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Wafer scale quasi single crystalline MoS₂ realized by epitaxial phase conversion

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Abstract

Vapor-solid phase reaction (VSPR) is a two-step process for synthesizing 2D MoS₂. In the first step, a precursor film such as molybdenum oxide is grown on a substrate, followed by a sulfurization process at elevated temperature. This process offers a scalable fabrication of wafer-scale film with feasible control in thickness and uniformity. However, the properties of MoS₂ films from this VSPR process often suffer from poor electrical properties. The major reason is their polycrystalline (PC) structure with large concentrations of defects and grain boundaries, which are inherited from the amorphous precursor films. Here, we report a new and scalable VSPR process in which epitaxial MoO₃ films (grown over a 2-inch wafers) are used as high-quality precursors, which are converted into quasi-single-crystalline (QSC) MoS₂. We demonstrate that the field effect mobility of transistors fabricated using a QSC MoS₂ channel is almost 35 times larger, compared to a PC MoS₂ channel, also better than most previously reported MoS₂ films by other two-step

MoS₂ formation processes. Our process presents a new approach in which the epitaxial growth of the precursor phase can be used to improve 2D semiconductor and device performance.

Keywords: Molybdenum dioxide, molybdenum disulfide, quasi-single crystalline, polycrystalline, wafer scale

Introduction

The fabrication of large-scale, single-crystalline, silicon wafers has enabled the modern electronics industry. Wafer-scale, single-crystalline, 2D graphene was first fabricated in 2014[1], an accomplishment that pushed 2D graphene electrodes into scalable industrial application. There is thus significant interest in growing single-crystalline, 2D semiconductors (e.g., MoS₂) at the wafer scale. However, MoS₂, which is one of the most promising 2D semiconductors with a tunable bandgap [2], has not yet been realized in 2D film with a single-crystalline structure at the wafer scale. Top-down exfoliation methods have only been able to realize single-crystalline flakes with a size of around tens of micron [3-5]. Chemical vapor deposition methods, on the other hand, could realize single-crystalline flakes with lateral sizes of around hundreds of microns [6, 7], but only PC films at the wafer scale (with a crystal domain size around several micron) [8, 9]. Furthermore, the two-step VSPR process reported previously has only been able to produce PC MoS₂ films at the wafer scale, with a nanometer-scale crystallite size, since their precursor films had an amorphous structure [10-13]. The other deposition methods, such as pulsed laser deposition (PLD) [14], atomic layer deposition [15], and sputtering [16], could also only realize PC MoS₂ films over large areas. Thus far, there have been no reports of single-crystalline, 2D chalcogenides grown at the wafer scale using the VSPR process.

Inspired by the recent work of synthesizing highly crystalline MoS₂ flakes converted from MoO₃ flakes by chemical vapor deposition [17], we decided to investigate the possibility of preparing

high-quality MoS₂ over 2-inch wafers through the VSPR process using MoO₂ as a precursor. To achieve this, we first developed an epitaxial MoO₂ film deposited on 2-inch wafers by PLD, and we then converted it to a QSC MoS₂ structure by annealing the wafer in sulfur vapor. Thin film transistors fabricated from the QSC and PC MoS₂ films, both grown over 2-inch wafers by the VSPR process, display a large difference in performance. The field effect mobility of QSC MoS₂ devices was approximately 35 times higher than that of the PC MoS₂ devices, and it could reach up to 10 cm²V⁻¹s⁻¹, which is among the best reported values for VSPR MoS₂ [13].

Experimental section

Growth of precursor epitaxial MoO₂ film by pulsed laser deposition (PLD). 2-inch (001) Al₂O₃ substrates of 0.5 mm thickness were used as received. Before PLD, the substrates were cleaned sequentially with acetone, IPA, and DI water for 5 min in each solvent, combined with sonication. After placing the sample inside the PLD main chamber, the vacuum was pumped down below 10⁻⁷ Torr. Furthermore, the MoO₃ target (purity 99.9%, Mateck) was used for the deposition, while O₂ was used as the deposition atmosphere, and the chamber pressure was kept at 10 mTorr during deposition. Low oxygen pressure was used during the growth to facilitate formation of MoO₂ film on the c-cut sapphire substrates. The temperature of the substrate during deposition was 400 °C, and the KrF laser source, with a 248-nm wavelength, was used and set to a constant energy mode using 210 mJ. The deposition rate was measured as 0.314 Å per shot, and the substrate was rotated during deposition at a speed of 36° per second to obtain MoO₂ film with thickness uniformity. After deposition, the sample was cooled down to room temperature naturally before being taken out of the PLD chamber.

Sulfurization process for epitaxial MoS₂ film. Precursor epitaxial MoO₂ films were placed in a cleaned quartz boat and loaded into the center of three-zone tube furnace. Argon was provided as the carrier gas during sulfurization, and sulfur powder (Fisher scientific, 700 mg) was placed in the upstream of the sample at a distance of 27 cm. During the high-temperature process, the sulfur powder would evaporate, and its vapor would be transported and incorporated into the epitaxial MoO₂, thereby converting it to epitaxial (or QSC) MoS₂ film. Before sulfurization, Ar was kept flowing through the quartz tube at 100 sccm for at least 40 min to completely remove the oxygen from the tube. The temperature increase rate of the middle zone was set as 20 °C/min from room temperature to the desired maximum values (700, 800, and 900 °C). After reaching the target value, the temperature was kept constant for 1 hr to complete the conversion of MoS₂ to MoO₂ and then cooled down to room temperature. The sulfurization pressure was maintained between 5 to 10 torr. The Ar flow was kept at 100 sccm throughout the process.

Transfer process. We used the stamp transfer process combined with chemical wet etching to transfer MoS₂ onto different substrates (a glass substrate is taken as the example in the following part). First, the as-prepared MoS₂/Al₂O₃ sample was submerged in a KOH (10% wt) liquid solution, keeping the temperature at 90 °C. The substrate was held there for liquid ions inset between the film and substrate to release the strain between them. The immersion time should be well controlled, always keeping the MoS₂ attached to the surface of the substrate. After removing the sample from the base solution, it was slowly rinsed with DI water several times and then dried by a Nitrogen gun to clean the aqueous alkali ions. A PDMS film was carefully attached to the MoS₂ film/sapphire and put into DI water for 10 min. Then, the PDMS/MoS₂ film was carefully and slowly detached from the sapphire substrate. Thereafter, the PDMS/MoS₂ film was attached to the glass substrate carefully and uniformly, Air bubbles should be eradicated during the attaching

process. The PDMS/MoS₂ film/glass was heated on a hot plate at 70 °C for 0.5-1 hr to reduce the viscosity of the PDMS, and it was then cooled down to room temperature naturally. After detaching the PDMS film, the MoS₂ film would be left on the target substrate.

Top-gate TFT device fabrication. The as-synthesized MoS₂ films on sapphire substrate were patterned using photolithography, followed by a dry etching process. Au/Ti S/D electrodes were grown on top of MoS₂ by e-beam evaporation (EBE) using a lift-off process. In addition, HfO₂ dielectric was grown by atomic layer deposition (ALD) (400 cycles, 60 nm). During the ALD process, the temperature was set as 160 °C, and deionized water was used as the oxidation source with a pulse/purge time of 0.015/8 s/s. Tetrakis(dimethylamido) hafnium (IV) precursor (Sigma-Aldrich) was used as the Hf source, with a pulse/purge time of 0.2/8 s/s. The top-gate electrode was grown by EBE and patterned by a lift-off process. Once the device structure was prepared, it was annealed at 200 °C for 2 hrs in a tube furnace. The annealing process was done in Ar/H₂ gas at a flow rate of 40/5 sccm, with the inner pressure kept at 1 torr. Before annealing, the tube was purged three times with the Ar/H₂ gas to remove any residual oxygen in the tube. The heating rate was set as 5 °C/min, and the furnace was naturally cooled to room temperature after the annealing process.

Characterization. The X-ray diffraction patterns of both epitaxial MoO₂ and 2D MoS₂ films (θ - 2θ scans and Φ scans) were measured using an X-ray diffractometer (Bruker, D8 DA Vinci) with a Cu $K\alpha$ source and a wavelength of 1.5418 Å. Raman spectra, including mapping (with a resolution of 1 μ m), and PL spectra were characterized in an ambient environment using a Horiba Aramis Raman spectrometer (Horiba Scientific) with an excitation source of visible light that had a wavelength of 473 nm. The PL spectra of the samples were measured in the dark, while the XPS spectra were measured in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic

Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multi-channel plate and a delay line detector under a vacuum of $\sim 10^{-9}$ mbar. Atomic force microscopy (AFM) (Bruker, Dimension Icon SPM) was used to obtain the surface morphologies of both the precursor MoO_2 and final MoS_2 films, and a line scan in AFM was used to obtain the MoS_2 film thickness information in area intentionally scratched by a tweezer. Then, TEM cross-section specimens were prepared using a focused ion beam system (Helios 400s, ThermoFisher USA [former FEI Co]), and TEM images and EELS elemental mapping were obtained at 80kV by a Titan 60-300kV TEM, ThermoFisher USA (former FEI Co), equipped with a high-brightness gun, a probe corrector, and a Gatan Quantum 966 imaging filter (GIF). The MoS_2 film was made totally free standing by etching the substrate in an aqueous alkali solution, and it was then transferred onto Cu grids with lacey carbon film. High resolution (HR) STEM images were recorded at 80kV with the ThermoFisher USA (former FEI Co) Titan Themis Z (40-300kV) TEM equipped with a double Cs (spherical aberration) corrector, a high-brightness electron gun (x-FEG), and a Gatan GIF 966. The performances of the top-gated TFT devices were measured using a semiconductor device analyzer (Agilent B1500A) at room temperature in the dark.

Results and Discussion

Molybdenum dioxide (MoO_2 , space group: $P2_1/c$ [14]) grown on the (001) surface of a 2-inch, single-crystalline Al_2O_3 substrate (space group: $R-3ch$ [167]) was selected as the precursor film, after calculating that lattice mismatches below 2% can be achieved. The lattice parameters along the $[120] \text{Al}_2\text{O}_3 // [001] \text{MoO}_2$ and $[100] \text{Al}_2\text{O}_3 // [010] \text{MoO}_2$ are 0.5720//0.5628 and 0.4762//0.4856 nm, respectively, and both are in (001) $\text{Al}_2\text{O}_3 // (200) \text{MoO}_2$ planes, as illustrated in Figures 1a-b. The former lattice mismatches are calculated to be -1.6% (tensile strain), and the latter are

calculated to be 2.0% (compressive strain). These strain values are negligible, and they motivated us to grow epitaxial (200) MoO₂ films on (001) Al₂O₃ [18].

Figure 1. Schematic structure of the (a) (100) Al₂O₃ surface and (b) (200) monoclinic MoO₂ lattice plane with the oxygen anions drawn on the top of the structures. (c) θ - 2θ scan of MoO₂ with different PLD shots. (d) Φ scan and (e) θ - 2θ of precursor MoO₂ with 1,500 PLD shots and final MoS₂ films on sapphire substrate. (f) Raman spectra of precursor MoO₂ with 1,500 PLD shots and final MoS₂ films on sapphire substrate. (g) MoO₂ with thickness 3 nm (left), 6 nm (middle), and 9 nm (right). (h) MoS₂ with thickness 3 nm (left), 6 nm (middle), and 9 nm (right).

Figure 1c depicts the θ - 2θ X-ray diffraction (XRD) pattern of epitaxial MoO₂ films deposited on (001) Al₂O₃ substrates at 400 °C using different numbers of PLD laser shots (100, 500, and 1,500). Only (200) MoO₂ ($2\theta = 37.95^\circ$) and (400) ($2\theta = 80.97^\circ$) diffraction peaks were observed for the films (500 and 1,500 shots), indicating that these films are epitaxial. A ϕ (Φ) scan was performed to further investigate the (200) MoO₂/(001) Al₂O₃ epitaxial film structure, which is presented in Figure 1d. The Φ -scan illustrates the 60° inter-spaced peaks of (011) MoO₂ planes

(red spectrum), indicating their six-fold symmetry, and the 120° inter-spaced peaks of (104) Al_2O_3 planes with three-fold symmetry (black spectrum). It can be seen that the (011) MoO_2 peaks are offset by 30° to those of (104) Al_2O_3 peaks, confirming the epitaxial nature of the MoO_2 growth.

Figure 1e depicts the θ - 2θ XRD scan of both the precursor MoO_2 film (1,500 PLD shots, 47.1 nm) and the final MoS_2 film (after sulfurization) on the (001) Al_2O_3 substrate. The XRD pattern of the MoS_2 film (the green one) displays peaks at 16.65° , 29.19° , 44.27° , and 60.32° , which can be assigned to the (002), (004), (006), and (008) planes of 2H MoS_2 , and the second peak at 41.80° can be assigned to the (001) planes of the Al_2O_3 substrate. However, the peak corresponding to (200) MoO_2 disappeared. This result indicates that the MoO_2 film has been converted to epitaxial MoS_2 . A Φ scan (the green pattern in Figure 1d) was performed to verify the epitaxial nature of the final MoS_2 film. It can be seen that the (107) MoS_2 planes exhibit six-fold symmetry and are offset by 30° from (104) Al_2O_3 peaks. The presence of small peaks (marked by black asterisks) in the Φ scan pattern indicates that the MoS_2 epitaxy might not be perfect, and some in-plane mismatch may exist. Raman spectroscopy was performed on both MoO_2 and MoS_2 films, as indicated in Figure 1f. [19, 20] No Raman peaks corresponding to MoO_2 were observed in the final MoS_2 film, which confirms the complete sulfurization. Visually, the films demonstrate good uniformity over 2-inch wafers, as illustrated in the optical images in Figures 1g and 1h for the precursor MoO_2 and the converted MoS_2 , respectively. The optical images of MoO_2 correspond to films deposited using 100, 200, and 300 PLD shots, and MoS_2 films with final thicknesses of ca. 3, 6, and 9 nm. The KAUST logo is more visible in the more transparent thinner films.

In addition, to the epitaxial films discussed above, we also prepared PC MoS_2 films over 2-inch wafers to compare their performance to QSC MoS_2 films. In this case, the precursor MoO_2 films are amorphous, as indicated in the XRD pattern in Figure S1, where no MoO_2 diffraction

peaks are observed. The amorphous MoO₂ structure can be obtained at different temperatures and on different substrates. For example, we prepared MoO₂ at two different temperatures (RT and 300 °C) on (001) Al₂O₃ (Figure S1a) and at 400 °C on (1-12) Al₂O₃ (Figure S1b black pattern). All of these amorphous MoO₂ films could be converted to PC MoS₂ after sulfurization at 900 °C. As an example, Figure S1b (the red pattern) presents the XRD pattern of one PC MoS₂ film converted from amorphous MoO₂ deposited at 400 °C.

Scherrer equation is used to estimate the grain size of polycrystalline films or powders and the crystalline quality of epitaxy films. [21] The equation can be expressed as $\tau = K\lambda/\beta\cos\theta$, where τ means the grain size of polycrystalline film or the effective coherence length of the epitaxial film relevant lattice plane. K is the shape constant, which usually has a value of 0.89, β is the full width at half maximum (FWHM) of the relevant XRD peak, θ is the Bragg angle of relevant peak. Gaussian Fitting of the (002) XRD peaks of both polycrystalline and epitaxial MoS₂ films prepared in this study are depicted in Figure S2. Using the Scherrer formula, the polycrystalline MoS₂ film is calculated to have a grain size around 20 nm. In comparison, the effective coherence length of (002) plane in the epitaxial film is 49.4 nm, which is consistent with the film thickness, indicating high-quality of epitaxial structure.

A schematic depicting the epitaxial phase conversion process from MoO₂ to MoS₂ is illustrated in Figure 2a. The MoO₂ epitaxial films grown by PLD were loaded into a tube furnace and annealed in a mixture of Ar and S at 900 °C for 1 hr at atmospheric pressure, resulting in 2D epitaxial MoS₂ films. The process's details are further discussed in the experimental section in the supporting information file. Furthermore, the optimization process is presented and characterized by Raman (Figure S3, Table S1), photoluminescence (PL) spectra (Figure S4), X-ray photoelectron spectroscopy (XPS) (Figure S5, Table S2), and atomic force microscopy (AFM)

(Figure S6), which verified that sulfurization at 900 °C for 1 hr yields the highest quality QSC MoS₂ film. The thinnest continuous MoS₂ film (ca. 3 nm) could be realized by sulfurizing MoO₂ film deposited using 100 PLD shots, as illustrated in Figure S (7-9). The details are discussed in the experimental section, in the supporting information.

Figure 2. (a) Schematic depicting the optimized sulfurization process. (b) STEM and (c) HR-STEM images of precursor MoO₂ epitaxial film formed using 100 PLD shots. (d) STEM and (e) HR-STEM images of cross section of final quasi-single-crystalline (QSC) MoS₂ epitaxial film. (f) Oxygen EELS elemental map with corresponding STEM image. (g) Sulfur and oxygen EELS elemental map with corresponding STEM image.

Figure 2b presents an image of a 3.15-nm thick (100 PLD shots) MoO_2 precursor film obtained with a high-angle annular dark-field (HAADF) detector in a scanning transmission electron microscope (STEM). The surface is atomically flat, which is consistent with the AFM data. A high-resolution (HR) STEM image of the epitaxial MoO_2 film is presented in Figure 2c, where the (200) MoO_2 planes are parallel to the (001) Al_2O_3 planes, further verifying the epitaxial nature of MoO_2 . The fast Fourier transformation (FFT) and line profile of the lattice spacing of the (200) MoO_2 precursor film with a calculated lattice spacing of 0.24 nm are illustrated in Figures S10a-b (standard spacing is 0.2406 nm from JCPDS#73-1249).

In comparison, the STEM image of the final MoS_2 film is displayed in Figure 2d, and the thickness was determined to be ca. 3 nm. According to the calculation of the volume expansion occurring during the epitaxial conversion process, there is almost no precursor evaporation away from the substrate. In other words, the chemical reaction and mass transfer occur predominantly on the substrate surface. The calculation of the volume expansion is given in detail in the supporting information in Figure S12. The HR STEM image in Figure 4e further displays the layer structure of the final film, with all layers parallel to the substrate surface, confirming the van der Waals epitaxy. Also, the FFT pattern and line profile of (001) MoS_2 with a lattice spacing of 0.58 nm (standard spacing is 0.615 nm from JCPDS#03-065-1951) are illustrated in Figures S9c-d. Figures 2f-g present the results of the electron energy-loss spectroscopy (EELS) elemental mapping (S and O) for the MoO_2 and MoS_2 films, plotted together with corresponding STEM images. Complete sulfurization of the MoO_2 film is confirmed by comparing the oxygen and sulfur elemental distributions. The relevant Mo and Al elemental mapping for the MoO_2 and MoS_2 film systems are illustrated in Figure S12.

Figure 3. (a) Low mag TEM and (b) SAEDs (red circle marked in [a]) from images of PC sample. (c) Low mag TEM and (d) SAEDs images of QSC sample (selected area marked with circle diameter about 20 μm as in [c]). (e-f) HR-STEM HAADF images with different magnification of QSC structure. (Red arrows marked in [a] and [c] towards lacy carbon film.)

The crystal structures of both PC and QSC MoS_2 were characterized by (S)TEM using transferred films on Cu grids with lacy carbon film (marked with red arrows in Figure 3a and 3c), as illustrated in Figure 3. Figure 3a presents the low-magnification TEM image of 3-nm thick PC MoS_2 , which is converted from amorphous MoO_2 film grown on (1-12) Al_2O_3 substrates. The PC MoS_2 structure is verified by the SAED pattern presented in Figure 3b, taken from the region marked by the red circle in Figure 3a. The observed ring pattern confirms the PC nature of these MoS_2 films. Additional SAED patterns of MoS_2 converted from amorphous MoO_2 films on (001) Al_2O_3 are depicted in Figure S13, and they also confirm the PC structure of MoS_2 . The low-magnification TEM image in Figure 3c displays the QSC MoS_2 film converted from the epitaxial MoO_2 film. The SAED pattern in Figure 3d indicates a single-crystal-like diffraction pattern with a hexagonal structure corresponding to MoS_2 . A comparison of the SAED patterns in Figures 3b and 3d reveals a distinct difference in the crystalline nature of these two films (PC vs QSC MoS_2). The PC MoS_2 has many random crystallite orientations, as evidenced by the ring diffraction pattern.

According to Figure S14a, the grain size is estimated to be 20 to 50 nm, which is consistent with the XRD analysis, indicating high density of grain boundaries, and large variations in the angles of the crystal domains as depicted in Figure S14b. On the other hand, the distinct diffraction spot pattern in Figure 3d (or inset in Figure S14d) indicates a single-crystal-like MoS₂ film, although the slight elongation of the diffraction spots points to the presence of small angle (1-2°) grain boundaries within MoS₂ monolayers as depicted in Figure S14c-d. This type of QSC structure has been observed before in the synthesis of other materials [22-25]. To verify that the QSC structure is uniform at the wafer scale, we selected five separate locations, marked with red circles in Figure S15a, to perform an electron diffraction analysis. Figures S15b-e (circle 1 in Figure 3d) confirm that in all five locations, the MoS₂ film exhibits a QSC structure. Also, we should emphasize that all the locations used to collect the SAED patterns have large diameters, up to 20 μm (illustrated in Figure 3c), which is the upper limitation of our TEM instrument. The total sample area from which we collected electron diffraction data for the QSC MoS₂ (depicted in Figure S15a) can thus be estimated to be around 1,500 μm², which indicates that the MoS₂ films indeed have a QSC structure at the wafer scale. Figure 3e presents the HR STEM HAADF images of the QSC MoS₂, with a zoom in on a specific area in Figure 3f. The honeycomb-like 2H MoS₂ phase structure is clearly evident in the image.

Figure 4. (a) Optical image of film before transfer with five marked areas. (b) Raman spectra measured at the five points marked in (a). (c) Optical image of the Raman mapping area. (d-f) Raman mapping of peak positions of E'_{2g} and A_{2g} vibration modes and the $\Delta\omega$. Scale: 10 μm . Optical images of 2-inch wafer-scale MoS_2 films transferred onto (g) 4-inch SiO_2 (300 nm)/ Si^{++} , (h) 2-inch glass, and (i) 2-inch PET substrates.

To verify the thickness uniformity of the MoS_2 films, five locations were chosen on the 2-inch wafer marked as 1), 2), 3), 4), and 5) in Figure 4a and used for the Raman and AFM line-scan characterizations. The Raman spectra at the marked points are indicated in Figure 4b. The positions of the Raman peaks are almost the same for all five spots, with a fixed peak separation of approximately 25 cm^{-1} . The AFM images and corresponding line profiles from these different areas are presented in Figure S14, which further confirms the thickness uniformity over a wafer

scale. The thickness of this MoS₂ film was found to be around 3 nm, which is consistent with the TEM characterization. Also, a randomly selected area (50×50 μm) was selected for Raman mapping. Figure 4c displays the optical image of the selected area, while Figures 4d-f display the Raman mapping results of the peak positions of E'_{2g} and A_{2g} vibration modes and their peak difference $\Delta\omega$. Uniform mapping contrasts and narrow distribution of the peak positions (Figure S15a-c) confirm the uniformity at the microscale. The QSC MoS₂ film deposited over the 2-inch wafer could be successfully transferred onto SiO₂ (300 nm)/Si, glass, and PET substrates, as illustrated in Figures 4g-i. The transfer process is illustrated in detail in the supporting information. This process indicates that the wafer-scale QSC MoS₂ film could be transferred and used in the fabrication of Si-based, transparent, and flexible electronics.

Figure 5. Output curves of (a) PC MoS₂ and (b) QSC MoS₂ TFTs. (c) Logarithmic for both and linear-scale transfer curves (d) PC and (e) QSC MoS₂ TFTs measured at gate voltage of 1 V. (f) distribution of PC MoS₂ for 34 devices and of QSC MoS₂ TFTs for 46 devices.

A comparison of the electronic properties between QSC and PC MoS₂ film was performed by fabricating thin film transistors. Top gate transistor device was fabricated on the as-synthesized MoS₂ film on sapphire substrate (both QSC and PC), using HfO₂ as gate dielectrics and Au/Ti as both the source/drain (S/D) contacts and gate (G). A typical device with channel length/width (L/W) = 90/50 μm was used for the transistor performance comparison in Figures 5a-e. The capacitance per unit area of HfO₂ dielectric (60 nm) was measured and calculated to be $2.7 \times 10^{-7} \text{ F/cm}^2$ with a metal/insulator/metal (MIM) structure. Figures 5a-b depict the output curves of the PC and QSC MoS₂ devices, where ohmic contact, linear, and saturation regions can be observed. In addition, both MoS₂ films display n-type semiconductor behavior. The logarithmic plots of the transfer curves with SD voltages of 1 V and 0.1 V (Figure 5c) demonstrate the on-current to off-current (I_{on}/I_{off}) ratio to be around 10^5 for QSC MoS₂ devices, but only 10^2 for the PC. The linear plots of the transfer curves are presented in Figure 5d for the PC and Figure 5e for the QSC TFTs. On the one hand, the field effect mobility of QSC TFTs was calculated to be $8.85 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which is comparable to that from CVD methods [26]; on the other hand, the mobility of the PC MoS₂ film was only $0.13 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for PC film, and this is a similar magnitude as that in previous reports.[12, 27] Figure 5f, which includes data from 46 QSC and 34 PC devices with different channel widths and lengths, indicates that the QSC MoS₂ devices have mobility that is about 35 times higher than that of PC MoS₂ devices. The large difference in electrical performance between the QSC and PC MoS₂ film devices can be attributed to at least two reasons. One factor is the quasi-single-crystalline quality of the MoS₂ films obtained using epitaxial MoO₃, which leads to only smaller angle grain boundaries or fewer planar defects. However, the high density of large angle grain boundaries and defects in PC MoS₂ film are formed and inherited from the amorphous precursor film. This can result in enhanced carrier scattering in the PC MoS₂ films. Furthermore, our results

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2
3 reveal that the surface roughness of the PC MoS₂ is twice as large as that of the QSC films, which
4 may lead to surface roughness-induced scattering of carriers, thereby leading to a lower mobility.
5
6
7

8 9 **Conclusion**

10
11 In conclusion, wafer-scale MoS₂ films were successfully prepared by a two-step vapor-solid
12 phase reaction (VSPR) process. Structure, morphology, and uniformity of the films were optimized
13 over 2-inch wafers by varying the laser deposition and sulfurization process conditions. By
14 controlling the precursor MoO₃'s film crystallinity, we could produce quasi single crystalline or
15 polycrystalline 2D MoS₂ at the wafer scale. The quasi single crystalline MoS₂ film on a 2-inch
16 wafer demonstrated significantly enhanced electrical performance, compared to PC MoS₂ films.
17 They also demonstrated better performance than all previously reported MoS₂ films prepared by
18 other two-step MoS₂ formation processes.
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46 **Notes**

47
48 The authors declare no competing financial interest.
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52 **Supporting Information**

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54 The Supporting Information is available free of charge on the IOP Publications website.
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Graphical information including XRD, Raman, PL and XPS, AFM images, TEM images, and additional graphica.

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Supporting Information

Wafer scale quasi single crystalline MoS₂ realized by epitaxial phase conversion

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Figure S1. (a) Amorphous MoO₂ growth on (001) Al₂O₃ at 300 °C and room temperature using 1,500 PLD shots. (b) Amorphous MoO₂ growth on (1-12) Al₂O₃ at 400 °C with 1,500 PLD shots and the converted PC MoS₂ films.

Figure S2. Gaussian fitting of XRD (002) peak of (a) epitaxial MoS₂ film (b) polycrystalline MoS₂ film

1. The Raman Spectra of MoS₂ Films Formed at Different Temperatures

To achieve higher-quality MoS₂ films, the sulfurization temperature was optimized using the 100 PLD-shot MoO₃ films. Specifically, three different sulfurization temperatures (700, 800, and 900°C) were evaluated to form quasi-single-crystalline (QSC) MoS₂. Raman and photoluminescence (PL) spectroscopy as well as X-ray photoelectron spectroscopy (XPS) were performed to evaluate the qualities of the resultant MoS₂ films. The Raman spectra in **Figure S2** demonstrate that two peak positions are always located at 384.6 and 409.6, regardless of the sulfurization temperature, corresponding to the E'_{2g} and A_{2g} modes of MoS₂, respectively. However, a higher conversion temperature results in a higher intensity of both peaks. These Raman spectra were further analyzed by Lorentz fitting of the peaks. It can be concluded that the full width at half maximum (FWHM) of these peaks becomes smaller at a higher sulfurization temperature (**Table S1**), indicating that a better quality MoS₂ film is obtained at a higher temperature. Actually, when a sulfurization temperature of 900 °C is used, the FWHM of the E'_{2g} peak is 3.74, which is close to the reported value (FWHM = 3.5) for few-layer, single-crystalline MoS₂ flakes prepared by CVD.[1]

Figure S3. Lorentz fitting of the Raman spectra of final MoS₂ films formed at (a) 700, (b) 800, and (c) 900 °C.

Table S1. FWHM obtained from Lorentz fitting of the Raman data of MoS₂ from Figure S1.

TEMPERATURE (°C)	FWHM (E' _{2G})	FWHM (A _{2G})
700	5.49	5.10
800	4.10	4.09
900	3.74	4.27

The reported FWHM (E'_{2g}) of single-crystal, few-layer MoS₂ from CVD process is **3.5**. [1]

2. The PL Spectra of MoS₂ Film Formed at Different Temperatures

A higher PL peak intensity can also be observed in MoS₂ films obtained at a higher sulfurization temperature (**Figure S3**), further confirming the higher quality of MoS₂ at a higher sulfurization

temperature. [2] Peaks marked with a star at 1.79 eV are actually from the sapphire substrate, while the peaks at 1.83 eV and 1.98 eV correspond to the A and B excitons of MoS₂ materials, respectively. [3]

Figure S4. PL spectra of the final MoS₂ film formed using 700, 800, and 900 °C sulfurization temperatures.

3. The XPS Spectra of MoS₂ Films Formed at Different Temperatures

Figure S4a indicates that S 2p_{1/2} and S 2p_{3/2} peaks are observed at 163.8 and 162.6, and Figure S4b displays XPS peaks at 232.9, 229.8, and 227, which correspond to Mo 3d_{3/2}, Mo 3d_{5/2}, and S 2s,

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3 respectively. These peaks' positions are consistent with those reported for crystalline MoS₂ films.^[2]
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5 It is interesting to note that the different sulfurization temperatures do not cause any peak shift in
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7 the XPS spectrum, which indicates that MoS₂ crystals can be obtained at all three temperatures. A
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9 further analysis was conducted on XPS spectra in **Figure S4b** by Lorentzian-Gaussian fitting to
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11 acquire the Mo/S ratio. As listed in **Table S2**, Mo/S ratios of 1/1.88, 1/1.90, and 1/1.94 are obtained,
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13 corresponding to the sulfurization temperatures of 700, 800, and 900 °C, respectively. These results
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15 demonstrate that the most stoichiometric MoS₂ could be obtained using the 900 °C sulfurization
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17 process. Besides, MoS₂, converted at 900 °C from an amorphous MoO₂ film with 100 PLD shots
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19 on (1-12) Al₂O₃ substrate, has the element ratio Mo/S = 1/1.936, which is similar to that on (001)
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21 Al₂O₃ substrate. This means the stoichiometry of MoS₂ depends mainly on the sulfurization
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23 process, and the quality of the precursor film has little influence on it. The lowest MoS₂ surface
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25 roughness was also obtained at 900 °C, as can be concluded from the root mean square (RMS)
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27 roughness analysis depicted in **Figure S5**. However, **PC** MoS₂ that is converted from an
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29 amorphous MoO₂ film on (1-12) Al₂O₃ substrate is rougher, compared with that converted from
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31 an epitaxial precursor film, as illustrated in **Figure S5d**. The above analysis clearly demonstrates
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33 that a higher sulfurization temperature improves the quality of 2D MoS₂; however, there is a limit.
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35 In fact, we found that further increasing the sulfurization temperature to more than 1,000 °C
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37 resulted in the evaporation of the precursor MoO₂ film.
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Figure S5. (a) XPS-S 2p. (b) Lorentzian-Gaussian fitting of XPS-Mo 3d spectra of final MoS₂ film XPS 700, 800, and 900 °C.

Table S2. Elemental ratios of Mo and S deduced from fitting the data in Figure S2.

Sulfurization temperature (°C)	700	800	900
Mo:S ratio	1:1.88	1:1.90	1:1.94

Figure S6. RMS roughness of final 2D MoS₂ films obtained using sulfurization temperatures of (a) 700 °C, (b) 800 °C, and (c) 900 °C on Al₂O₃ (001), and (d) 900 °C on (1-12) Al₂O₃ substrate. Scale bar: 1 μm.

4. Roughness and Thickness of MoS₂ Film Formed at Different Temperatures with Different Thickness

To investigate the sulfurization process in more detail, the surface morphology of the precursor MoO₂ films deposited using different PLD shots (40, 60, 80, 100, 120, 140, 160, 200, and 300 shots) and their corresponding final MoS₂ films were studied using an atomic force microscope (AFM). **Figure S6** illustrates the typical AFM surface morphology of MoO₂ films, where the RMS roughness changes from 0.147 to 0.270 nm as the thickness increases. It can be seen that an excellent surface smoothness of precursor films was achieved (RMS < 0.27 nm), although the RMS roughness increases slightly with the number of PLD shots. **Figure S7** depicts the typical AFM surface morphologies of final MoS₂ films. The RMS roughness changes from 2.554 to 0.178 nm under 100 shots and up to 0.542 nm again from 100 to 300 shots. Interestingly, the RMS roughness of the final 2D MoS₂ films changed significantly with the thickness (the number of PLD laser shots) of MoO₂, as is also indicated in **Figure S8**. The precursor MoO₂ films deposited using 40 PLD shots resulted in isolated islands of MoS₂, as illustrated in **Figure S7a**. As the number of PLD shots of MoO₂ increased, the islands began to coalesce; however, continuous MoS₂ films were not formed until the number of MoO₂ PLD shots reached 100, as indicated in **Figure S7d**. The RMS roughness of the 2D MoS₂ films decreased before the formation of a continuous film, and it increased again after the formation of a continuous 2D MoS₂ film. **Figure S8** presents the RMS roughness change of both the precursor MoO₂ and the final MoS₂ films as a function of the MoO₂ film thickness (the number of PLD shots). The converted MoS₂ films basically always demonstrated higher roughness than the corresponding MoO₂ precursor. The only exception occurred when the number of MoO₂ laser shots was 100 (3.15 nm MoO₂), where the continuous MoS₂ film had just formed. The thickness of the MoS₂ films obtained for different MoO₂ precursor

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3 thicknesses (PLD shots) was studied using AFM, as illustrated in **Figure S8**. Before the formation
4 of the continuous MoS₂ film, the thickness increased nonlinearly with the number of MoO₂ laser
5 shots, but once a continuous film formed, it began to increase linearly with the number of laser
6 shots, as depicted in **Figure S8**. However, the precursor MoO₂ film thickness always increased
7 linearly with the number of laser shots, as expected for the PLD process.
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15 Here, we should emphasize that the thickness of 2D MoS₂ film, converted from MoO₂ film
16 with 100 MoO₂ PLD shots, is approximately 3 nm (four to five layers). We attempted to further
17 scale down the thickness of a continuous 2D MoS₂ film by using a thinner MoO₂ thickness (a
18 lower number of PLD shots, e.g., 80, 60, and 40 shots); however, no continuous MoS₂ film could
19 be formed thinner than four to five layers. This indicates that, at this stage, it is not feasible to
20 fabricate a large-area, continuous, monolayer MoS₂ film based on the sulfurization of a (200)
21 MoO₂ // (001) Al₂O₃ epitaxial film system. As we analyzed in the beginning, there is a lattice
22 mismatch that exists in this epitaxial film system. The mismatch is -1.6% for [001] MoO₂ // [120]
23 Al₂O₃, which causes tensile strain, and 2.0% for [010] MoO₂ // [100] Al₂O₃, which causes
24 compressive strain. We believe that these lattice strains limit the thickness of the resulting MoS₂
25 obtained from the sulfurization of MoO₂ that is 3 nm or higher. However, if an epitaxial precursor
26 system with a smaller film/substrate lattice mismatch can be developed, then large-area, monolayer
27 MoS₂ films could be realized using our method.
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Figure S7. RMS roughness of precursor MoO₂ film with (a) 40, (b) 60, (c) 80, (d) 100, (e) 120, (f) 140, (g) 160, (h) 200, and (i) 300 PLD shots.

Figure S8. RMS roughness of final MoS₂ films sulfurized from precursor MoO₃ film with (a) 40, (b) 60, (c) 80, (d) 100, (e) 120, (f) 140, (g) 160, (h) 200, and (i) 300 PLD shots.

Figure S9. Curves illustrating RMS roughness change for precursor MoO₂ and final MoS₂ films with different precursor thicknesses (PLD shots).

Figure S10. Line profile on HR STEM images. (a) HR STEM images of MoO₂ film and FFT. (b) Line profile indicating the lattice spacing in (a). (c) HR STEM images of MoS₂ film and FFT. (d) Line profile depicting the lattice spacing in (c).

Figure S11. EELS elemental mapping. (a) The HAADF STEM image of MoO₂ for EELS mapping area. (b) Al (c) Mo EELS mapping from the area in (a). (d) The HAADF STEM image of MoS₂ for EELS mapping area. (e) Al (f) Mo EELS mapping from the area in (d).

Figure S12. Cell Model of (a) monoclinic MoO₂ (b) 2H-MoS₂.

5. Calculation of volume expansion during the epitaxial phase conversion process

If we presume that the epitaxial MoO₂ film has a perfect single crystal structure without defects or strains. The volume expansion from MoO₂ film to MoS₂ film is calculated as follows:

Suppose there was no evaporation, Mo element is the only element which always stays on the substrate during sulfurization process. Our calculation will be based on the areal density of Mo atoms.

The unit cell of MoO₂ monoclinic crystal is shown in Figure S12(a), with the following lattice parameters(JCPDS#73-1249):

$$a = 0.5536 \text{ nm (along [100])}, b = 0.4856 \text{ nm (along [010])}, c = 0.5628 \text{ nm (along [001])};$$

$$\alpha = 90^\circ, \beta = 119.683^\circ, \gamma = 90^\circ$$

There are 3 Mo atoms on average (2 inside the cell, 2 on the surface of the cell, as shown in the inset side-view cell along [001] direction) in one MoO₂ unit cell.

As MoO₂ epitaxial film grows with (100) lattice plane parallel to the substrate surface:

The height h of one MoO₂ cell normal to the substrate surface should be as follow:

$$h = a \cdot \sin\beta = 0.5536 \times \sin 119.683^\circ = 0.481 \text{ nm}$$

For 3 nm thick MoO₂ film, the average number of stacking unit cells should be: 6.23

The area of one MoO₂ unit cell occupied on the substrate should be:

$$Area = b \times c = 4.856 \times 5.628 = 27.33 \text{ \AA}^2 = 2.733 \times 10^{-19} \text{ m}^2$$

3nm thick MoO₂ film on only one unit cell area should have the number of Mo atoms:

$$6.23 \times 3 = 18.69$$

Then the areal density of Mo atoms of 3 nm thick MoO₂ film should be:

$$\frac{18.69}{2.733 \times 10^{-19}} = 6.81 \times 10^{19} \text{ m}^{-2}$$

The unit cell of 2H MoS₂ crystal is shown in Figure R4(b), with the following lattice parameters(JCPDS#03-065-1951):

$a = 0.316 \text{ nm}$ (along [100]), $b = 0.316 \text{ nm}$ (along [010]), $c = 1.229 \text{ nm}$ (along [001]);

$\alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ$

From the unit cell of 2H MoS₂, we could figure out there are 2 Mo atoms in one unit cell:

The area of (001) plane for one unit cell is:

$$Area = a \times b \times \sin\gamma = 0.316 \times 0.316 \times \sin 120^\circ = 8.647 \text{ \AA}^2 = 8.67 \times 10^{-20} \text{ m}^2$$

Since 2 layers are included in one unit cell of 2H MoS₂, there is only one Mo atom in one unit cell area occupied on the substrate, therefore, the areal density of Mo atoms in one layer film should be:

$$\frac{1}{8.67 \times 10^{-20} \text{m}^2} = 1.16 \times 10^{19} \text{m}^{-2}$$

The Mo atoms transferred from MoO₂ to MoS₂ film should be also $6.81 \times 10^{19} \text{m}^{-2}$, assuming no Mo evaporation:

Then the layer number of MoS₂ should be: $\frac{6.81 \times 10^{19} \text{m}^{-2}}{1.16 \times 10^{19} \text{m}^{-2}} = 5.87$ layer

So MoS₂ converted from 3nm thick MoO₂ film should have 5.87 layers on average. According to our TEM cross section characterization, the layer distance is 0.582 nm. Then the calculated thickness of MoS₂ is $5.87 \times 0.582 = 3.42 \text{ nm}$, which is a little higher than the 3 nm obtained from the TEM characterization. This is reasonable, since our calculation of MoO₂ film is based on ideal single crystalline structure. However, any deposited epitaxial film should contain some defects or strains. These defects and strains inside the 3 nm thick MoO₂ film means that the actual number of Mo atoms per area is less than $6.81 \times 10^{19} \text{m}^{-2}$, MoS₂ film thickness is actually smaller.

According to the non-ideal single crystal structure of real epitaxy MoO₂ film and our calculation about the volume expansion based on the ideal single crystal model, we conclude that almost no precursor film evaporates away from the substrate.

Figure S13. (a) Low mag TEM. (b) SAED for MoS₂ converted from MoO₂ growth at room temperature. (c) LR TEM. (d) SAED characterization for MoS₂ converted from MoO₂ growth at 300 °C. (Red arrows towards lacey carbon film.)

Figure S14. (a)LR STEM image (b) atomic resolution STEM image and inset SAED of PC MoS₂ film. (c)LR STEM image (d) atomic resolution STEM image and inset SAED of QSC MoS₂ film.

Figure S15. (a) Low mag TEM images marked with five red circles. (b-e) SAED characterized from red circle areas marked with 2, 3, 4, and 5. (SAED from circle area 1 is presented in main manuscript in Figure 2[c-d], all with the selected area with the diameter 20 μm .)

Figure S16. AFM line scans at five points marked in Figure 4a. Scale bar: 1 μm .

Figure S17. (a-c) The frequency counts for all the data in the Raman mappings from Figure 4 (d-f), respectively.

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