Surface morphology engineering of metal oxide-transition metal dichalcogenide heterojunction

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ABSTRACT
A tremendous effort has been made to develop 2D materials-based FETs for electronic applications due to their atomically thin structures. Typically, the electrical performance of the device can vary with the surface roughness and thickness of the channel layer. Therefore, a two-step surface engineering process is demonstrated to tailor the surface roughness and thickness of MoSe\textsubscript{2} multilayers involving exposure of O\textsubscript{2} plasma followed by dipping in (NH\textsubscript{4})\textsubscript{2}S(aq) solution. The O\textsubscript{2} plasma treatment generated an amorphous MoO\textsubscript{x} layer to form a MoO\textsubscript{x}/MoSe\textsubscript{2} heterojunction, and the (NH\textsubscript{4})\textsubscript{2}S(aq) treatment tailored the surface roughness of the heterojunction. The ON/OFF current ratio of MoSe\textsubscript{2} FET is about 1.1 × 10\textsuperscript{5} and 5.7 × 10\textsuperscript{4} for bare and chemically etched MoSe\textsubscript{2}, respectively. The surface roughness of the chemically treated MoSe\textsubscript{2} is higher than that of the bare, 4.2 ± 0.5 nm against 3.6 ± 0.5 nm. Conversely, a 1-hour exposure of the multilayer MoO\textsubscript{x}/MoSe\textsubscript{2} heterostructure with the (NH\textsubscript{4})\textsubscript{2}S(aq) solution removed the amorphous oxide layer and scaled down the thickness of MoSe\textsubscript{2} from ~92.2 nm to ~38.9 nm. The preliminary study shows that this simple two-step strategy can obtain a higher surface-area-to-volume ratio and thickness engineering with acceptable variation in electrical properties.

1. Introduction
Two-dimensional (2D) transition metal dichalcogenides (TMD) are well-studied layered materials with unique physical properties, widely used in next-generation electronic and optoelectronic devices such as chemical sensors [1,2], memory devices [3,4], batteries [5,6], phototransistors [7], and photodetectors [8]. Molybdenum diselenide (MoSe\textsubscript{2}) is an excellent choice for low-power electronic applications and exhibits relatively low internal resistance and high electron and hole mobilities of about 200 and 150 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} [9], respectively, enabling it to be a promising material for field-effect transistors (FETs). Furthermore, the vertical MoSe\textsubscript{2}-MoO\textsubscript{x} heterojunctions exhibit current rectifying characteristics and better photoresponse performance and have wide applications in electronic and optoelectronic devices [10].

Surface engineering and thickness tailoring of MoSe\textsubscript{2} is of great practical interest in preparing various devices. It is well known that the electronic structure of layered semiconductors can be altered by tuning the thickness; typically, the bandgap of MoSe\textsubscript{2} can be tuned by changing the thickness with an indirect bandgap of ~1.1 eV for bulk and a direct bandgap of 1.5 eV for monolayer, which is smaller than MoS\textsubscript{2} and comparable to Si [9]. In addition, the \textit{l}_{\text{on}}/\textit{l}_{\text{off}} ratios can be pushed to extremely high levels [11,12], 10\textsuperscript{6}–10\textsuperscript{9} by varying the thickness of semiconducting TMDs from monolayer to multilayer. In TMD-based FETs, the gate control of the electron density is limited with the increase in channel thickness. For a channel thickness greater than \textit{W}_{\text{max}} (maximum depletion depth), the electrostatic gate voltage loses control over the electrons in the extra thickness of the channel beyond \textit{W}_{\text{max}}. Thus for multilayer films beyond the \textit{W}_{\text{max}}, a leakage current is generated, and it will lead to an increased OFF current, and correspondingly the \textit{l}_{\text{on}}/\textit{l}_{\text{off}} ratio decreases [13]. Therefore, obtaining a proper thickness for the channel is necessary for achieving better electrical characteristics of the FET. However, the thinning down process of TMDs via exfoliation has poor efficiency and yield [14–17].

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Moreover, recent research shows that MoSe\textsubscript{2} can be a potential candidate for sensory applications \cite{18,19}. The sensitivity of semiconductors can be significantly enhanced by engineering surface morphology with the improvement of molecular adsorption behavior on channel surfaces \cite{20–24}. However, the sensitivity of these MoSe\textsubscript{2} sensors is limited due to the weak van der Waals attraction between MoSe\textsubscript{2} and gas molecules. Several researchers tried to increase the sensitivity of the MoSe\textsubscript{2} gas sensors by incorporating heterostructures \cite{20,21}, defect engineering \cite{22,23}, and by increasing the surface area-to-volume ratio using MoSe\textsubscript{2} porous nanowalls \cite{24}. Therefore, engineering MoSe\textsubscript{2} to achieve a proper thickness and roughness is necessary for obtaining better performance. Several approaches, such as post-growth thermal annealing \cite{25}, plasma etching \cite{26}, and laser etching techniques \cite{27}, are widely used for morphology and thickness engineering \cite{16,28,29}. Especially the plasma etching based on CF\textsubscript{4} or SF\textsubscript{6} is a well-known technique for surface engineering of semiconductors; however, this etching process includes the bombardment of energetic ions with the semiconductor surface, which may deteriorate the electrical properties of the semiconductor \cite{30}. In addition, CF\textsubscript{4} or SF\textsubscript{6} plasma etching is expensive and requires sophisticated instruments. Chemical etching with KOH is an exceptional candidate for selective etching of oxide layers \cite{31}. However, the K\textsuperscript{+} ions released during the etching process can contaminate the SiO\textsubscript{2} substrate, thereby affecting the durability of the device. Moreover, the KOH creates H\textsubscript{2} gas bubbles, which can destroy the microstructure \cite{31,32}. Conversely, the chemical etching with (NH\textsubscript{4})\textsubscript{2}S(aq) solution does not induce potential byproducts, which can degrade the semiconductors material, and this application can be broadened to other TMDCs \cite{33,34}.

We demonstrated a versatile and effective two-step process involving an O\textsubscript{2} plasma treatment followed by chemical etching with (NH\textsubscript{4})\textsubscript{2}S(aq) solution to tailor the surface roughness and thickness of MoSe\textsubscript{2} multilayers for various applications. The two-step process in this work is carried out in ambient conditions at room temperature. In addition, it does not require any complex instrumentation. The O\textsubscript{2} plasma treatment on MoSe\textsubscript{2} leads to the formation of an amorphous MoO\textsubscript{x} layer. With this two-step process, the surface roughness and thickness of the MoSe\textsubscript{2} can be tuned. The change in roughness and thickness can influence the electrical properties of the system. Oxidation of MoSe\textsubscript{2} surfaces can be confirmed using Raman and X-ray photoelectron spectroscopy. The FET characteristics of the surface engineered MoO\textsubscript{x}/MoSe\textsubscript{2} heterostructure can be conducted after the O\textsubscript{2} plasma treatment and chemical etching. The surface morphology of MoSe\textsubscript{2} after the O\textsubscript{2} plasma and (NH\textsubscript{4})\textsubscript{2}S(aq) treatment was analyzed by atomic force microscopy.

2. Experimental detail

2.1. Device fabrication

The CVT-grown multilayer MoSe\textsubscript{2} was mechanically exfoliated by the scotch tape method. The flakes were transferred onto a 300 nm thick SiO\textsubscript{2} layer thermally grown on a heavily p-doped Si substrate. E-beam lithography and wet etching were employed to fabricate the source and drain electrodes with Ti/Au (20 nm/200 nm). Finally, to reduce the contact resistance between the electrodes and the MoSe\textsubscript{2} multilayer, the fabricated devices were annealed at 200 °C under a 5% H\textsubscript{2} environment diluted by Ar for 2 hours.

2.2. The two-step treatment

The O\textsubscript{2} plasma treatment was performed on multilayer MoSe\textsubscript{2} FETs using a plasma generator (PDC-32 G-2, Harrick plasma). During O\textsubscript{2} plasma, the power, the chamber pressure, and the oxygen flow rate were maintained at 10.5 W, 2.33 torr, and 60 sccm, respectively, for 20 min. After the O\textsubscript{2} plasma treatment, the multilayer MoSe\textsubscript{2} FETs were fully dipped in (NH\textsubscript{4})\textsubscript{2}S(aq) (Sigma-Aldrich, 20% diluted in H\textsubscript{2}O) for 30 min at 323 K; followed by thorough rinsing in IPA.

2.3. Measurement and analysis method

The electrical properties of bare, O\textsubscript{2} plasma-treated, and (NH\textsubscript{4})\textsubscript{2}S(aq) solution-treated multilayer MoSe\textsubscript{2} FETs were performed under ambient pressure using a semiconductor parameter analyzer (4200A-SCS, Keithley). The Raman spectra were obtained at room temperature under ambient pressure using a Raman spectrometer (DXR2xi, Thermo fisher scientific) with a laser excitation wavelength of 532 nm and an incident laser power of 6.1 mW. The X-ray photoelectron spectroscopy (XPS) (Nexsa, Thermo fisher scientific) using Al K\textsubscript{α} radiation was performed to analyze the chemical configuration of MoSe\textsubscript{2}. The surface morphology of MoSe\textsubscript{2} after the O\textsubscript{2} plasma and (NH\textsubscript{4})\textsubscript{2}S(aq) treatment was analyzed by atomic force microscopy (XE-100, Parksystems) using a noncontact mode.

3. Result and discussion

The formation and surface engineering of MoO\textsubscript{x}/MoSe\textsubscript{2} heterostructure are described in the schematic diagram of Figure 1(a). When the MoSe\textsubscript{2} layer is exposed to O\textsubscript{2} plasma, the Mo atoms react with atomic oxygen to form the MoO\textsubscript{x} layer. The MoO\textsubscript{x}/MoSe\textsubscript{2} samples are further dipped in 25% (NH\textsubscript{4})\textsubscript{2}S(aq) diluted in H\textsubscript{2}O to tune the surface morphology of MoO\textsubscript{x}. Even though the functionalization induces partial oxidation and etching of the topmost MoSe\textsubscript{2} layer, the initial shape of the MoSe\textsubscript{2} flake can be maintained, as shown in the optical images of Figures 1(b). The
MoO$_x$/MoSe$_2$ heterojunction formation via O$_2$ plasma can be confirmed by transmission electron microscopy (TEM) image, as shown in Figure 1(c). The figure shows that a 20 min O$_2$ exposure yielded a 3 nm thick amorphous MoO$_x$ layer. It is noted that the diffusion length of atomic oxygen into MoSe$_2$ is about 3 nm in the TEM result; therefore, multilayer MoSe$_2$ devices are employed here to prevent the complete oxidation of MoSe$_2$ with O$_2$ plasma treatment. Therefore, only a few top layers of MoSe$_2$ are oxidized to MoO$_x$ to maintain the MoO$_x$/MoSe$_2$ heterojunctions. After the amorphous MoO$_x$ layers are obtained, the surface of MoO$_x$ is partially etched by dipping in (NH$_4$)$_2$S(aq) solution to increase the surface roughness.

Structural transition of MoSe$_2$ surface upon applying O$_2$ plasma is elucidated using Raman spectroscopy. A 532 nm laser is irradiated onto the surface of bare multilayer MoSe$_2$ in ambient conditions. The prominent vibrational mode in Figure 1(d) (black curve) is observed at 239.7 cm$^{-1}$, consistent with the out-of-plane vibration A$_{1g}$ [10,35–40]. However, the A$_{1g}$ peak is shifted to 241.8 cm$^{-1}$, and the intensity is reduced by 70% after the exposure to O$_2$ plasma, as shown in the red curve of Figures 1(d,e). The intensity decay of the peak around 240 cm$^{-1}$ is consistent with the chemical transition of a few nanometer thick MoSe$_2$ into MoO$_x$ at the surface; thereby, the Raman signal from MoSe$_2$ is screened by the plasma-induced MoO$_x$ layers. After the oxidation, MoSe$_2$ is dipped in (NH$_4$)$_2$S(aq) for 30 min at 323 K. Although the intensity of the A$_{1g}$ peak slightly increases with respect to MoO$_x$/MoSe$_2$, the position of the peak remains constant. In addition, the E$_{1g}$ peak is also observed in all spectra, as shown in Figure 1(f). Regardless of the oxidation process and chemical etching, the E$_{1g}$ peak remains unchanged. The peak-to-peak distance of the chemically treated MoSe$_2$ is about 74.2 cm$^{-1}$, similar to the value of bare MoSe$_2$, indicating that only a few top layers are oxidized by plasma treatment, and the MoSe$_2$ structure exists under the MoO$_x$ layers.

The chemical transition of MoSe$_2$ surfaces is probed using XPS. The spectra of Mo 3d and O 1s for bare bulk MoSe$_2$ are shown in Figures 2(a,b), respectively. As shown in the black curve of Figure 2(a), two distinct peaks can be observed at 231.6 eV and 228.5 eV, corresponding to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ signals originating from Mo-Se chemical bonding [41–44]. A broad peak (purple curve) corresponding to Se 3s is also detected at 229.4 eV [38]. A weak and broad peak of oxygen signal (black curve) is also observed in the
range from 529 eV to 534 eV, shown in Figure 2(b). The MoSe₂ bulk samples are probed using XPS without an annealing process to prevent unintentional chemical transition induced by thermal energy. It can be hypothesized that multiple chemical configurations of oxygen exist on the MoSe₂ resulting from the adsorption of oxygen-containing molecules introduced from ambient conditions, such as CO or O₂ [42], as shown in the red curve of Figure 2(b). A broad peak observed at 530.5 eV in Figure 2(b) (blue curve) reveals the presence of partial oxidation states in the bulk MoSe₂ sample [45].

Applying O₂ plasma onto the surface of MoSe₂ induces the formation of amorphous MoO₃ layers, which is consistent with the generation of XPS peaks corresponding to MoO₃ at high binding energy, as shown in Figure 2(c). Apart from the Mo 3d signal originating from the Mo-Se bond in MoSe₂, two new peaks are observed at 232.5 eV and 235.5 eV due to the exposure of MoSe₂ with energetically activated O, which is consistent with the transition of top MoSe₂ layers to MoO₃ [42,46,47]. The position of the Mo 3d signal at higher binding energy is the result of oxygen atoms pulling electrons from Mo atoms in MoO₃. As shown in Figure 2(c), the Mo-O peaks corresponding to MoO₃ are broadened, which is expected due to the absence of post-annealing processes and is consistent with the coexistence of multiple chemical configurations in MoO₃. Also, it can be hypothesized that the plasma-induced MoO₃ is amorphous and substoichiometric, based on the previous report [42]. The chemical transition from MoSe₂ to MoO₃ can also be confirmed by probing O 1s spectra, as displayed in the blue curve of Figure 2(d). Based on the O 1s signal assigned to Mo-O bonding, the O to Mo ratio also increased to 1.2, which agrees with the oxidation of Mo in the topmost MoSe₂ layers. Compared to O 1s spectra of bare MoSe₂ in Figure 2(b), the intensity of the O 1s signal of MoO₃/MoSe₂ significantly increases with the appearance of shoulder peaks in the range of 530 eV to 534 eV [42,48]. The strong peak noticeable at 530.5 eV in the O 1s spectrum (blue curve) of Figure 2(d) is assigned to Mo-O bonding, and the low-intensity peak observed at 531.8 eV (red curve) indicates the O atoms adsorbed on MoO₃/MoSe₂.

Dipping MoO₃/MoSe₂ samples in (NH₄)₂S(aq) caused the reduction of oxygen signal in XPS. Figure 2(e) shows that the Mo 3d signal of chemical-treated MoO₃/MoSe₂ can be observed at a nearly identical position to the O₂ plasma-treated MoSe₂ sample; however, the intensity of Mo 3d corresponding to Mo-O bonding decreases significantly. The Mo 3d (MoO₃) to Mo 3d (MoSe₂) elementary ratio of O₂ plasma exposed sample of Figure 2(d) is obtained as 0.4, while that of (NH₄)₂S(aq) treated sample is reduced to 0.25. The reduction of the O signal is confirmed in the O 1s XPS spectra shown in Figure 2(f). Two distinct peaks are observed at 532 eV and 530.4 eV after the (NH₄)₂S(aq) treatment, corresponding to surface adsorbed O and Mo-O chemical bonds. As a result of the reduction of MoO₃ with (NH₄)₂S (aq) treatment, O (Mo-O bonding) to Mo ratio decreased to 0.3. The chemical analysis based on XPS reveals that the (NH₄)₂S(aq) dipping process induces the partial etching of MoO₃ in O₂ plasma-induced MoO₃/MoSe₂.

The electrical characterization of mechanically exfoliated multilayer MoSe₂ FETs is investigated at room temperature (300 K) under ambient conditions to
explore the impact of the chemical transition. Figure 3(a) illustrates the schematic of a back-gated multilayer MoO$_x$/MoSe$_2$ FET fabricated on 300 nm thermally grown SiO$_2$/Si substrates. The fabricated device’s channel length (L) and width (W) are 0.75 µm and 10 µm, respectively. Details of the device fabrication process are described in the experimental section. The log $I_D$-$V$ transfer characteristics of multilayer MoSe$_2$ FET measured at $V_{DS} = 1$ V while applying back gate control over 300 nm SiO$_2$ is shown in Figure 3(b). It is noted that the back-gate voltage $V_{BG}$ is swept in both the forward (negative bias to positive bias) and backward direction (positive bias to negative bias), while the source and drain voltage are kept constant for all measurements. As shown in the black curve of Figure 3(b), the as-fabricated FET displays an n-dominant behavior with Ti/Au contacts [49,50]. The OFF and ON current is about $7.2 \times 10^{-5}$ µA and 7.9 µA, respectively, which is consistent with a gate dependent ON/OFF ratio of $1.1 \times 10^3$ for applied gate voltages ($V_{BG}$) ranging from −50 to 50 V. The threshold voltage ($V_{TH}$) of forward and backward transfer curves are also measured at −6.9 V and −26.2 V; thereby, the 19.3 V width of hysteresis of bare MoSe$_2$ FET is extracted, as shown in linear $I_D$ vs. $V_{BG}$ of Figure 3(c).

However, after the O$_2$ plasma treatment, the transfer characteristic of pristine MoSe$_2$ (red curve in Figures 3(b,c)) is drastically changed. It is clear from the figures that the drain current is independent of the gate voltage in the $V_{BG}$ range of −50 to 50 V. Therefore, it can be hypothesized that the oxidation of MoSe$_2$ via O$_2$ plasma generates a high density of O vacancies; thereby, a defect-associated conducting channel is induced at the MoO$_x$/MoSe$_2$ interfaces between the metal contacts, resulting in a gate voltage-independent transfer curve [42,51,52].

The electrical characteristics of bare MoSe$_2$ after the (NH$_4$)$_2$S(aq) chemical treatment is shown in the supplemental material, Figure S1. As shown in Figure S1, the increase of current at the p-branch is observed, consistent with p-doping via -SH species molecular adsorption [34]. Conversely, after the (NH$_4$)$_2$S(aq) chemical treatment on O$_2$ plasma treated MoSe$_2$, a pronounced difference in the measured transfer characteristic is observed as compared to O$_2$ plasma, as shown in Figure 3(b) (blue curve) [33]. The drain current dependence on back gate bias is observed. The maximum n-branch current at 50 V is 9.7 µA, similar to the n-branch current of bare MoSe$_2$, while the p-branch current at −50 V is 0.02 µA, which is much smaller than that of bare MoSe$_2$. Therefore, the minimum current level of chemical treated MoO$_x$/MoSe$_2$ FET is higher than the OFF current of bare MoSe$_2$. Therefore, the ON/OFF current ratio of chemically etched MoSe$_2$ FET is about $5.7 \times 10^4$, consistent with nearly half of the ON/OFF ratio of bare MoSe$_2$ FET. The threshold voltage ($V_{TH}$) of forward and backward transfer curves in treated MoO$_x$/MoSe$_2$ FET is measured as −15.5 V and −25 V, respectively, with a hysteresis of 40.5 V. The higher OFF current level and increased hysteresis after the chemical etching leads to the conclusion that plasma-induced defects still exist at the MoO$_x$/MoSe$_2$ interface.

To elucidate the topographical change in MoSe$_2$ upon oxidation and chemical treatment, the surface of bulk MoSe$_2$ is probed using atomic force microscopy (AFM). As shown in Figures 4(a,b), a flat surface of bare bulk MoSe$_2$ is observed across the entire scan area (10 µm × 10 µm). The line trace corresponding to the yellow line of Figure 4(a) shows no noticeable variation of topography except at the step edges of MoSe$_2$ multilayers [44,53,54]. After applying O$_2$ plasma, Figures 4(c,d) reveal the formation of particle-like features. The particles are distributed across the entire surface with variable diameters (0.12 nm to 0.89 nm), and the particles’ height ranges from 1 nm to 60 nm. These particle-like features are also observed on transferred WSe$_2$ treated with UV-O$_3$ and confirmed it as...
WO\textsubscript{x} particles without any polymer residues [34]. Furthermore, the intensity reduction of the carbon peak after O\textsubscript{2} plasma treatment (supplemental figure S2) compared to bare MoSe\textsubscript{2} indicates that the carbon-contained residue or adsorbates can be removed during O\textsubscript{2} plasma [55,56]. Therefore, we can conclude it as MoO\textsubscript{x} particles without any polymer residues. However, after dipping in (NH\textsubscript{4})\textsubscript{2}S(aq) solution for 1 hr, the MoO\textsubscript{x} particles are entirely removed from the surface of MoO\textsubscript{x}/MoSe\textsubscript{2}. In contrast, small-sized particles remain on MoSe\textsubscript{2}, as shown in Figures 4(e,f). It is assumed that the agglomerated MoO\textsubscript{x} particles are removed mainly by the (NH\textsubscript{4})\textsubscript{2}S(aq) chemical treatment, and the oxidized layers are etched in the (NH\textsubscript{4})\textsubscript{2}S(aq) solution; thereby, the underlying MoSe\textsubscript{2} surface is exposed to ambient atmosphere. Consequently, sub-5 nm-sized particles are uniformly distributed on the MoO\textsubscript{x}/MoSe\textsubscript{2} surface, consistent with the formation of nanostructures.

An AFM topographic image of mechanically exfoliated MoSe\textsubscript{2} flake on SiO\textsubscript{2} substrate after 30 mins of chemical treatment is shown in Figure 5(a). Static root-mean-square (RMS) roughness analysis is performed on 20 AFM images for each condition, as shown in Figure 5(b). The RMS roughness of the bare MoSe\textsubscript{2} surface is about 1.48 ± 0.2 nm and dramatically increases to 4.9 ± 0.5 nm after the O\textsubscript{2} plasma exposure of MoSe\textsubscript{2}, as shown in Figure 5(b). Furthermore, the chemical treatment of MoO\textsubscript{x}/MoSe\textsubscript{2} decreases the RMS roughness (4.2 ± 0.5 nm) compared to the plasma-treated samples; however, it was still higher than the bare sample. These results are consistent with the height profile analysis.

Figure 4. AFM images and height profiles (size 10 \(\mu\)m × 10 \(\mu\)m) of MoSe\textsubscript{2} flakes. (a) and (b) bare MoSe\textsubscript{2}, (c) and (d) after applying O\textsubscript{2} plasma for 20 min, (e) and (f) after dipping in (NH\textsubscript{4})\textsubscript{2}S(aq) for 1 hour at 323 K.

Figure 5. (a) AFM topographic image (size 10 \(\mu\)m × \(\mu\)m) of a chemical treated MoSe\textsubscript{2} flake surface for 30 min and (b) The RMS-roughness variation of MoSe\textsubscript{2} flake with two-step chemical treatment.
The scaling down of the thickness of MoSe₂ using the chemical treatment with (NH₄)₂S(aq) solution is demonstrated using AFM. The thickness of the bare multilayer MoSe₂ was about ~88.4 nm, as shown in the AFM and height profile of Figures 6(a,b), respectively. However, after the O₂ plasma treatment for 20 min, the multilayer thickness increased to ~92.2 nm, indicating an amorphous MoOₓ layer of thickness of ~3.8 nm, which agrees well with the TEM image in Figure 1(c). The multilayer thickness is further scaled down after 30 mins of chemical etching with (NH₄)₂S(aq) solution. The total thickness of MoSe₂ after the chemical etching was ~86.3 nm indicating the removal MoOₓ layer, which is shown in Figures 6(e,f). A drastic decrease in the total thickness to ~38.9 nm was observed after the chemical etching for 1-hour, as shown in Figures 6(g,h).

It is noted that the etching with (NH₄)₂S(aq) dipping processes occurs only at the metal oxide surface. For bare MoSe₂ surface without formation of MoOₓ, thickness and surface roughness of MoSe₂ flake is nearly identical after dipping in (NH₄)₂S(aq) solution, as shown in the supplemental material, Figures S3-S6. Therefore, it can be concluded that the (NH₄)₂S(aq) dipping process induces the selective etching of the oxidized layers. However, a significant thickness reduction (~53 nm) surpassing the oxide layer is observed after 1-hour of chemical treatment (Figures 6g,h). It is understood that the O₂ plasma treatment generates an ultra-thin MoOₓ layer on bare MoSe₂. In addition, it can be possible that certain energetically activated atomic oxygen can further penetrate the MoSe₂ and form the oxidized defect sites [42,57–59]. Therefore, (NH₄)₂S(aq) can react with the underlying MoSe₂ layer containing atomic oxygen, resulting in thinning down of underlying MoSe₂. It is noted that the electrical properties of the FETs after the 30 mins and 1-hour chemical treatments required the additional optimization of devices fabrication processes; whereby, it will be the future scope of this work.

4. Conclusion
In the present report, the surface engineering and thinning down of MoSe₂ is carried out through a two-step process involving exposure to O₂ plasma followed by chemical etching with (NH₄)₂S(aq) solution. The O₂ plasma treatment resulted in the formation of an ultra-thin (3 nm) amorphous MoOₓ layer on the surface of MoSe₂ due to the reaction of Mo atoms with oxygen. The surface roughness of the amorphous MoOₓ layer is increased by partially reducing the MoOₓ/MoSe₂ heterostructure with (NH₄)₂S(aq) chemical treatment. A 40 min exposure of the multilayer MoOₓ/MoSe₂ heterostructure with the (NH₄)₂S(aq) solution removed the amorphous oxide layer and scaled down the thickness of MoSe₂ from ~92.2 nm to ~38.9 nm. The structural transition of the few layers of MoSe₂ into MoOₓ is confirmed using Raman spectroscopy and XPS. The topographical changes and thickness of multilayer MoSe₂ after oxidation and chemical treatment were determined using AFM. Due to the chemical and topographical transition of the surface, the RMS roughness of MoOₓ/MoSe₂ significantly increased, resulted in an increase in the surface area-to-volume ratio. The electrical characterization of multilayer MoSe₂ FET is conducted to explore the effect of two-step functionalization on the chemical transition of the surface. A gate voltage-independent transfer characteristic is obtained for the O₂ plasma-treated MoSe₂ samples. The negligible gate voltage dependence of I_D is expected due to the formation of defect-associated amorphous MoOₓ conducting channels. Moreover, the (NH₄)₂S(aq) chemical etching demonstrated a back gate bias-dependent drain current like
bare MoSe$_2$. The gate dependent ON/OFF current ratios of about $1.1 \times 10^5$ and $5.7 \times 10^4$ were obtained for bare MoSe$_2$ and chemically etched MoSe$_2$, respectively. In this work, a 10s chemical etching gives a surface roughness of 4.2 $\pm$ 0.5 nm without significant degradation in the ON/OFF current ratio.

Therefore, the surface roughness and thickness of the MoO$_x$/MoSe$_2$ heterostructure can be tailored using the two-step process. An increase in roughness, in turn, increases the surface-area-to-volume ratio of MoSe$_2$. A 10s chemical etching has yielded a higher surface roughness for the MoO$_x$/MoSe$_2$ heterostructure than the bare MoSe$_2$. A more extended chemical etching removed the oxide layer and scaled down the thickness of the multilayer MoSe$_2$. The analysis shows that a higher surface-area-to-volume ratio can be obtained with an acceptable variation in the electrical properties. Therefore, this work can be extended to fabricate a highly functional electronic device based on layered materials. Since the present two-step treatment involves the formation of transition metal oxide followed by the reduction of the metal oxide in (NH$_4$)$_2$ S(aq), this surface engineering via the present two-step treatment can be applied to various TMDCs such as WSe$_2$ and MoS$_2$ [33,34].

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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