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Two-dimensional MoO₃ via a top-down chemical thinning route

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Abstract: Two-dimensional MoO₃ is a versatile planar material, whose properties can be readily tuned, rendering it anywhere from a wide bandgap semiconductor to semi-metallic. This makes it a desirable candidate for a wide range of applications. However, to utilise its full potential, a repeatable process to produce high-quality two-dimensional (2D) crystals is yet to be reported. Here, we report a wet chemical etching process to controllably thin down bulk crystals of MoO₃. This process does not result in any structural or compositional changes, while retaining the desirable intrinsic electronic properties of the material. Field effect transistors based on post-etched crystals exhibit switching ratios of over three orders of magnitude. As such, the proposed thinning process opens pathways to exploit the exotic properties of planar MoO₃ to create versatile 2D systems.

1. Introduction

Two-dimensional (2D) materials yield a high specific surface area with quantum confinement of charge carriers, which offer extraordinary mechanical, optical and electronic properties in comparison to their bulk counterparts.^[1, 2] Graphene has been the most investigated 2D material, since its discovery more than a decade ago. However, the lack of an intrinsic energy band gap has hindered the widespread deployment of graphene in nano-electronic applications.^[3] Hence, an extensive effort has been applied into the exploration of other

semiconducting 2D materials, from both scientific and application point of view. Reliable production of high purity, crystalline 2D materials is a crucial aspect for studying them and translating their electronic and optical properties into a viable technology.

Typically, 2D materials can be realized by bottom-up synthesis and top-down exfoliation methods. Chemical vapour deposition (CVD) has been the most effective and widely adopted bottom-up technique, commonly used in the large area growth of 2D crystals (graphene,^[4] MoS₂^[5]). However, obtaining the desired thickness of 2D materials using CVD is rather complicated as it involves several parameters to be optimised such as amount of precursor, deposition temperature/pressure, and carrier gas flow rate. The top-down synthesis methods include mechanical^[2, 6] and liquid^[7, 8] phase exfoliation processes. Liquid phase exfoliation has a higher yield of 2D crystals, but generally carries significant traces of contaminants from the solvents which tend to affect the intrinsic properties of the material. As a result, the structural and electronic quality of liquid phase exfoliated 2D materials are compromised. Mechanical exfoliation is the simplistic traditional process to achieve 2D crystals, first demonstrated for graphene.^[9] This process provides crystals of high purity, which is ideal for electronic device applications and fundamental research. However, the exfoliated crystals are found in random lateral sizes and thicknesses, making it challenging to obtain single crystals with desired thicknesses on-demand. As a result, post-deposition etching of the multi-layered crystals is a promising avenue towards the sustainable production of 2D crystals with desired thicknesses. Recently, wet chemical thinning of MoS₂ using HNO₃,^[10] laser thinning,^[11] and layer-by-layer thinning of MoS₂ by using XeF₂^[12] has been reported.

Molybdenum trioxide (MoO₃), a member of the 2D materials family is an *n*-type, wide bandgap (~3 eV), high dielectric (*k*) material. The band structure of MoO₃ can be readily tuned through ionic intercalation that enables control over its characteristics, which can be engineered to render it semi-metallic to insulating on-demand.^[2] Typically, ion intercalation changes the stoichiometry of the material by introducing oxygen vacancies, subsequently

enhancing the charge carrier concentration, as a result of increasing density of states at the Fermi level.^[13] Such aspects of 2D MoO₃ makes it promising in a variety of potential applications such as field effect transistors,^[14] gas sensors,^[15] bio-sensors,^[7] light emitting diodes,^[16] supercapacitor electrodes,^[17] flexible photodetectors,^[18] and memristors.^[19] However, there has not been any reported post deposition thinning method to controllably obtain 2D MoO₃ crystals.

This work explores a facile and low-cost, top-down, wet chemical etching method to obtain 2D crystals of MoO₃. The reliability and repeatability of the chemical etching process is investigated. Extensive characterisations of the MoO₃ crystals are carried out pre- and post-etching, in order to establish the retention of the material's compositional integrity through the etching process. Field effect transistors (FETs) based on these etched crystals has been demonstrated to assess the transport properties of the post-etched material.

2. Results and Discussion

In this study, we employ mechanically-exfoliated MoO₃ crystals. Thermodynamically stable orthorhombic α -MoO₃ phase, possesses double layers of MoO₆, stacked together through weak van der Waals forces along the [010] vertical direction (**Figure 1**). Each double layer consists of edge-sharing MoO₆ octahedra along the [001] direction and corner-sharing rows along the [100] direction. This configuration allows easy exfoliation of layers from the parent crystal. Mechanical exfoliation preferentially breaks large crystals of MoO₃ along the [001] direction resulting in long rectangular crystals (Figure 1a,b). This can be attributed to the doubly-coordinated O₍₂₎ being weaker than the triply-coordinated O₍₃₎ (Figure 1a,b).

Figure 1. Crystal structure of MoO_3 crystal along (a) 001 direction and (b) 100 direction.

Typically, base (OH^-) solutions are known to be solvents for metal oxides. Hence, we utilise a KOH-based buffer solution to controllably etch MoO_3 . Multiple etching experiments were conducted on mechanically-exfoliated MoO_3 crystals, with varying concentrations of the etchant (in water) at a constant etch duration (5 s), in order to determine an optimum etchant concentration for controlled crystal thinning. **Figure 2a** shows the change in thickness (Δt), obtained using atomic force microscopy, of the crystals with respect to etchant ratio. As seen in the graph, Δt is very large (~ 65 nm) for a 5 s etch duration, at an etchant ratio of 1:100, where controllability of the change in thickness is minimal. The etchant is further diluted with water and, Δt is significantly lower (~ 5 nm) for the same etch duration, at an etchant ratio of 1:500. An overall decreasing trend of Δt with respect to the etchant ratio was observed, with the highest controllability achieved at an etchant to water ratio of 1:500. This is expected, as

fewer number of cations in the etchant result in a weaker reaction with the edge sharing oxygen atoms in the crystal; thereby, providing controllability over the thinning process with respect to etch duration. As such, a ratio of 1:500 is adopted as the ratio for further characterisation of the thinning process.

Subsequently, the MoO_3 crystals were subjected to increasing etch durations using an etchant to water ratio of 1:500. It is to be noted that in the experimented thickness range (up to 100 nm), the etch rate was independent of the initial crystal thickness. The etch rate was calculated, by assessing the corresponding Δt . Figure 2b presents the variation in the etch rate with respect to the etch duration, depicting a non-linearly rising trend in the etch rate. The non-linearity is expected due to the non-uniform distribution of the initial dimensions of the subjected crystals. The exponentially rising trend in the etch rate can be attributed to two factors: (i) the non-linearly increasing number of exposed dangling oxygen bonds in the crystal with progressing etch durations, and (ii) the exothermic process of the etching reaction results in moderately increased temperatures, which would accelerate the reaction rate with time.^[12] To confirm the repeatability of the process, the experiments were conducted multiple times and the etch rate was confirmed to be consistent with the observed trend at a confidence level of 95%.

Figure 2. (a) Change in MoO₃ crystal thickness *vs.* ratio of the etchant to water, at a fixed etch duration of 5 s. (b) The etch rate *vs.* etch duration, at the optimum etchant ratio (1:500). Error bars in both (a) and (b) represent a confidence interval of 95%. (c) Atomic force micrographs of a MoO₃ crystal before and after 25 s of etching using the optimum ratio (1:500) of the etchant. The scale bar denotes 1 μm. The corresponding thickness profiles of the crystal along the dashed lines reveal the reduction in thickness.

Figure 2c shows the surface atomic force microscopy (AFM) scans of a MoO₃ crystal prior to and after 25 s of etching. The corresponding cross-sectional thickness profile (indicated by the dotted lines) of the MoO₃ crystal pre- and post-etching (at two etching steps) are indicative of the change in thickness. Cross-sectional profiles indicate that ~3 and ~33 mono layers of MoO₃ have been etched after 5 and 25 s of etching, respectively. Based on the AFM analysis of the etched crystals, it can be seen that the top-down thinning process results in the bulk crystals of MoO₃ being stripped down into 2D layers. The etch process is observed to start from the crystal edges and move inwards with time, resulting a slight reduction in lateral dimensions, as seen from the cross-sectional profile (Figure 2c). However, for longer etch durations (25 s) the change in thickness is uneven with bulges at the edges, which might result from the bending of unremoved MoO₃ due to strong adsorption between the substrate and the material, at the edges of the crystals.^[20]

The proposed two-step etching mechanism can be described as follows:^[21]

There are three distinct oxygen sites in each octahedra: $\text{O}_{(1)}$ is the singly-coordinated terminal oxygen, $\text{O}_{(2)}$ is the asymmetrically-bonded bridging oxygen with the two neighbouring Mo atoms, and $\text{O}_{(3)}$ is the triply-coordinated asymmetric oxygen with two Mo atoms oriented along the (001) plane and one sublayer Mo atom^[22] (Figure 1a,b). The etching process can be seen as the breaking of the MoO_6 octahedron to form a MoO_4 tetrahedron after reacting with the hydroxyl group (OH^-) present in the etchant. The difference in the bonding structure of Mo and O along the (100) and (001) planes^[22] results in different reactivities towards the etchant. The Mo and O atoms are unsaturated in the (100) planes, as the bridging oxygen $\text{O}_{(2)}$ between two Mo atoms becomes a terminal oxygen on the (100) plane after exfoliation. The OH^- reacts with these new terminal oxygen atoms forming $\text{H}-\text{O}-\text{MoO}_3^-$ and eventually produces MoO_4^{2-} . As such, an entire chain of MoO_6 octahedron, that shares edges and vertices through cross-linking oxygen atoms, can be peeled off sequentially from the plane. As described by the reaction mechanism, etching occurs at the terminal oxygen. Since the (010) edge plane is solely composed of terminal oxygen atoms, the highest etch rate is seen along this plane. The (100) edge plane has combination of molybdenum and terminal oxygen atoms, whereas (001) edge plane is composed of molybdenum, doubly coordinated and terminal oxygen atoms. As such, the etch rate along the various planes can be sequenced as: $(001) < (100) < (010)$.

Raman spectroscopy was employed to characterise the structural integrity of the material post-etching. **Figures 3a-c** show spatial map of the dominant Raman peak (820 cm^{-1}) intensity of a pristine MoO_3 crystal, sequentially subjected to the etching process. The 820 cm^{-1} peak in the Raman spectrum denotes the stretching mode for doubly-coordinated oxygen.^[6, 23] The results indicate a reduction in Raman peak intensity with the etching process, which is

attributed to the reducing number of MoO₃ layers present in the crystal. Full-range Raman spectra (Figure 3d) show the other characteristic peaks for MoO₃ at 115, 157, 197, 283, 336, 363, 666, 819, and 995 cm⁻¹ [6] pre- and post-etching. The sharp nature of the peaks suggests that the corresponding vibrational modes are from a highly-ordered structure. No shift in the positions of the peaks is observed post-etching, which suggests that the composition of MoO₃ crystals is preserved.^[14, 24] To verify the consistency and reproducibility of aforementioned observations, Raman analyses carried out on multiple MoO₃ crystals are presented in Figure 3e. As seen in Figure 3e, a decrease in normalised peak intensity is indicative of the reduction in MoO₃ crystal thickness,^[6] whereas the average peak shift observed (~ 0.35 cm⁻¹) is negligible (being less than the resolution of the equipment 0.5 cm⁻¹). It can be concluded that the compositional integrity of the MoO₃ crystal remains intact post-etching.

Figure 3. Micro-Raman maps of (a) pristine and (b) 5 s and (c) 25 s etched MoO₃ crystal. Scalebar denotes 2 μm . Micro-Raman spectra of mechanically-exfoliated a MoO₃ crystal before and after etching steps. The etching was carried out using the optimum ratio (1:500) of

the etchant for 5 s and 25 s. (e) The normalised Raman peak (820 cm^{-1}) intensity and peak shift observed in multiple crystals subjected to the etch process.

High-resolution transmission electron microscopy (HRTEM) was utilised to compare the crystallinity of the pristine and etched MoO_3 crystals. **Figure 4a** shows a pristine MoO_3 crystal with its corresponding selected-area electron diffraction (SAED) pattern (inset). Figures 4b and 4c present MoO_3 crystals that were subjected to 5 s and 25 s of chemical etching, respectively. The SAED patterns acquired on multiple locations of the etched crystals are in agreement with that of the pristine MoO_3 crystal. The lattice parameters calculated from the SAED patterns of the pristine and etched (5 s and 25 s duration) MoO_3 crystals show identical values, confirming there are no structural defects present initially or introduced by the etching process.

Figure 4. Transmission electronic micrographs with SAED patterns (as insets) of the mechanically-exfoliated and etched MoO_3 crystals: (a) pristine, (b) 5 s etched, and (c) 25 s etched. The optimum ratio (1:500) etchant was utilised.

To quantify the charge transport properties of the obtained 2D MoO_3 (following 25 s of etching), field effect measurements were carried out in a back-gate configuration at room temperature. Ion intercalation was carried out in order to introduce sub-stoichiometry in the channel, making it ideal for FET applications.^[14] Typical drain current vs. voltage (I – V) characteristics of a MoO_3 FET at an applied gate voltage in the range of -2.6 to 7 V are

shown in **Figure 5a**. At a channel bias of 300 mV, an ON/OFF ratio of $\sim 4,000$ was observed (Figure 5b). The field effect carrier mobility was calculated using the following equation:

$$\mu = \frac{\Delta I_{DS}}{\Delta V_{GS}} \times \frac{l}{C \cdot w \cdot V_{DS}} \quad (3)$$

where $\Delta I_{DS}/\Delta V_{GS}$ is the transconductance, l is the channel length, w is the channel width, and C ($\sim 4.3 \times 10^{-8} \text{ F/cm}^2$) is the gate capacitance per unit area V_{DS} is the drain–source voltage (300 mV). The carrier mobility was calculated to be $\sim 175 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The room temperature ON/OFF ratio and carrier mobility values of $\sim 4,000$ and $175 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively are comparable to other 2D dichalcogenide-based FETs.^[25] However, by adopting alternate device architectures and dielectric capping, carrier scattering can be further reduced, improving the carrier mobility.

Figure 5. The experimental I – V characteristics of a 25 s etched MoO_3 FET. (a) I_{DS} vs. V_{DS} characteristics of the FET with varying back-gate voltages (V_{GS}) in steps of 0.2 V from -2.6 V to $+7$ V. Inset shows an optical micrograph of the FET. (b) Corresponding I_{DS} – V_{GS} curves of the FET acquired at V_{DS} values of 300 mV.

3. Conclusion

In conclusion, the adopted wet chemical etching process provides a low-cost and easily deployable method to obtain high quality 2D crystals of MoO₃. No compositional and structural changes in the MoO₃ crystal are introduced as a result of the etching process. This is also evidenced by the demonstration of FETs which exhibit low-voltage switching ratios that are $>10^3$. This provides a controllable and simple process to integrate 2D MoO₃ as the functional and tunable material in 2D electronics.

4. Experimental Section

Preparation of MoO₃ crystals: Mechanical exfoliation of MoO₃ crystals was conducted using polydimethylsiloxane (PDMS) as an alternative to the conventional scotch-tape method.^[26] Mechanical exfoliation was carried out on bulk crystals synthesized from chemical vapour deposition, using MoO₃ powder as the precursor.^[2,6] Firstly, 80 nm SiO₂/Si substrates were cleaned using acetone and isopropyl alcohol, followed by drying with compressed N₂. Subsequently, the substrates were subjected to 5 min of oxygen plasma treatment, ensuring all organic residues are completely removed. The MoO₃ crystals were then cleaved using flexible pieces of PDMS and transferred onto the SiO₂/Si substrates. The samples were further subjected to oxygen plasma treatment for 2 min to remove any residue from PDMS.

Chemical etching process: A potassium hydroxide buffer solution was utilised as the etchant to thin the exfoliated MoO₃ crystals. This was chosen as a commercially available solution AZ400K (AZ Chemicals), which is routinely used as a developer in photolithography processes. A range of solutions with varying ratio of etchant:water content (1:100, 1:200, 1:300, 1:400, and 1:500) were prepared to identify the best ratio for controllable etching. The exfoliated MoO₃ crystals were etched for a fixed duration of 5 s, at various etchant concentrations and the solution with the slowest etch rate was adopted for further experiment and characterisation. The thinning process was then repeated multiple times to establish repeatability.

Characterisation: The change in thickness of MoO₃ crystals was measured using Digital Instruments D3100 atomic force microscope under tapping mode. LabRam HR Evolution Raman Spectrometer (laser excitation at 532 nm with a 50× objective) was utilised to assess composition of MoO₃ crystals before and after etching. A high resolution transmission electron microscope (JEOL 2100F at 200 KV) was utilised to characterise and compare the crystal structure of MoO₃ before and after etching. The devices were characterised for their electronic transport properties in a back-gated FET configuration using semiconductor parameter analyser (Keithley 4200SCS).

Field effect transistor fabrication: Device fabrication was carried out on the etched crystals by adopting standard photolithography. Source and drain electrodes (Au 100 nm with Cr 10 nm to promote adhesion) were deposited using electron beam deposition. The fabricated devices were subjected to liquid phase H⁺ intercalation using 0.5 M H₂SO₄ in a propylene carbonate (PLC) solution at a constant bias voltage of 0.5 V.

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