore, both the density of charge carriers and the electronic band gap of WSe₂ can be tuned by defect engineering utilizing $(NH_4)_2S(aq)$ solution. Based on the averaged STS data, a greater enhancement in hole concentration than electron concentration can be predicted over the chemically treated ML WSe₂ surface. It is noted that the detectable limit of tunneling current is about ± 1 nA in the *I*–*V* curves during STM/STS probing. Therefore, current levels above ± 1 nA cannot be measured, and, instead, they are only shown as a steady current of ± 1 nA.

To determine the exact mechanism underlying the aforementioned electronic transition in WSe₂ after $(NH_4)_2S$ -(aq) chemical treatment, DFT calculations were performed to



Figure 5. Spectroscopic and electrical characterization of a chemically treated back-gated FL WSe₂ FET. (a) Optical image and schematic illustration of the back-gated FL WSe₂ FET with Ni/Au top contact electrodes. (b) Raman spectra taken on a FL WSe₂ device flake (\sim 3–4 nm thickness) before (black curve) and after (red curve) (NH₄)₂S(aq) chemical treatment. (c) Room-temperature back-gated transfer characteristics of the FL WSe₂ FET shown in (a) before (black curve) and after (red curve) (NH₄)₂S(aq) chemical treatment. A clear enhancement of I_{ON} in the p-branch is observed after (NH₄)₂S(aq) chemical treatment. (d) Qualitative equilibrium band diagrams along the FL WSe₂ FET channel before (top; bare FET) and after (NH₄)₂S(aq) chemical treatment (bottom; treated FET) explaining the enhanced p-type behavior and hole field-effect mobilities observed in chemically treated back-gated FL WSe₂ FETs.

compare the electronic band structures of ML WSe₂ before and after $(NH_4)_2S(aq)$ chemical treatment. The surface interaction between WSe2 and various chemically generated molecular species in the $(NH_4)_2S(aq)$ solution was determined; calculations were performed to model all the possible adsorbates (S, SH, H₂S, NH₃) from the sequence of reactions in (1), but only the "SH" adsorbates produced an electronic surface structure consistent with the experiments. As shown in Figure 4a, the adsorption of SH molecule on the WSe₂ surface exhibits a noticeable change in its electronic band structure; it induces the formation of acceptor-like in-gap states as well as an increase in the density of states (DOS) right below the WSe₂ VBE and shifts the Fermi level toward the WSe₂ VBE. Conversely, the adsorption of elementary S introduces additional states near both band edges without a Fermi level shift and slightly reduces the electronic band gap from 1.55 to 1.49 eV. When a H₂S or NH₃ adsorbate is applied on WSe₂, the DOS of WSe₂ is nearly consistent with extremely weak interactions. The effect of SH adsorbates on the WSe₂ band structure was investigated in more detail. The calculated electronic band structure of bare ML WSe₂ is shown in Figure 4b; an electronic band gap of about 1.55 eV is calculated with the Fermi level positioned closed to the middle of the band gap. However, as shown in Figure 4c, the adsorption of SH on WSe₂ induces the electronic band structure modification due to an increase in the DOS right below the WSe₂ VBE and formation of additional acceptor-like states in the band gap,

thereby, causing a shift of the Fermi level toward the WSe_2 VBE. It is noted that the calculated binding energy of SH molecules at the Se atom site of WSe_2 is 0.48 eV. Introduction of the second SH molecule onto the surface of WSe_2 induces an additional increase in both the DOS below the WSe_2 VBE and acceptor-like in-gap states, as shown in Figure 4d. The details of the DFT calculations are included in Section 4 of the Supporting Information. Based on the DFT modeling results, it can be hypothesized that the adsorption of "SH" molecules is responsible for the p-type doping and electronic band gap reduction observed in WSe₂ after $(NH_4)_2S(aq)$ chemical treatment.

It is noted that in the STS curves shown earlier in Figure 3e, quantification of the exact change of ML WSe₂ electronic band gap with $(NH_4)_2S(aq)$ chemical treatment is challenging because of the limited energy resolution and relatively high sample temperature (100 K). In addition, STM lacks chemical selectivity, and, thus, identifying a chemically induced adsorbate using STM is challenging. However, as shown in Figure 4, DFT reveals that as SH molecules adsorb on the surface of WSe₂, additional electronic states are introduced in the band gap as well as right below the VBE consistent with pdoping and band gap narrowing. Therefore, it is hypothesized that the p-doping and electronic band gap reduction in $(NH_4)_2S(aq)$ -treated ML WSe₂ results from the introduction of additional energy states in the WSe₂ band structure with the adsorption of a large density of SH molecules.^{57–59} It is noted that the present DFT model is simplified with a limited number of SH adsorption sites (only one and two) on the WSe₂ surface, because a DFT calculation with a large density of SH adsorption on WSe₂ would require an enormous processing time and complicated models. Conversely, as shown earlier in the STM images of $(NH_4)_2S(aq)$ -treated ML WSe₂, a large coverage of adsorbate-like CTI defects is observed on the WSe₂ surface which includes SH molecular adsorbates among others, and, therefore, it can be inferred that multiple adsorbed SH molecules induce the generation of a large DOS in the WSe₂ band structure consistent with p-type doping and electronic band gap reduction.

To further substantiate the STS and DFT results, the hole doping induced in WSe₂ by the one-step $(NH_4)_2S(aq)$ chemical treatment process was also investigated via the electrical characterization of FL WSe2-based FETs. Details of the device fabrication process can be found in the Methods section. Figure 5a illustrates the schematic of a back-gated FL WSe₂ FET along with an optical micrograph of a typical FET used in this study. The FL WSe₂ flake is first characterized using Raman spectroscopy (see Methods section for details of the Raman measurement). Figure 5b shows the Raman spectra acquired on the FL WSe₂ device flake before (black curve) and after (red curve) $(NH_4)_2S(aq)$ chemical treatment (10 min at 300 K + quick IPA rinse + air-dry), revealing a negligible change in the peak positions or sharpness of the characteristic Raman modes of FL WSe₂, that is, the A_{1g} , 2LA(M), and B_{2g}^1 modes,⁶⁰ suggesting that the material/structural quality of the FL WSe₂ flake, much like the case of ML WSe₂ as shown in Figure 2c, remains unaffected by the $(NH_4)_2S(aq)$ chemical treatment.

The back-gated FL WSe2 FETs were electrically characterized at room temperature (300 K) under vacuum (base pressure: 6×10^{-6} mbar) in the dark, utilizing a Lakeshore probe station and a Keysight B1500A semiconductor parameter analyzer. The back-gate voltage V_{BG} was swept from negative to positive for all the current-voltage transfer characteristic measurements presented in the manuscript and Supporting Information, unless otherwise noted. The source and drain electrodes were kept constant for all measurements taken on any given FET. The flake thickness used in our FL WSe₂ FETs was in the range of 3-4 nm, corresponding to 4-5atomic layers. Figure 5c shows the semilog transfer characteristics (i.e., log I_{DS} vs V_{BG}) of the back-gated FL WSe₂ FET shown in Figure 5a, measured at $V_{DS} = 1$ V. The channel length (L) and width (W) of this device are 0.75 and 10 μ m, respectively. Before the $(NH_4)_2S(aq)$ chemical treatment, the as-fabricated FET displays an ambipolar behavior, typical of FL WSe_2 FETs with Nickel (Ni) contacts,⁶¹ as shown by the black curve. The I_{ON} in the p-branch and the n-branch are comparable, consistent with the contact metal Fermi level being pinned close to the midgap of FL WSe2. After the $(NH_4)_2S(aq)$ chemical treatment, the measured transfer characteristic shows a pronounced difference as evidenced by the red curve in Figure 5c. The back-gate voltage at which the p-branch current starts to emerge is slightly shifted toward more positive V_{BG} values after $(NH_4)_2S(aq)$ chemical treatment, suggesting a positive threshold voltage shift indicative of p-type channel doping. There is a large increase (~70×) in the p-branch $I_{\rm ON}$ (from ~200 nA/ μm to ~14 $\mu {\rm A}/$ μ m), whereas the n-branch I_{ON} remains largely unchanged (~100–150 nA/ μ m). Note that the present WSe₂ FETs display ambipolar behavior even after chemical treatment with fairly significant n-branch ON-currents. This is expected because the Fermi level of Ni typically pins slightly above the midgap in WSe₂ at the Ni/WSe₂ contact interface,⁶¹ and the present chemical treatment is done after complete FET fabrication (*i.e.*, after the fabrication of Ni/Au top source/drain (S/D) electrodes), implying that the p-doping is effective only on the exposed WSe₂ channel regions and not the channel extensions underneath the Ni/Au top contacts. Moreover, as elucidated via the STS and DFT results discussed before, the $(NH_4)_2S(aq)$ chemical treatment also induces a reduction in the overall electronic band gap of WSe₂, and it is likely that this electronic band gap reduction in the chemically treated WSe₂ channel regions contributes to such sustained n-branch currents in the present FETs. Therefore, owing to these reasons, ambipolarity is expected in our FL WSe2 FETs even after chemical treatment.

Since only the p-branch of the FL WSe₂ FET shows significant relative changes after $(NH_4)_2S(aq)$ chemical treatment, it is analyzed in more detail. As can be seen in Figure 5c, due to the increase in the p-branch $I_{\rm ON}$ after $(NH_4)_2S(aq)$ chemical treatment, the p-branch $I_{\rm ON}/I_{\rm OFF}$ ratio increases by 2 orders of magnitude (from ~10⁷ to ~10⁹). The extrinsic or two-point (2-pt.) field-effect hole mobility ($\mu_{\rm FE-h}$) is calculated from the linear transfer curves of the FET data shown in Figure 5c, using the expression:

$$\mu_{\rm FE} = (\delta I_{\rm DS} / \delta V_{\rm BG|max}) (L/W) (1/C_{\rm OX}) (1/V_{\rm DS})$$

where $\delta I_{\rm DS}/\delta V_{\rm BG}$ I_{max} is the maximum back-gated transconductance, L and W are the length and width of the channel, respectively, C_{OX} represents the geometric back-gate capacitance, and $V_{\rm DS}$ is the drain/source voltage. The present chemical treatment induces p-doping consistent with molecular SH adsorption on the WSe₂ FET channel. Since doping the channel near the contact regions reduces the contact resistance and increases the field-effect mobility of charge carriers in TMD-based FETs, the 'extrinsic' or '2-pt.' mobility equation (which includes the voltage drop across the series resistance of the contacts) was employed to estimate the relationship between the p-doping and changes in the hole field-effect mobility ($\mu_{\text{FE-h}}$) in the back-gated WSe₂ FETs. The $\mu_{\rm FE-h}$ of the bare FL WSe₂ FET was extracted to be ~3.5 cm²/ V s (*i.e.*, before $(NH_4)_2S(aq)$ chemical treatment), while the $\mu_{\text{FE-h}}$ after (NH₄)₂S(aq) chemical treatment was ~22.7 cm²/V s, showing about a $6 \times$ enhancement in the hole field-effect mobility. Similar device results, that is, enhancement of the pbranch I_{ON} and improvement in μ_{FE-h} , were obtained on four different back-gated FL WSe₂ FETs after (NH₄)₂S(aq) chemical treatment. The ambient stability of this $(NH_4)_2S(aq)$ chemical treatment process was studied by remeasuring the FET transfer characteristics after a period of 10 days following the initial measurement post-chemical treatment. The FETs displayed good ambient stability as they retained a majority of the chemical treatment-induced enhanced p-type behavior. Moreover, the $(NH_4)_2S(aq)$ chemical treatment process shows reversibility as the WSe₂ FET transfer characteristic almost returns to its initial state after subjecting the samples to a highvacuum annealing step at 340 °C. The repeatability, stability, and reversibility of the $(NH_4)_2S(aq)$ chemical treatment process can be seen in the transfer characteristics of another similar back-gated FL WSe₂ FET as discussed in Section 5, and shown in Figure S5, of the Supporting Information.

To understand the mechanism of WSe_2 FET operation before and after $(NH_4)_2S(aq)$ chemical treatment, simple qualitative equilibrium band diagrams along the FL WSe₂ FET channel are illustrated in Figure 5d. Before $(NH_4)_2S(aq)$ chemical treatment, the FL WSe₂ FET shows typical ambipolar behavior as the Ni Fermi level pins slightly above the midgap in WSe₂ at the Ni/WSe₂ contact interface, resulting in large Schottky barrier heights for both electron and hole injections as represented by Φ_N and Φ_P , respectively, in Figure 5d. After $(NH_4)_2S(aq)$ chemical treatment in the exposed channel region, the band profile along the channel changes due to the enhanced p-doping induced by the adsorbed SH species on the WSe₂ surface. This chemical p-doping results in an enhanced "upward" band bending in the entire WSe₂ channel region, resulting in a narrowing of the p-type Schottky barrier width as illustrated by the shaded light red oval regions in the bottom band diagram of Figure 5d. Note that the WSe₂ channel extensions directly underneath the Ni contacts are not affected by the $(NH_4)_2S(aq)$ chemical treatment, and, thus, the chemical p-doping is confined only to the exposed WSe₂ channel/access regions in this study. The overall effect of this $(NH_4)_2S(aq)$ chemical treatment-induced p-doping in the WSe₂ channel and access regions is that when similar negative back-gate voltages are applied (which causes an upward band bending in the WSe₂ layer due to electrostatic p-doping), it makes it relatively easier for the holes to get injected into the valence band of WSe2 via tunneling through the p-type Schottky barrier width present at the Ni/WSe2 contact interface. In other words, after $(NH_4)_2S(aq)$ chemical treatment on our WSe2 FETs, the combined effect of the chemical p-doping and electrostatic p-doping by the negative back-gate voltage results in an enhanced upward band bending in the WSe₂ channel leading to enhanced narrowing of the ptype Schottky barrier width, as opposed to the case before chemical treatment where the band bending is effected only by the negative back-gate voltage. Thus, enhanced p-branch ONcurrents and hole field-effect mobilities were obtained in our FL WSe₂ FETs after chemical treatment. Since Schottky barriers result in large contact resistances, it can be said that the $(NH_4)_2S(aq)$ chemical p-doping helps alleviate the p-type Schottky barrier-induced contact resistance in our FL WSe₂ FETs. This is consistent with other reports on TMD-based FETs where chemical doping in the channel/access regions has been shown to improve the FET performance by alleviating the Schottky barrier-induced contact resistance.⁶²

This contact resistance improvement effect after $(NH_4)_2S$ -(aq) chemical p-doping can be clearly observed in the detailed p-branch output $(I_{DS}-V_{DS})$ characteristics of another Nicontacted FL WSe₂ FET as shown in Figure S8 of Supporting Information Section 6, wherein the transfer characteristics (Figure S7), hysteresis behavior (Figure S10), and optical images (Figure S6) of the same FL WSe₂ FET before and after $(NH_4)_2S(aq)$ chemical treatment are also compared. Although the chemical treatment leads to an improvement in the ONcurrents and linearity of the p-branch $I_{\rm DS}-V_{\rm DS}$ curves at low $V_{\rm DS}$ values, some nonlinearity is still present in the p-branch output characteristics of the FL WSe₂ FET consistent with non-ohmic or Schottky-type contacts even after chemical treatment (see Figure S8 of Supporting Information Section 6). This signifies that the chemical p-doping technique used in this study only converts the p-type contacts from being "more" Schottky-type before chemical treatment (i.e., more nonlinearity in the output curves) to relatively "less" Schottky-type after chemical treatment. It is noted that Ni S/D contact electrodes were used in this study which typically pins slightly

above midgap in WSe2, resulting in ambipolar FET behavior and large Schottky barrier heights for hole injection.⁶¹ Consequently, Ni contacts are not optimized for efficient hole injection in WSe₂ and are partly responsible for the Schottky-type behavior observed in the p-branch of the FL WSe₂ FETs even after chemical treatment. Moreover, a $(NH_4)_2S(aq)$ solution with a fixed starting concentration $(20\% \text{ in } H_2O)$ was utilized for the chemical p-doping. In principle, the starting concentration as well as the treatment time of the $(NH_4)_2S(aq)$ solution can be varied to achieve different concentrations of adsorbed SH species on the WSe₂ surface, thereby, resulting in different p-doping levels ranging from nondegenerate doping in the channel region to degenerate doping in the S/D contact and access regions (as proof of concept, the p-doping evolution with increasing chemical treatment time using the 20% $(NH_4)_2S(aq)$ solution is demonstrated in Figure S9 of Supporting Information Section 6, along with an estimation of the 2D hole doping concentration after chemical treatment). Therefore, with the proper choice of the S/D contact electrode (e.g., high work function Pd or Pt), p-type ohmic contacts and highperformance WSe₂ PFETs might be fabricated with the simple one-step $(NH_4)_2S(aq)$ chemical functionalization technique.

CONCLUSIONS

The band structure engineering of 2D layered WSe₂ via the one-step $(NH_4)_2S(aq)$ chemical treatment method is demonstrated to enhance its p-type electrical performance. Molecularly resolved STM and STS reveal that chemical treatmentinduced defect adsorption on the WSe₂ surface induces this band structure transition; the electronic band gap of ML WSe₂ decreases from 2.1 to 1.1 eV, and the position of the Fermi level is shifted toward the WSe₂ VBE. The underlying mechanism responsible for this WSe₂ band structure modification is elucidated via DFT calculations which reveal that the adsorption of chemically generated "SH" molecules on the bare WSe₂ surface is consistent with the formation of additional acceptor-like states in the WSe₂ band gap as well as states right below the WSe₂ VBE, resulting in the overall electronic band gap reduction and shifting of the Fermi level toward the WSe₂ VBE. As a result of this electronic band structure transition in chemically treated WSe₂, an enhancement of the p-branch I_{ON} (up to 2 orders of magnitude) as well as the hole field-effect mobilities (up to $6\times$) is observed in back-gated ambipolar FL WSe₂ FETs. The facile nature of this one-step $(NH_4)_2S(aq)$ chemical functionalization process to tune the band structure of layered WSe₂ at room temperature, without requiring additional vacuum or other complicated processes, can provide a potential pathway to easily integrate the band structure engineering of TMDs into the conventional TMD transistor fabrication process.

METHODS

MBE and STM/STS Method. For STM/STS experiments, the WSe₂ layers were grown by molecular beam epitaxy (MBE) in an ultrahigh-vacuum (UHV) system (RIBER, MBE 32) on HOPG substrates. HOPG substrates were first cleaned by multiple exfoliation cycles. Afterward, the cleaned substrates were transferred immediately into the UHV chamber. WSe₂ layers were grown while the HOPG substrates were held at 1073 K for 20 min. Elemental W and Se were simultaneously dosed onto the HOPG surface using an electron beam source and a Knudsen cell, respectively. After the growth of WSe₂ layers on the HOPG substrates, about 20 nm Se capping layers were deposited on the WSe₂/HOPG samples to prevent unintentional

oxidation of the samples during transfer to the separate STM/STS UHV chamber (Omicron, base pressure: $<1 \times 10^{-10}$ Torr). After transferring the WSe2/HOPG samples into the STM chamber, Se capping layers were removed from the WSe2/HOPG samples by annealing at 750 K for 120 min. STM and STS measurements were performed using electrochemically etched tungsten tips.

Device Fabrication Process, Chemical Treatment Method, and Raman Characterization. Back-gated FL WSe₂ FETs were fabricated by first mechanically exfoliating WSe₂ flakes from commercially available bulk crystals (source: HQ Graphene) onto a degenerately doped p-type Si-100 substrate with 90 nm of thermally grown SiO₂. Upon exfoliation, the samples were subjected to a highvacuum annealing step (340 °C for 6 h; base pressure: 10⁻⁶ mbar) to minimize tape residues as well as trapped adsorbates between the WSe₂ flakes and the underlying SiO₂ substrate. FL WSe₂ flakes (3-4 nm, i.e., 4-5 atomic layers thick) were identified using a combination of optical microscopy and atomic force microscopy (AFM) imaging. Top contact electrodes were patterned using standard electron-beam lithography (EBL) utilizing a poly methyl(methacrylate) (PMMA) resist, following which Ni/Au (20/30 nm) metal electrodes were deposited using electron-beam evaporation and solvent lift-off steps to serve as the source/drain (S/D) electrodes. After device fabrication, the WSe₂ FET samples were dipped in the 20% $(NH_4)_2S(aq)$ solution for a specified time period, following which the samples were rinsed in IPA and dried in air. All chemical treatments were performed for 10 min unless otherwise noted. Note that, although acetone is a widely employed solvent to remove hydrocarbon residues, IPA does remove hydrocarbons as well, and, thus, a single step rinsing process with IPA was utilized in the present study. It is noted that the effect of $(NH_4)_2S(aq)$ chemical treatment on layered TMDs persists even after washing with acetone and water, as reported in previous publications (see refs 35 and 36). Raman spectroscopy measurements were taken with a Renishaw inVia micro-Raman system with an excitation wavelength of 532 nm and a grating of 3000 l/mm.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b09351.

Further discussion on the STM/STS measurements of MBE-grown WSe₂, detailed AFM and XPS study of $(NH_4)_2S(aq)$ -treated WSe₂, details about the DFT computational method, and additional FL WSe₂ FET results showing the repeatability, stability, and reversibility of the $(NH_4)_2S(aq)$ chemical treatment, evolution of p-doping with chemical treatment time, as well as a detailed comparison of the optical images, transfer characteristics, p-branch output characteristics, and hysteresis behavior before and after $(NH_4)_2S(aq)$ chemical treatment (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: akummel@ucsd.edu. **ORCID**

Jun Hong Park: 0000-0001-5138-1622 Amritesh Rai: 0000-0002-2639-711X Andrew C. Kummel: 0000-0001-8301-9855

Author Contributions

[¶]J.H.P and A.R. contributed equally to this manuscript. J.H.P., A.R., and A.C.K. conceived and designed this experiment. J.H.P. performed STM/STS and AFM experiments on MBEgrown WSe2. J.H.P. and A.C.K. analyzed the STM/STS data. XPS was performed by I.K. and S.W. Fabrication of exfoliated FL WSe₂ devices and their AFM, Raman, and electrical characterizations were performed by A.R. under the supervision of S.K.B. A.R. performed the PL studies on exfoliated ML WSe2. J.H. and C.Z. performed DFT calculations, and K.J.C. reviewed the calculations. Growth of MBE WSe₂ was performed by S.V., X.L. under the supervision of J.F., M.D., and H.G.X. All data were thoroughly discussed and analyzed by J.H.P., A.R., and A.C.K. J.H.P. and A.R. largely wrote the manuscript with contributions from all the authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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