

Contact Engineering of Layered MoS₂ via Chemically Dipping Treatments

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The performance of electronic/optoelectronic devices is governed by carrier injection through metal–semiconductor contact; therefore, it is crucial to employ low-resistance source/drain contacts. However, unintentional introduction of extrinsic defects, such as substoichiometric oxidation states at the metal–semiconductor interface, can degrade carrier injection. In this report, controlling the unintentional extrinsic defect states in layered MoS₂ is demonstrated using a two-step chemical treatment, (NH₄)₂S(aq) treatment and vacuum annealing, to enhance the contact behavior of metal/MoS₂ interfaces. The two-step treatment induces changes in the contact of single layer MoS₂ field effect transistors from nonlinear Schottky to Ohmic behavior, along with a reduction of contact resistance from 35.2 to 5.2 kΩ. Moreover, the enhancement of I_{ON} and electron field effect mobility of single layer MoS₂ field effect transistors is nearly double for *n*-branch operation. This enhanced contact behavior resulting from the two-step treatment is likely due to the removal of oxidation defects, which can be unintentionally introduced during synthesis or fabrication processes. The removal of oxygen defects is confirmed by scanning tunneling microscopy and X-ray photoelectron spectroscopy. This two-step (NH₄)₂S(aq) chemical functionalization process provides a facile pathway to controlling the defect states in transition metal dichalcogenides (TMDs), to enhance the metal-contact behavior of TMDs.

due to its low fabrication cost and outstanding performance.^[1] However, with the scaling of the channel length of Si field effect transistors (FETs) to a few nanometers, a fundamental limitation has arisen from the intrinsic challenges related to the 3D bulk body of the Si channel, such as power consumption and short channel effects.^[2] Intrinsically atomic-thin channel materials have been proposed as ultrathin channel bodies to enhance the gate control and suppress short-channel leakage.^[3] Coupling an intrinsically atomically thin body with a finite bandgap, layered transition metal dichalcogenides (TMDs) have been employed as semiconducting channel platforms with large ON/OFF ratio and near theoretical subthreshold swing.^[3b,4] TMDs demonstrate a finite bandgap which spans from 0.9 to 2.5 eV; therefore, they have been studied as alternative semiconductor channels. Additionally, the band structure of TMD can be governed by controlling the number of layers or surface functionalization, while the mobility of TMDs is comparable to existing heavily

doped thin Si channels;^[5] therefore, the applications of TMDs can be expanded to logic devices and optoelectronics.^[6]

Typically, the output performance of electronic/optoelectronic semiconductor devices can be altered by a change of

1. Introduction

Si-based complementary metal–oxide–semiconductors (CMOS) technology has driven the growth of the semiconductor industry

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resistance at the channel surface or the contact junctions.^[7] To fabricate electronic and optoelectronic transistors, it is crucial to form low resistance metallic electrodes (source/drain) on semiconductor channels to inject the charge carriers through metal–semiconductor interfaces. Afterward, when a carrier pathway is opened by electrostatic gate control or optical stimulation, injected charge carriers are transported via the semiconductor channel. The charge transfer process and the carrier mobility values can be degraded by existence of resistance sources at the contact interfaces or near the metal–semiconductor interfaces,^[7a,b,f] consistent with strong dependence of performance on existence of electrical resistance at the channel surfaces or metal–semiconductor interfaces.

One of known sources for resistances of the TMD devices is unintentional oxidation/interfacial states at the channel surface or contact interfaces formed during TMDs growth and the device fabrication process.^[8] Typically, the growth of TMDs via chemical vapor deposition/transport (CVD) is initiated from the reduction of solid metal oxides (MO_x or WO_x) by reaction with elementary S or Se to induce the formation of crystalline TMDs.^[9] The TMDs are transferred to ambient air for standard semiconductor devices fabrication processing.^[10] It has been reported that the deposition of metal contacts on TMD surfaces in high vacuum (about 10^{-5} – 10^{-7} Torr) involves the formation of metal oxide at the metal/TMDs interface due to metal–background gas reactions.^[8a,b] Therefore, during these growth and fabrication processes, the defective metal oxides or byproducts including other possible contaminants (e.g., hydrocarbon) can be unintentionally introduced in the TMDs. These nonstoichiometric metal oxides can have dipoles and defect states near Fermi energy level; therefore, the carriers can be trapped or scattered by metal oxides located at the channel surfaces or at the metal/TMDs interfaces.^[11] Moreover, existence of chemical disorder can induce the Fermi level pinning, consistent with degradation of contact performance.^[12] Therefore, it is crucial to control the chemical states at the TMD surfaces and remove the defective states to enhance the electric and optical properties of TMDs. However, there are few reports of the selective removal of these oxides from TMDs without degradation of pristine TMDs crystallinity because the metal oxides at the TMDs are thermodynamically more stable than the crystalline TMDs.

In this report, an effective chemical method to remove MoO_x from layered MoS_2 surfaces leading to enhancement of electrical output performance is demonstrated. The present technique is composed of two steps: surface chemical reaction, using an $(\text{NH}_4)_2\text{S}$ (aq), and annealing in vacuum. Using scanning tunneling microscopy (STM) and spectroscopy (STS) of bulk MoS_2 before and after the two-step $(\text{NH}_4)_2\text{S}$ (aq) treatment is employed to elucidate the effects of treatment on atomic scale topographical and electronic properties of MoS_2 . To track the chemical transition from the two-step treatment of MoS_2 , X-ray photoelectron spectroscopy (XPS) is employed; both STM/STS and XPS results reveals that the oxidation states are removed after dipping MoS_2 into $(\text{NH}_4)_2\text{S}$ (aq) and vacuum annealing, while the crystal structure and Mo/S ratio of MoS_2 are maintained. As a result of the removal of oxygen defects by the two-step process on MoS_2 , the Schottky contact behavior of bare

single layer MoS_2 FETs with Au/Cr metal contact transitions to Ohmic contact behavior with a reduction of contact resistance by 6 X. Moreover, this two-step treatment induces mobility enhancement of MoS_2 by about 3 X, as well as an increase of 4 X in ON state driving current. That data is consistent with defect engineering via a simple and facile chemical treatment to enhance metal-TMDs contacts, thereby enabling relatively simple integration of this chemical functionalization into conventional semiconductor processing.

2. Result and Discussion

2.1. Raman and Photoluminescence Analysis of Two-Step Treated MoS_2

The process of two-step functionalization to enhance of the electronic performance of MoS_2 is described in the schematic diagram of **Figure 1a**. Commercially available $(\text{NH}_4)_2\text{S}$ is employed with dilution in H_2O to 20%; bare MoS_2 flakes are dipped in the $(\text{NH}_4)_2\text{S}$ (aq) solution for 10 s, then the treated samples are washed for 60 s with isopropanol. Afterward, the samples are transferred to the vacuum for the annealing process. During the annealing process of treated MoS_2 , the temperature is held at 473 K in the vacuum ($P < 5 \times 10^{-6}$ torr) and annealing duration is limited in 10 min.

To elucidate the effect of two-step treatment on MoS_2 flakes, CVD grown single layer MoS_2 is spectroscopically probed using Raman spectroscopy. As shown in **Figure 1b**, Raman spectroscopy of a bare CVD single layer MoS_2 sample is performed in ambient with excitation at 532 nm; two prominent vibrational modes can be observed at 384.8 and 402.9 cm^{-1} , referred as the in-plane vibrational mode E_{2g}^1 and out-of-plane vibrational mode A_{1g} respectively, and the peak-to-peak distance is about 18.1 cm^{-1} , consistent with the Raman spectra of single layer MoS_2 in previous reports.^[13] After the two-step treatment of single layer MoS_2 , similar Raman vibration behavior can be observed as shown the red curve; the E_{2g}^1 and A_{1g} peaks are detected at 384.7 and 402.7 cm^{-1} respectively and are at nearly identical positions to the peaks in the Raman spectra of bare MoS_2 ML. The peak-to-peak distance of the chemically treated MoS_2 ML is 17.9 cm^{-1} similar to the value of bare MoS_2 ML, indicating the present two-step treatment does not induce transformation of the crystal structure of single layer MoS_2 .

The efficacy of exciton generation is improved with the present two-step treatment as determined by photoluminescence (PL) spectroscopy. As shown in **Figure 1c**, the change in PL of MoS_2 is tracked with constant laser power (1 mW) and wavelength on the same CVD single layer MoS_2 flake upon two-step treatment. Prior to $(\text{NH}_4)_2\text{S}$ treatment and annealing, the MoS_2 single layer has two prominent broad peaks at 672 nm and 628 nm, referred to as A and B respectively, consistent with previous reports.^[14] The two major peaks, A and B, result from the spin-orbit splitting of the valence band in MoS_2 single layers. After the two-step treatment of the MoS_2 single layer sample, the intensity of both A and B peaks greatly increases as shown by the red curve. Although the position of PL peaks for treated MoS_2 ML are

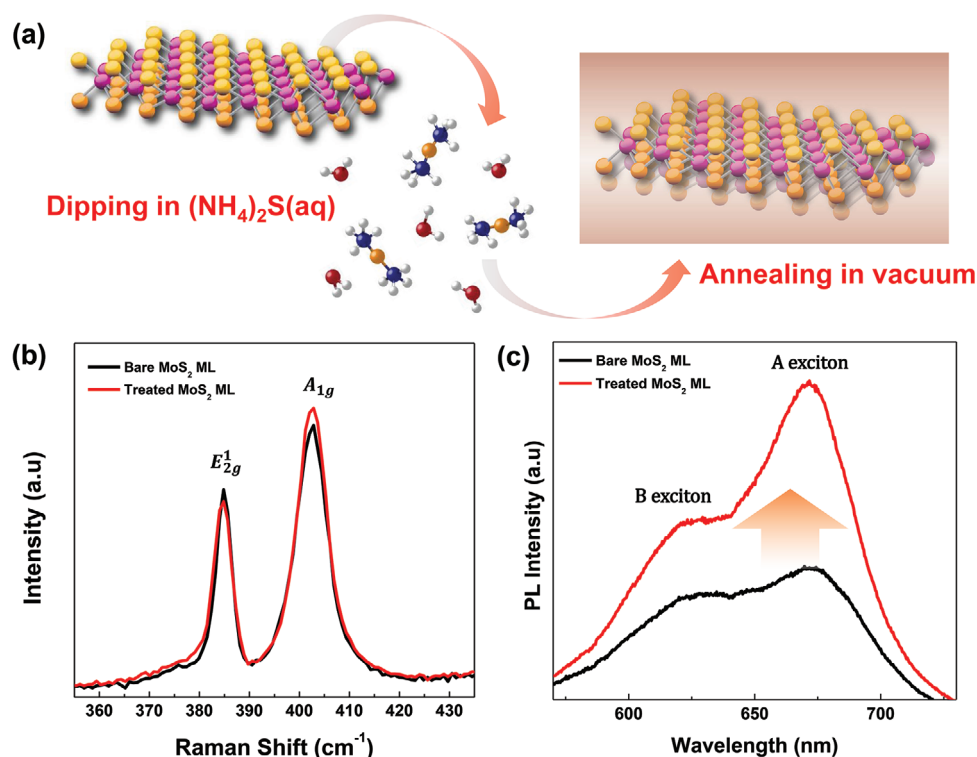


Figure 1. Raman and photoluminescence (PL) spectra of single layer MoS₂ before and after (NH₄)₂S(aq) chemical treatment and annealing at 473 K. a) Schematic diagram illustrating the two-step chemical treatment process, consisting of (NH₄)₂S(aq) treatment and followed annealing processes. b) Raman spectra of single layer MoS₂ with 532 nm laser excitation. c) PL spectra of single layer MoS₂ under a 532 nm laser excitation with 1 mW incident power.

nearly identical to the position of PL peaks for bare MoS₂ ML, the intensity of PL peak A increases 50% with chemical treatment, while the intensity of PL peak B is enhanced more than 100% with chemical treatment. The improvement of PL is consistent with an increase of quantum yield for exciton formation by removal of optically unfavorable defects at the surface of MoS₂,^[9c] which is confirmed below.

2.2. Electrical Characteristic of Two-Step Treated MoS₂: Transition of Contact Behavior

The electronic impact of two-step treatment to MoS₂ ML is elucidated by electronic characteristic of back-gated MoS₂ FETs at 300 K under vacuum (1×10^{-5} torr) in the absence of light. The back-gated FETs are fabricated with the CVD grown single layer MoS₂ on SiO₂/Si substrates. Once the MoS₂ single layer is located at the desired place on SiO₂/Si, the MoS₂ layer is trimmed to a rectangular shape (channel width of 3 μ m) using electron beam lithography and SF₆ reactive etching. Afterward, Au/Cr pads (total thickness: 50 nm) are defined by electron-beam deposition (P : 1×10^{-6} torr) and lithographic patterning to carry out transfer length measurement (TLM), as shown in Figure 2a. The schematic diagram in Figure 2b reveals three different channel lengths, denoted as the L1 (1.68 μ m), L2 (5.50 μ m), and L3 (13.72 μ m) channels; these are employed to determine the total resistance (R_T) between two successive metal contacts.

The transfer characteristics of channels L1, L2, and L3 are shown in Figure 2c with forward (negative to positive) and backward (positive to negative) sweeping of the back-gate bias V_{BG} , while the drain bias V_{DS} is kept at 0.01 V. As shown in the transfer curve of the single MoS₂ FETs, bare MoS₂ reveals n -dominant behavior for all channel L1, L2 and L3, consistent with typical single layer MoS₂ FETs.^[3c,15] The measured transfer characteristic of two-step treated MoS₂ FETs is shown in the dotted curve; the position of back-gate voltage where the n -branch current starts to emerge is shifted toward negative V_{BG} values (about -35 to -39 V) after (NH₄)₂S(aq) chemical treatment, consistent with a negative threshold voltage shift. It is noted that to prevent the thermal damage during metal-MoS₂ contact formation, the annealing temperature is limited to 473 K. However, since elementary S is highly volatile in ambient due to formation of SO_x,^[16] the impact of elementary S adlayer from (NH₄)₂S(aq) on the MoS₂ surface in electric enhancement of MoS₂ transistors can be considered to be negligible. Although I_{OFF} of L1, L2, and L3 is nearly constant, I_{ON} at the n -branch increases with negative shift of threshold voltage; therefore, the I_{ON}/I_{OFF} ratios between $V_{BG} = -60$ and $+60$ V of all treated channels are improved 4 X. It is noted that the present two-step treatment involves vacuum annealing at 473 K; therefore, it is hypothesized that molecular adsorbates, such as HS,^[17] would be mostly removed from MoS₂ surface by annealing in vacuum. Moreover, NH₃ or H₂S have negligible effects on the electronic structure of TMDs as shown in previous report.^[17] Since the Raman spectra in Figure 1b

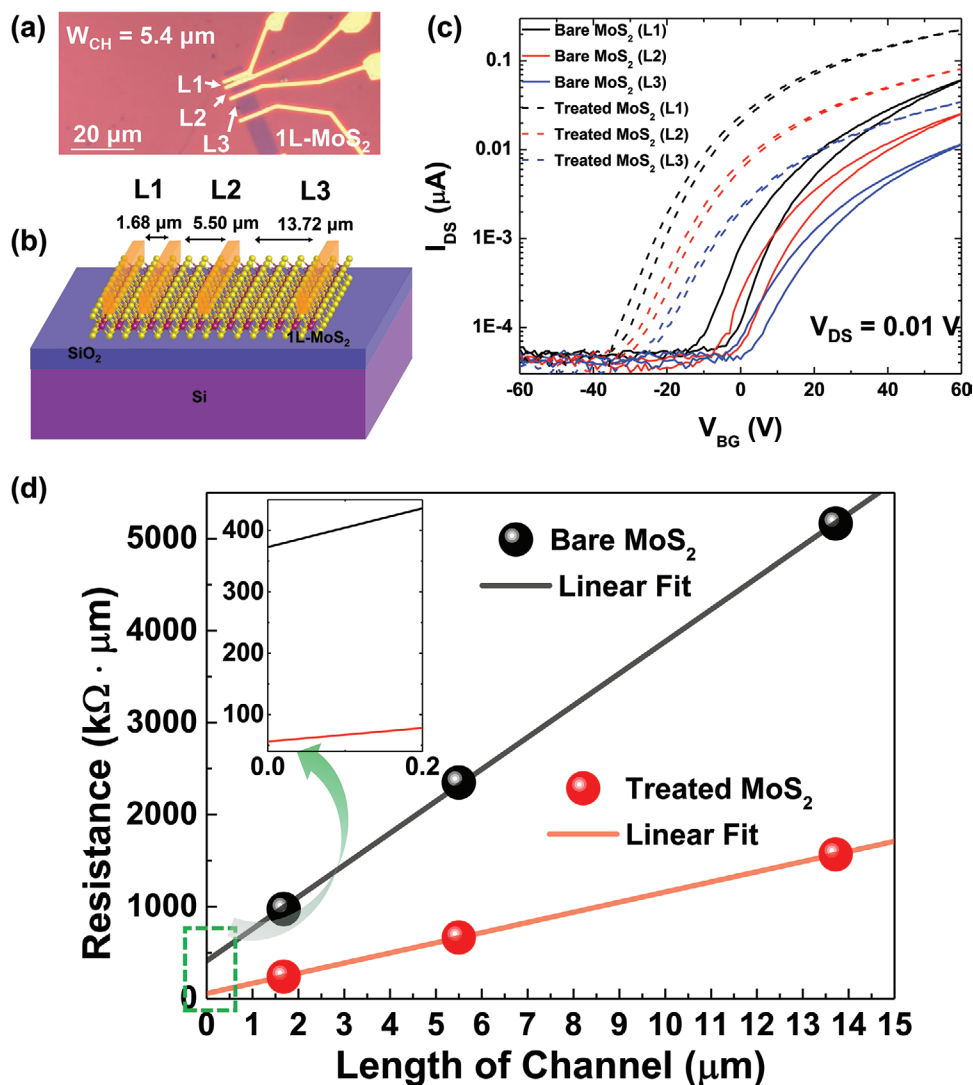


Figure 2. Transfer length measurement of single layer MoS₂ before and after (NH₄)₂S(aq) chemical treatment and annealing at 473 K. a) Optical image of TLM structure for MoS₂ with channel length L1, L2, and L3. It is noted that the channel width (W_{CH}) is 5.4 μm. b) Schematic illustration of the MoS₂ TLM FET. The channel lengths of L1, L2, and L3 are 1.68, 5.50, 13.72 μm, respectively. c) Back-gated transfer curves of channel L1, L2, and L3 in log scale. Solid curves correspond to bare single layer MoS₂, while dotted curves correspond to treated single layer MoS₂. d) Resistance versus channel lengths of single layer MoS₂ for Au/Cr contacts. The resistance of bare MoS₂ is shown as a black line, while the resistance of treated MoS₂ is shown as a red line. Inset is enlarged R_{TOT} versus L_{CH} near $L = 0$ to determine zero-distance contact resistance of MoS₂.

reveal that the two-step treatment does not induce structure changes in MoS₂, the shift of threshold voltage in Figure 2c is unlikely to be the result of surface or substitutional doping of MoS₂. Instead, improvement of carrier transport behavior with the two-step treatment is likely one of the sources of source of the threshold voltage shift, as shown in Figure S7 (Supporting Information). As a result of the improved ON/OFF ratio, the subthreshold swing (SS) below the V_{TH} are improved from 8.19 to 3.4 V dec⁻¹ with the two-step chemical treatment.

The field effect mobility of electron (μ_{FE-e}) is extracted using linear I - V transfer curves from the back-gated transistors, using Equation (1)

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

where $\delta I_{DS} / \delta V_{BG} |_{\max}$ is the maximum back-gated transconductance. L and W are the length and width of the channel, respectively. $C_{OX} (= \epsilon_0 \cdot \epsilon_r / d; \epsilon_r = 3.9)$ represents the back-gate capacitance of SiO₂ (285 nm). Using this equation, the μ_{FE-e} of the bare single layer MoS₂ FET is determined as 7.4–11.42 cm² V⁻¹ s⁻¹, while the μ_{FE-h} of treated single layer MoS₂ FET is estimated to be 13.6–17.69 cm² V⁻¹ s⁻¹, consistent with about over 60% enhancement in the electron mobility.

To elucidate the origin of enhancement in the electric performance of single layer MoS₂, total resistance (R_T) of MoS₂ as a function of channel length is determined using a TLM configuration. The total resistance (R_{TOT}) of bare single layer MoS₂ is plotted as a function of distance between electrodes in Figure 2d. After the two-step treatment of same MoS₂ FET, the

total resistance of treated MoS₂ at L1, L2, and L3 is reduced, as shown in the red line in Figure 2d. The contact resistance (R_C) of bare MoS₂ with Au/Cr contact is about 35 k Ω , while the R_C of treated MoS₂ with Au/Cr is determined to 5.2 k Ω , consistent with decreases of R_C by a factor of ≈ 6 . Consequently, the present two-step treatment induces the improvement of carrier transfer behavior at the metal-MoS₂ channel contact junctions, resulting in reduction of contact resistance.

The reduction of contact resistance via the two-step treatment is confirmed with output characteristics curves with tracking of the degree of linearity in I_D - V_{DS} . All gate-dependent output characteristics in Figure 3 are measured with same sweep rate 0.2 V s⁻¹. Figure 3a reveals that I_D is nonlinearly correlated with V_{DS} , consistent with a Schottky behavior of metal contacts on single layer MoS₂. For $V_{BG} = 40$ V, the output current (I_{ON}) is ≈ 3.2 μ A, when V_{DS} is 1.0 V, consistent with the existence of n-branch Schottky barrier across the path from

the metal pad to the single layer MoS₂ channel. Moreover, as V_{DS} is swept forward (negative to positive branch) and backward (positive to negative branch), a large hysteresis can be observed as shown in Figure 3b. It has been reported that the hysteresis of transistors originates from extrinsic defects, such as molecular adsorption on the semiconductor channel or sub-stoichiometric oxide/carbide in the channel because these "extrinsic defects" can act charge trapping/scattering centers^[18] to degrade the efficiency of carrier injection over contact barriers. Conversely, as shown in Figure 3c, the two-step chemical treatment induces an increase of I_D by a factor of ≈ 3 X ($I_{ON} \approx 13$ μ A for $V_{BG} = 40$ V and $V_{DS} = 1.0$ V), and I_D linearly increases upon sweeping V_{DS} from negative to positive bias, consistent with near-Ohmic behavior of single layer MoS₂ FET. This significant improvement of contact behavior is consistent with the present two-step chemical treatment inducing the removal of oxidative defects access region of MoS₂ channel. This implies

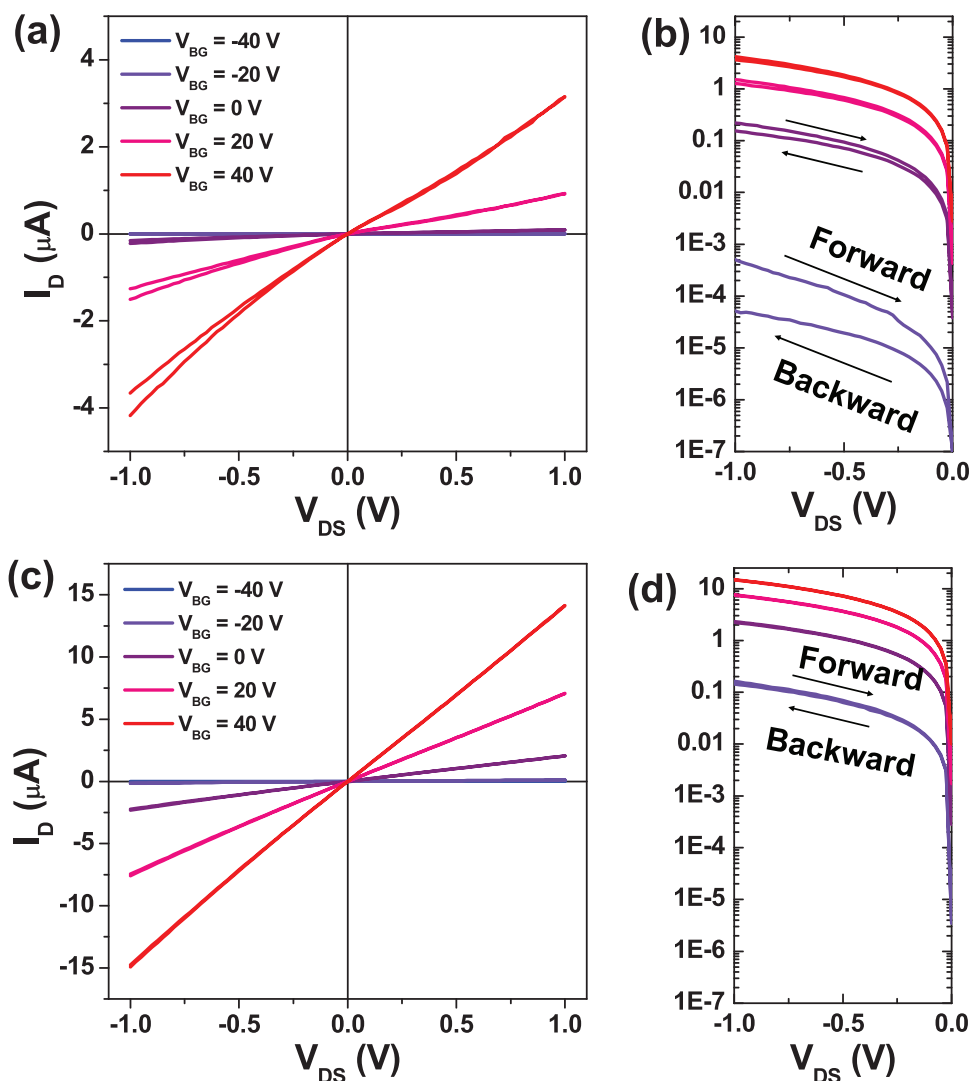


Figure 3. Output and hysteresis characteristic of bare single layer MoS₂ FET and treated single layer MoS₂ FET. a) Output characteristic of bare single layer MoS₂ FETs (channel L2 of Figure 4) with a linear scale. b) Expanded output characteristic plot of (a) from -1.0 to 0 V with a logarithmic scale. c) Output characteristic of treated single layer MoS₂ FET (L2) with a linear scale. d) Expanded output characteristic plot of (b) from -1.0 to 0 with a logarithmic scale.

that electron injection from the Au/Cr contacts into the MoS₂ is facilitated with removal of carrier trapping/scattering centers. The electric enhancement in MoS₂ FETs can be also confirmed with the significant reduction of hysteresis, as shown in Figure 3d; the removal of oxidative defects in MoS₂ results in facile electron transfer with suppression of carrier trapping/scattering near extrinsic defects.

2.3. Surface Chemistry of MoS₂ during Two-Step Treatment

To confirm that removal of oxidative defects is the origin of enhanced metal contact behavior of MoS₂ FETs with the present two-step (NH₄)₂S(aq) treatment, STM and STS are performed on the MoS₂ surface before and after (NH₄)₂S treatment and annealing. Prior to treatment, two different areas of MoS₂ bulk are probed to verify the initial properties of MoS₂ surface. As shown in Figure 4a,b, two different types of defects are observed on bare surface of MoS₂ bulk at 2 V (empty states) and at -2 V (filled states); bright features (white circles) can be observed on the surfaces of MoS₂, while dark features (yellow circles) are detected with smaller density than white corrugation. The bright features are visible in both empty and filled state imaging modes, consistent with a structural protrusion, rather than an electronic effect. Previous reports reveal that the surface of MoS₂ with low defects density is typically smooth and atomically flat on various substrates, opposite to the present MoS₂ STM images. It is noted that previous reports reveal that metallic defects on MoS₂ are observed in only empty state or filled state imaging modes^[19] and molecular adsorption on MoS₂ typically involves the dark circles surrounding the adsorbates, consistent with the electron depleted regions. Consequently, it is hypothesized that observed protrusions arise from the formation of extrinsic defects in synthesis or ambient

conditions, rather than existence of metallic defects or adsorption defects.

After verification of MoS₂ surface using STM and STS, the two-step chemical treatment is performed with the same MoS₂ bulk sample. After dipping bulk MoS₂ in (NH₄)₂S(aq) at 300 K without annealing process, the large area empty state STM image in Figure 4c shows the surface of treated MoS₂ with horizontal noise;^[20] this is consistent with weak interactions between molecular adsorbates and the STM metal tip at 100 K. The status of STM tip can be chemically and physically altered, resulting in STM tip noise along the scan direction. To elucidate the effect of aqueous (NH₄)₂S treatment on the surface of MoS₂, excess adsorbates are removed from the MoS₂ by thermal annealing at 523 K for 5 min in the ultra high vacuum (UHV) chamber. As shown in Figure 4d, the flat surface of treated MoS₂ is shown without observation of white defects. After additionally annealing the same sample in the UHV chamber at 673 K, a hexagonal array of S atoms in MoS₂ surface is observed in an atomically resolved STM image (Figure 4e), consistent with the hexagonal pattern observed in the Fourier transform image of the inset; the interatomic distance of S atoms is about 0.33 ± 0.01 nm, which is consistent with previous reports.^[21] The large area images with two different areas in the Supporting Information show that there are no “white protrusion” defects in the two-step treated MoS₂ surface and only dark metallic defects can be observed in two-step treated MoS₂.

The electronic structure transition of the MoS₂ surface upon chemical treatment and vacuum annealing is probed using STS. As shown in Figure 4f, the initial band structure is shown as a black curve; the measured bandgap is ≈1.2 eV with the Fermi level positioned near conduction band edge.^[19a,22] After aqueous (NH₄)₂S treatment, the bandgap is expanded about 1.8 eV and the Fermi level is positioned in the middle of bandgap. The expanded bandgap (≈1.8 eV) of the MoS₂ surface remains after UHV annealing at 523 K, while the Fermi level position is

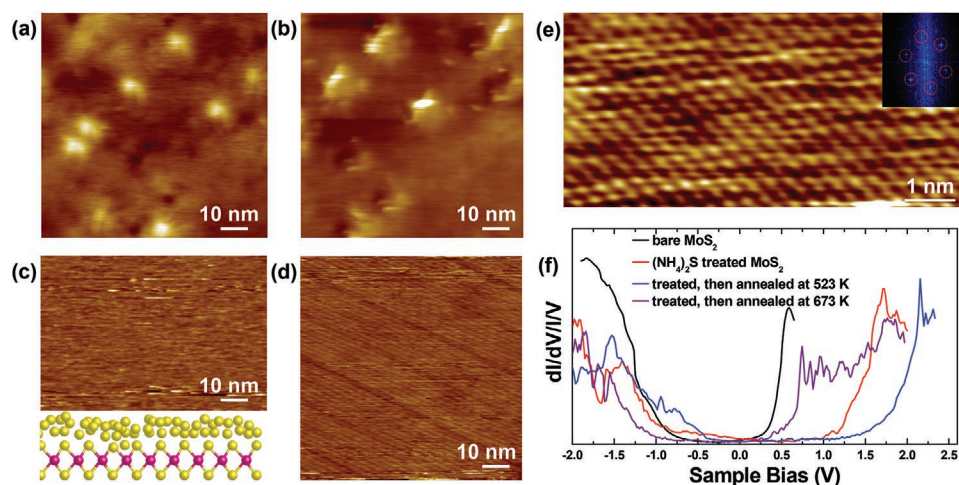


Figure 4. Scanning probe microscopy and spectroscopy of bulk MoS₂ before and after (NH₄)₂S treatment and annealing processes. a) Empty state STM image of bare bulk MoS₂ ($V_S = 2$ V, $I_T = 40$ pA). b) Filled state STM image of bare bulk MoS₂ ($V_S = -2$ V, $I_T = 40$ pA). It is noted that STM images in (a) and (b) probe different areas on the same sample. c) Empty state STM image of (NH₄)₂S(aq) treated MoS₂ with no anneal ($V_S = 2$ V, $I_T = 20$ pA). d) Empty state STM image of (NH₄)₂S(aq) treated MoS₂, after annealing 473 K in the UHV chamber for 30 min ($V_S = 2$ V, $I_T = 20$ pA). e) Atomically resolved STM image of (NH₄)₂S(aq) treated MoS₂, after annealing 573 K in the UHV chamber for 30 min ($V_S = -0.8$ V, $I_T = 380$ pA). Inset displays the Fourier transform of the STM image. f) Local density of states (LDOS) of bulk MoS₂ surface probed via STS after two-step treatment. Each curve is averaged from five to seven individual STS curves.

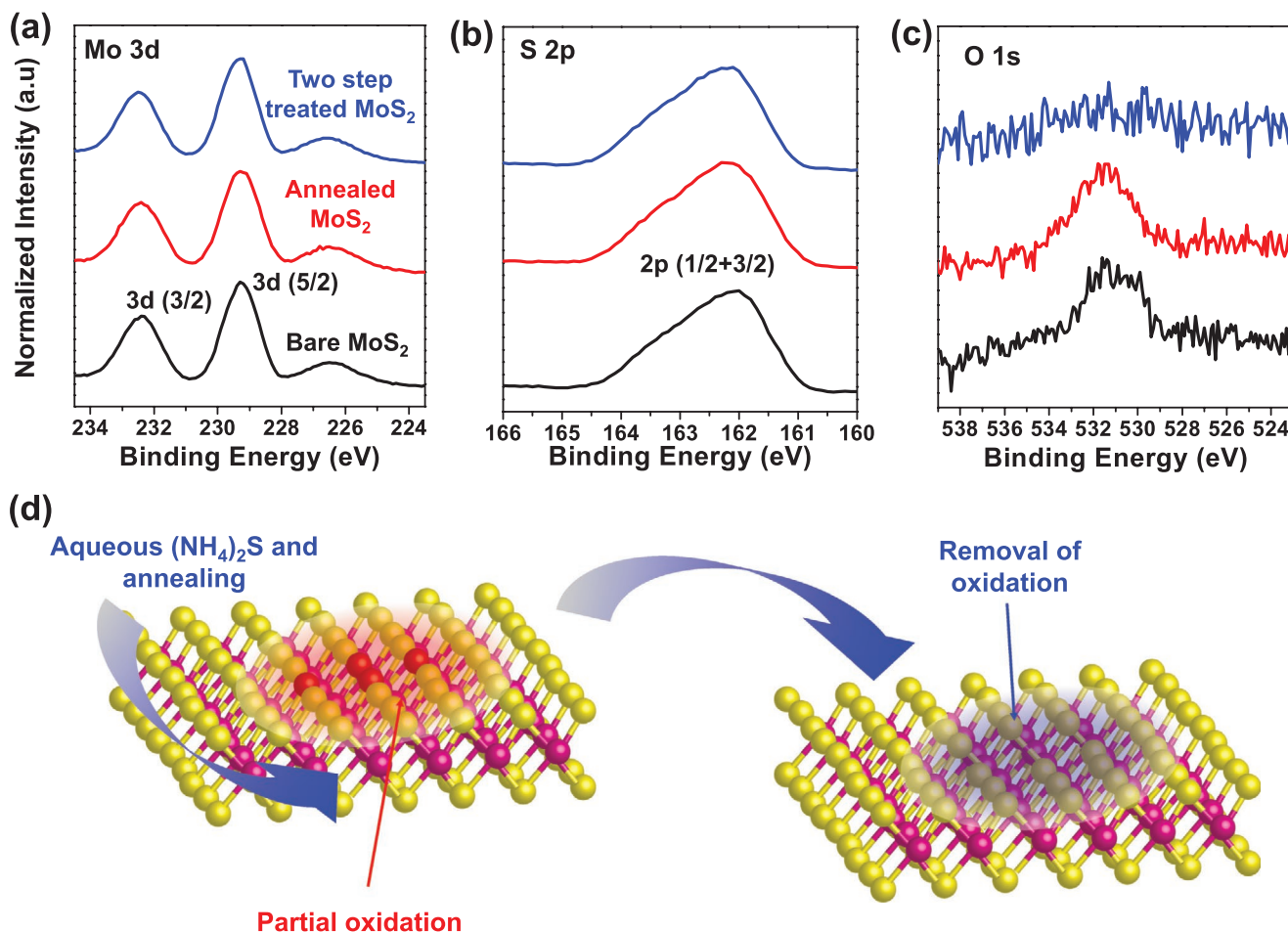
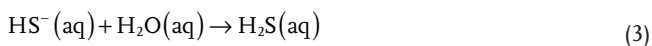
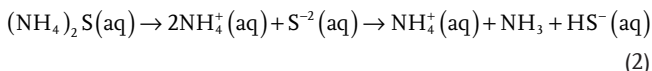
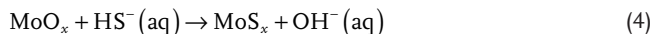


Figure 5. XPS spectra of bulk MoS₂, before and after (NH₄)₂S(aq) chemical treatment and annealing at 423 K in UHV. The black curves correspond to the bare bulk MoS₂, and the red curves correspond to the annealed bulk MoS₂ without (NH₄)₂S(aq) treatment. Finally, the blue curves correspond to bulk MoS₂ after (NH₄)₂S(aq) treatment and followed annealing at 423 K for 30 min in UHV chamber. a) Spectra of Mo 3d. b) Spectra of S 2p. c) Spectra of O 1s. d) Schematic diagram shown the removal of partial oxidation states in MoS₂ with two-step treatments.

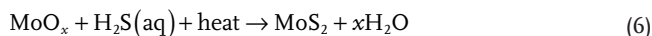
slightly shifted to valence band. It is known that the elementary S has a 1.65 eV bandgap;^[23] therefore, it can be hypothesized that an S or S contained molecules adlayer exists on top of MoS₂ surface with (NH₄)₂S treatment. However, after annealing at 673 K in UHV chamber, the measured bandgap of the treated MoS₂ surface decreases to ≈1.3 eV, consistent with removal of S adlayer from MoS₂ surface. Consequently, based on STM/STS results and previous reports, (NH₄)₂S in H₂O is expected to be dissociated into NH₃, HS, and H₂S as the follow chemical reactions^[24]



Therefore, it is hypothesized that NH₃, NH₄⁺, H₂S, or HS⁻ adsorbs on the MoS₂ surface during (NH₄)₂S dipping treatment. In second stage of the two-step treatment, (NH₄)₂S(aq) treated MoS₂ is annealed above 473 K in vacuum chamber; therefore, the adsorbates can react with MoO_x in MoS₂, consistent with thermally activated chemical reaction with following possible reactions



Or



It is noted that this is speculative,^[25] and DFT modeling is required for determination of a realistic mechanism.

To track the chemical change in bulk MoS₂ after two-step treatment, the surface of MoS₂ is probed using X-ray photoelectron spectroscopy (XPS). The spectra of Mo 3d and S 2p for bare bulk MoS₂, annealed MoS₂, and the two-step treated is shown in **Figure 5a,b**, respectively; there is negligible change in the position, width and intensity of each peaks. Furthermore, the atomic ratio of elementary S 2p to Mo 3d in the two-step treated bulk MoS₂ (2.32:1) is found to be nearly identical to S 2p/Mo 3d ratio of bare bulk MoS₂ (2.51:1) and annealed bulk MoS₂ (2.50:1), consistent with the absence of change of the chemical composition and binding configuration of the atoms in MoS₂ with the two-step

treatment. It is noted that the precision of elementary ratio can be variable by a few percent, depending on the sample surfaces status.^[26]

The chemical transition of oxygen in MoS₂ upon two-step treatment can be observed in the XPS spectra and compared to bare and annealed MoS₂ samples. As shown in Figure 5c, the XPS spectra of bare MoS₂ (the black curve) reveals a broad O1s peak in the range from 528 to 534 eV. After annealing the bare MoS₂ sample in UHV chamber at 523 K, a broad O 1s peak is detected as shown by the red curve. It can be hypothesized that the broad peak of O1s is consistent with the existence of multiple chemical configurations of oxygen in MoS₂. Based on the previous reports, adsorption of O on MoS₂ is observed around 531 eV,^[27] and the O single in MoO_x has been observed in the range from 529 to 532 eV.^[8b,28] It is noted that the origin for O in bare and annealed MoS₂ is not clear, but it can be assumed that O associated defects in MoS₂ are formed when the MoS₂ samples are stored in ambient air. However, after the two-step chemical treatments, the blue curve in Figure 2c shows the disappearance of O signal in the range from 536 to 528 eV. Therefore, it can be concluded that the (NH₄)₂S treatment and annealing process induces near-completed removal of oxygen from MoS₂. As a result of removal of oxidative defects from MoS₂, the carrier transport behavior is enhanced with transition from Schottky behavior to Ohmic behavior of metal-MoS₂ contact, confirmed by electric characteristic of Figures 2 and 3.

3. Conclusion

The two-step chemical treatment of layered MoS₂ using (NH₄)₂S(aq) is demonstrated to enhance the contact behavior of metal/TMDs via controlling the unintentional extrinsic defect states. Using STM/STS, sequent observation of the MoS₂ surface at molecular level upon chemical treatment reveals that the defect states, which are shown as bright protrusions in both empty and filled states, are nearly completely removed by dipping in (NH₄)₂S(aq) and annealing at 523 K in vacuum, without inducing atomic structural damage in MoS₂. This removal of oxygen defects can be confirmed by XPS results; after two-step treatment, Mo/S ratio is nearly constant, while the oxygen signal completely disappears, consistent with removal of oxygen species in MoS₂. These oxidative defects can be introduced in MoS₂ during the synthesis process of MoS₂ or the fabrication processes in ambient conditions; therefore, it is hypothesized that these defect states can degrade electric performance of MoS₂ FETs with act as trapping/scattering center for carrier. However, as a result of the removal of unintentional oxygen defects from MoS₂, the optical and electronic performance of single layer MoS₂ is significantly enhanced. The PL intensity of single layer MoS₂ is doubled with chemical treatment, consistent with improvement of quantum yield for exciton formation by removal oxidation defects at the surface of MoS₂. Moreover, as the contact behavior changes from non-linear Schottky behavior to nearly linear Ohmic behavior in output I_D versus V_{DS} characteristic of single layer MoS₂ FET, the contact resistance of Au/Cr/MoS₂ junction decreases from 35 to 5.2 kΩ, indicating facilitated injection of electron from metal pads to MoS₂ channels. As a result, the *n*-branch I_{ON}

increases 3 X, and the electron field effect mobility is enhanced up to 3 X. Therefore, this two-step (NH₄)₂S(aq) chemical functionalization process provides a facile pathway to engineering the surface defect states in atomically thin TMDs to tune the contact behavior of metal/semiconducting TMD junctions.

4. Experimental Section

Device Fabrication Process, Chemical Treatment Method, and Electrical & Optical Characterization: The CVD-grown single layer MoS₂ flakes were transferred using a wet transfer method on a SiO₂/Si substrate. The average flake size was 50 μm × 50 μm as observed by OM. E-beam lithography was employed to make the open area for deposition of Cr (5 nm/Au 50 nm), which was deposited using an E-beam evaporation system. For exact electrical characteristics of MoS₂ back-gate transistors, single layer MoS₂ flakes were etched to a rectangular shape using SF₆ (20 sccm, 20 s, 20 W) and O₂ (15 sccm, 15 s, 15 W) plasma. Finally, the back-gated MoS₂ FET was fabricated. After electrical measurements, the MoS₂ FET samples were fully dipped in the (NH₄)₂S(aq) solution for a specific time period, following which the samples were rinsed in IPA and dried by N₂ gas. The electrical properties were measured by a vacuum probe system (4200, Keithley) at high vacuum (≈10⁻⁶ Torr). For Optical properties, PL and Raman measurements were performed by an optical microscope system (NTEGRA Spectra, NT-MDT) using a 532 nm laser with high magnification objective lens (100×, NA = 0.7). The gratings with 150 and 1800 grooves were used for PL and Raman, respectively.

STM/STS Method: Bulk MoS₂ purchased from SPI supplies (Structure Probe, Inc.) was mechanically exfoliated multiple times in ambient conditions to obtain clean surface. The bulk MoS₂ was transferred to an Omicron multipurpose UHV chamber (<2 × 10⁻¹⁰ torr). For STM/STS experiments, MoS₂ samples were annealed in UHV at 737 K for 30 min to remove the possible ambient contaminants or adsorbates, such as hydrocarbon, H₂O or CO. For STM/STS experiments, the samples were transferred into Omicron VT STM chamber without exposure to ambient air. All STM/STS experiments were carried out using electrochemically etched tungsten tips.

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

contact engineering, oxide defects, surface science, transition metal dichalcogenides, two-step chemical functionalization

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