High-Performance Monolayer MoS₂ Films at the Wafer Scale by Two-Step Growth

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To realize multifunctional devices at the wafer scale, the growth process of monolayer (ML) two-dimensional (2D) semiconductors must meet two key requirements: (1) growth of continuous and homogeneous ML film at the wafer scale and (2) controllable tuning of the properties of the ML film. However, there is still no growth method available that fulfills both of these criteria. Here we present the first report on the preparation of continuous and uniform ML MoS₂ films through a two-step process at the wafer scale. Unlike in previous ML MoS₂ film growth processes, the ML MoS₂ film could be uniformly modulated across the wafer in terms of material structure and composition, exciton state, and electronic transport performance. A significant result is that the high-quality wafer-scale ML MoS₂ films realized superior electronic performance compared to reported two-step-grown films, and it even matched or exceeded reported ML MoS₂ films prepared by other processes. The transistor performance of the optimized ML film achieves a field effect mobility of 10 to 30 cm²/Vs, an on/off current ratio of about 10⁷, and hysteresis as low as 0.4 V.

1. Introduction

Two-dimensional (2D) single monolayer (ML) chalcogenide films are more remarkable than their fewer-layered counterparts. Because reducing the thickness of 2D chalcogenide film to only single layer breaks the lattice inversion symmetry,^[1] and the band gap is transformed from an indirect to a direct gap.^[2] This transformation endows it with novel optical and electrical properties.^[3] Particularly, excitons in ML 2D chalcogenides are not only present as electroneutral (i.e. the same as other materials)^[4, 5] but can also be bonded with electrons and holes (charged excitons or trions) with giant exciton binding energies, which are unique in 2D ML films.^[6-8] These novel physical phenomena of ML MoS₂ can be excited by light and controlled by an electric field.^[8, 9] Therefore, the mutual conversion of light and electrical signal can enable data processing and storage on the sole basis of ML 2D chalcogenides. In fact, besides traditional optoelectronic devices, novel devices that are based on controlling excitons (i.e. exciton flux) have recently been reported.^[10, 11] Although such properties of ML chalcogenide have been verified, they may not require exactly the same quality of ML 2D films. For example, transistors may need high-quality films with fewer electron scattering centers,^[12] while luminescent devices may need more active sites for an exciton recombination luminescence center,^[13, 14] and some chemical sensing devices may require more defective sites to sense special molecules.^[15] Thus, to grow 2D ML films that are suitable for various device applications, two conditions are necessary in the 2D ML film growth process: (1) Two-dimensional ML films should be continuous and homogeneous at the wafer scale, and (2) tuning the structural, excitonic, and electronic properties of the ML films should be possible during the growth process to achieve the optimal ML film properties for the desired application.

Previous research has yielded continuous and homogeneous ML MoS₂ films that were grown at the wafer scale through a variety of methods, such as metal-organic chemical vapor deposition (MOCVD),^[12] magnetron sputtering (MS),^[16] molecular-beam epitaxy (MBE),^[17] chemical vapor deposition (CVD),^[18, 19] and layer-resolved splitting (LRS).^[20] Most of these reports have focused on an attempt to realize continuity and uniformity at the wafer scale. However, the uniformity of these films is sensitive to fluctuations in the growth parameters, which has made it difficult to tune their properties in scaled-up processes. Therefore, it is necessary to develop methods to engineer the structural, excitonic, and electronic properties of 2D ML chalcogenide without compromising continuity and homogeneity. The present report details a two-step growth process that is based on a sulfurization process of molybdenum (Mo)-containing (Mo metal,^[21] oxides,^[22] or compounds^[23, 24]) precursor films at an elevated temperature.

The two-step process of creating 2D ML films has consistently suffered from two major drawbacks (see Table S2): (1) discontinuity when film thickness is reduced to a single layer, and (2) poor-quality films, which result in inferior electronic device performance. However, in this study, we have developed a novel two-step process that resolves both of these issues. The ML MoS₂ films were successfully prepared continuously and homogeneously on a 2-inch sapphire substrate. Electronic devices of the optimized ML film revealed high performance that is comparable to that of the ML film that was prepared through aforementioned methods. Our process is capable of maintaining the continuity and homogeneity of the ML films at the wafer scale, and modulating the structural, excitonic and electronic properties, and laser-induced photoluminescence (PL) enhancement.

2. Results and Discussion

2.1. Homogeneity and continuity of ML MoS₂ film at the wafer scale

The growth of wafer-scale ML MoS₂ film has always posed a challenge, especially in the two-step process. Diverse precursor films have been developed for sulfurization, but most of them yield discontinuous films in the process of conversion (sulfurization) into ML MoS₂ film (Table S2). However, through our process, we realized a ML MoS₂ film with wafer-scale continuity by carefully controlling the Ar/S vapor flow during sulfurization. We discovered that minimizing the Ar/S flow dynamic disturbance of the sulfurization step could produce homogeneous and continuous ML film at the wafer scale (see Figure S1). The supporting information shows process optimization details. In principle, with access to a large enough space in a sealed reactor with a highly pure and static Ar/chalcogens atmosphere, high-quality ML chalcogenide film wafers could be easily realized in batch production.

The uniformity of the MoS₂ film is confirmed in **Figure 1**. Since the two-step process offers the outstanding advantage of controlling the layer number (thickness) at the wafer scale, we verified both the bilayer (BL) and ML film uniformity at the wafer scale. Figure 1a depicts BL and ML films grown at the wafer scale; the left is a 2-inch BL film with a thickness of 1.46 nm, the middle is a 2-inch ML film with a thickness of 0.72 nm, and the right is the bare sapphire substrate (see AFM line scan inset). The color difference between the BL and ML MoS₂ films can be clearly identified. Both samples appear uniform, as confirmed by Raman spectroscopy. Figure 1b depicts the Raman peaks of the BL film, which were obtained from the seven selected points that are marked in Figure S2. Notably, all locations exhibit a Raman peak difference of 21.3 cm⁻¹, which is consistent with the value reported for BL MoS₂ flakes.^[25] The Raman characterization in Figure 1c indicates that the sample in the middle of Figure 1a has a peak difference of 19.2 cm⁻¹ across all seven points, which confirms that single-layer MoS₂ was also uniformly grown at the wafer scale. Figure 1d reveals that the middle sample has a much stronger PL intensity which is almost

20 times higher than the intensity of the left sample in Figure 1a. This result is consistent with the previously reported unique ML MoS₂ PL properties.^[26] It also indicates that the MoS₂ film with one ML thickness was successfully grown at the wafer scale. Figure 1e and Figure S3 present patterns of ML MoS₂ with different shapes, which were patterned by dry etching as described in the methods section. The patterns were collected (at the sub-millimeter scale) through an optical microscope at several multiple locations on the wafer. All of these large-scale patterns present uniform color contrast, which illustrates the uniformity of the films at the wafer scale.

To verify the continuity, we performed PL mappings on the unpatterned ML MoS₂ film on four selected areas (see red marking in **Figure 2a**). Figure 2b-e provide the relevant PL intensity mappings with a 200-nm spatial resolution. The strong PL intensity in Figure 2b-e, which originated from the unique ML chalcogenide film luminescence property, was uniform for all four mapping areas. In addition, the corresponding PL peak positions are uniformly located at 1.86 eV (see maps in Figure S4), which is the direct band gap of ML MoS₂ film. This result further indicates the uniform and continuous nature of the ML film.^[27] Further characterization was performed on randomly selected concentric circular, square, and triangular patterns. In their optical images in Figure 2f and Figure S5e, i, and m, the color contrast is uniform and monochromatic. The AFM height (see Figure 2g and Figure S5a, h, and q) and phase (see Figure S5b, c, i, and p) images demonstrate continuous smoothness of these shapes compared to the discontinuous dot-like area, which resulted from dry etching. In addition, the E_{2g} and A_{1g} Raman peak position (see Figure 2h, Figure S5d, f, j, h, and o) and intensity mappings (Figure 2i, Figure S5g and k) were characterized with a nanometer-scale resolution (200 nm) to capture the color uniformity in these patterned shapes. All of these optical, AFM, Raman, and PL mappings resulted in different shapes and locations of the wafer, which evidences the uniformity of our ML films at the wafer scale.

2.2. Composition modulation of ML MoS₂ film

One of the remarkable advantages of the two-step process is that this method can realize the composition and structure engineering of ML MoS₂ film without losing the uniformity and continuity. X-ray photoelectron spectroscopy (XPS) spectra in **Figure 3** semi-quantitatively indicate the compositional change of ML MoS₂ films that were grown at different temperatures. Figure 3a presents the intensity-normalized XPS curves with Lorentzian-Gaussian fitting of both Mo-3*d* (left curves) and S-2*p* (right curves) elements when the precursor MoO₃ films were sulfurized in the range of 500 to 1,000°C. By fitting and analyzing the Mo-3*d* curves, the Mo element peaks with both the oxidation state (Mo⁶⁺-3*d*) and sulfurization (Mo⁴⁺-3*d*) could be discerned. Mo⁴⁺-3*d*_{3/2}, Mo⁴⁺-3*d*_{5/2}, and S-2*s* exhibit peak positions at 232.8, 229.7, and 226.6, respectively. Also, S-2*p*_{1/2} and S-2*p*_{3/2} peaks are observed at 163.7 and 162.5 eV, respectively, in the S-2*p* spectra. It should be noted that the peak positions do not display obvious change under different sulfurization temperatures. These results indicate that the MoS₂ film could be obtained in the entire temperature range (500-1,000°C). However, the Mo⁶⁺-3*d* and Mo⁴⁺-3*d* reflect a clear intensity change, which implies that a change occurred in the oxidation state ratio. To determine the composition change, we plotted the integral intensity ratios between Mo⁶⁺ and Mo⁴⁺ peaks versus the sulfurization temperature in Figure 3b. Through nonlinear curve fitting, we discovered that the oxidized state in MoS₂ film attenuates exponentially with an increase in temperature from 500 to 1,000°C.

2.3. Excitons modulation of ML MoS₂ film

The structural variation of the ML MoS₂ film under different temperatures was further monitored through Raman and PL (see **Figure 4**). Meanwhile, the resulting change in the exciton and optoelectronic properties could be explored from these spectra. Figure 4a depicts the Raman

spectra with peaks at E'_{2g} and A_{1g} , which correspond to in-plane and out-of-plane vibration of S–Mo–S, respectively.^[25] From the line width of E'_{2g} , we could derive information about the crystalline quality of ML films.^[28] As Figure 4b illustrates, the line width of E'_{2g} decreased as the sulfurization temperature increased from 500 to 800°C, which suggests that the crystalline quality was enhanced by increasing the sulfurization temperature. However, the E'_{2g} line width hardly changed at temperatures higher than 800°C; therefore, a high crystalline quality of ML MoS₂ can be achieved by using a sulfurization temperature above 800°C. The E'_{2g} peak position (black curve in Figure 4c) conveys almost no shift as sulfurization temperature changes. However, an obvious red shift was observed in the A_{1g} peak position (orange curve in Figure 4c) when the temperature was between 800 and 1,000°C, which implies that films obtained above 800°C have a more n-type doping level.^[29, 30] Thus, exciton-related optoelectronic properties might also be modulated when preparing the ML MoS₂ film under different sulfurization temperatures.

To modulate the excitons of small-size ML MoS₂ flakes, various methods have been applied, including chemical treatment (TFSI,^[13] p-type F4TCNQ and n-type NADH^[31]), plasma treatment,^[14] molecular physisorption (O₂, H₂O),^[32] thermal-annealing,^[14] α -particle^[33] or laser irradiation,^[34, 35] electric field tuning^[36], dielectric screening,^[37] and changing substrates with different electron affinities.^[38] All of these reported exciton modulation methods are based on additional physical and chemical treatment on the exciting small-size ML flakes.

Our process differs from the above methods is that we realized the exciton modulation by directly modifying the growth parameters of ML films at the wafer scale. This outcome can facilitate the fabrication of exciton-based optoelectronic integrated devices. Figure 4d depicts the PL curves with Lorentzian-Gaussian fitting of ML MoS₂ films converted at different temperatures. The peak A in PL spectra (Figure 4d) were deconvoluted into peaks of negatively charged excitons

(or trions) (X^- , dark yellow curves) and neutral excitons (X , orange curves). B peaks (violet curves) correspond to the valance band splitting that was induced by spin-orbital coupling.^[31] Figure 4e depicts the positions of X (orange dots) and X^- (dark yellow dots) versus sulfurization temperatures. The average position difference between X and X^- is about 40 meV, which is usually taken as the trion binding energy, and this value is consistent with previous reports.^[20, 36] The inset in Figure 4e presents the change in integrated intensity ratios of I_{X^-}/I_{total} alongside the different conversion temperatures. Figure 4f displays the relation between n_{el} and I_{X^-}/I_{total} (calculation shown in SI). Thus, the values of electron doping density n_{el} corresponding to certain I_{X^-}/I_{total} could be extracted from Figure 4f. The electron doping level increased from 1.07×10^{13} to a maximum of 7.7×10^{13} cm^{-2} , when the sulfurization temperature increased from 600 to 800°C. Then, it dropped to 2.8×10^{13} cm^{-2} with a further temperature increase to 1,000°C. Figure 4g provides a comparison of n_{el} values in this work versus previous reports. The red points are the n_{el} values as derived by PL photoexcitation.^[31, 34, 39-41] The black points are the n_{el} values obtained through electronic device drain currents.^[40, 42-46] Notably, all of these reports used single crystalline ML MoS₂ flakes (exfoliated or CVD grown) as research objects. Since n_{el} values in this work are also derived from PL photoexcitation, it is more reasonable to compare them tjko the red-point n_{el} values (Figure 4g). Apparently, ML MoS₂ films that were grown at 800 and 900°C in this work have n_{el} values that are close to those of ML single crystalline MoS₂ flakes. However, ML films that were grown at 600, 700, and 1,000°C possess much lower electron doping densities. Moreover, Figure 4g indicates that the reported n_{el} values derived from electronic device drain currents exhibit almost one order of magnitude less than that of PL spectra, which is a recently reported phenomenon.^[40] Through analysis of the PL characterization above, we demonstrated that the electron doping level

of the wafer-scale ML MoS₂ film could be engineered by simply varying the experimental parameters in the two-step growth process.

Laser irradiation has been employed as a method for realizing PL enhancement and quenching in ML MoS₂ flakes (deposited by CVD and exfoliation).^[34, 35] This PL dynamic change induced by laser irradiation could help to infer the dynamic evolution of the excitons and, thus, corresponding changes in surface absorption and the material structures of ML flakes. A similar PL evolution phenomenon was detected in our two-step-grown ML film. Initially, we tried to perform a PL measurement repeatedly on the same position of 900°C-grown ML film. The measurement was performed for 48 seconds with a laser wavelength of 473 nm and a laser power of 6.2 mW. We realized PL enhancement in the first nine repetitions, as depicted in Figure 4h. However, PL quenching occurred in the subsequent measurements (PL spectra are presented in Figure S6). Figure 4i illustrates the PL intensity (orange curve) and position changes (dark yellow curve) versus the measurement repetition. The PL intensity exhibited rapid enhancement in first four counts and then slowly increased until the ninth count, which is likely due to p-type doping that results from the physical and chemical absorption of O₂ and H₂O. Thus Fewer excitons were charged as trions, which led to enhanced PL intensity.^[35] This effect could be indirectly inferred from the shift in the PL peak toward the X exciton peak position (dark yellow curve in Figure 4i). Damage to the ML film structure due to laser-heating-induced oxidization might have been the catalyst for the subsequent PL quenching between the 9th and 19th measurements.^[35] The inset of Figure 4i contains the PL measurement with lower laser intensity (power of 3.1 mW) and two consecutive measurements at the same points of the film (the waiting time was 1.5 hours between first and second measurements). Photoluminescence (PL) enhancement in the second measurements (orange curve) started at a PL intensity that was 40% less than that of the 9th

measurement of the first run. This result might indicate laser-induced absorption of O_2 and H_2O is partly reversible.^[34] Figure S7 illustrates the PL enhancement under different laser intensity measurements. We performed the same PL measurements on ML film that was converted at other temperatures. As Figure 4j depicts, the PL enhancement degree differed when the films were prepared at different sulfurization temperatures. For example, the 600°C-prepared film displayed only PL quenching with repeated measurement, which may be due to higher risk of damaging the less crystallized structure under laser irradiation, as the Raman spectra in Figure S8 confirm. The films prepared between 700 and 900°C exhibited some PL enhancement with repeated PL measurement, while almost no PL intensity changes occurred with repeated PL measurements on the 1,000°C-prepared films. The relevant physical-chemical evolution and corresponding structure, exciton, and electron changes with repeated PL measurement are still unclear, as only two papers have reported on these phenomena.^[34, 35] This inquiry warrants further systematic experimental and theoretical study. However, from our initial observations, we could conclude that using different temperatures to grow films by our two-step process can clearly influence the structure and exciton dynamic evolutions under laser irradiation.

2.4. Electronic property modulation of ML MoS_2 film

The ML MoS_2 is considered one of the most promising candidates for post-Moore's Law electronics in view of its relatively high mobility,^[3] excellent stability,^[47] and lack of short-channel effect during device operation.^[48] Thus, it is necessary to evaluate the transistor performance using our two-step-grown ML MoS_2 films. **Figure 5** demonstrates the performance of top-gated (TG) thin-film transistors (TFTs) that were fabricated with ML MoS_2 films as channel layers. All of the tested devices had a channel width (W) and length (L) $L/W=10/200\ \mu m$ (see Figure S9). Figure 5a displays the logarithmic plots of the dual-sweep transfer curves that were obtained with $V_{SD} = 1\ V$. As expected, the temperature of the ML film conversion from MoO_2 into MoS_2 obviously

influenced device performance. The on-current increased, while the off-current decreased alongside an increase in the conversion temperature from 600 to 800°C. As Figure 5b indicates, this effect in turn enhanced the on/off current ratio. This outcome indicates that higher crystalline quality ML film achieved a superior field effect transport performance. However, further increasing the sulfurization temperature to 1,000°C did not affect the on/off current ratio. This phenomenon may be due to the previously discussed lack of a clear change in the crystalline quality in the range of 800 to 1,000°C. Figure 5c and Figure S10 illustrate the subthreshold swing (SS) variation versus film sulfurization temperature. These values (for both forward and reverse sweeps) decreased as the temperature increased from 600 to 900°C, but they rose when the temperature was further increased to 1,000°C. The smallest values of SS_f and SS_r were 0.94 and 0.74, respectively, and were realized at 900°C. An inset in Figure 5c presents the difference between SS_f and SS_r as derived from the hysteresis. The change in SS may be explained by the effect of the sulfurization temperature on the native defect trap states of ML MoS₂ films,^[49] the MoS₂/HfO₂ interface trap states,^[50] or both. Apparently, films that were converted at 900°C exhibited the smallest trap density. The forward threshold voltage (V_{THf}) also changed with the sulfurization temperature (see inset in Figure 5c, Figure S11). It displayed monotonous variation from -3.8 to 0.7 V as the temperature increased from 600 to 1,000°C. Therefore, a higher conversion temperature of the ML MoS₂ film leads to diminished n-doping, which initially appears to conflict with the above PL analysis. A possible reason for this paradox might be that the interface formation during the HfO₂ ALD-deposition on ML MoS₂ film dominates the doping behavior in the case of devices.^[51] As Figure 5d indicates, the field effect mobility (μ_{FE}) also changed. When the sulfurization temperature increased from 600 to 900°C, the average mobility increased from 1.4 to 22 cm²/Vs and subsequently dropped to 10 cm²/Vs at 1,000°C. This interesting result implies

that the electric performance of our ML MoS₂ films could be engineered by directly tuning the growth parameters in our two-step process. The best transistor performance was achieved when the ML MoS₂ film was prepared at a conversion temperature of 900°C, and it could realize a maximum μ_{FE} of up to 27 cm²/Vs.

Besides the intrinsic quality of the 2D MoS₂ film,^[49] the device structure has been known to influence 2D channel transistor performance.^[50, 52] Thus, we modified the device structures to study the potential of our two-step-grown ML MoS₂ film for various TFT device configurations. To this end, we varied the channel pattern and dielectric thickness to fabricate TFTs with three distinct structures: a global-MoS₂ channel with an HfO₂ thickness of 30 nm (G - t_{diel}-30 nm), a global-MoS₂ channel with an HfO₂ thickness of 60 nm (G - t_{diel}-60 nm), and a patterned-MoS₂ channel with an HfO₂ thickness of 60 nm (P - t_{diel}-60 nm). **Figure 6** describes their relevant TFT performance. Insets in Figure 6a, b, and c display schematics for G - t_{diel}-30 nm, G - t_{diel}-60 nm, and P - t_{diel}-60 nm devices, respectively. For the sake of comparison, we specifically chose devices with the same channel length and width ($L/W = 10/200$ μm; see Figure S9). Their logarithmic dual-sweep transfer curves were measured with $V_{SD} = 1$ V (see Figure 6a-c). The comparison indicates that the P - t_{diel}-60 nm device exhibited the largest on/off current ratio up to 10⁷. This result might be due to the fact that the patterned channel has the smallest overlap area between MoS₂ channel and the top gate electrode; this small overlap can suppress the leakage current (I_{GS}), as verified in Figure 6h. The smallest SS (no matter SS_f or SS_r) was realized in G - t_{diel}-30 nm device, with the value 0.50 (both SS_f and SS_r). This is because thinner HfO₂ layer could achieve larger dielectric capacitance, thus better gate voltage tunability. Linear transfer curves and corresponding output curves are depicted in Figure 6d-f and their insets, respectively. Output curves of all these devices illustrated the ohmic-like contact between S/D electrode and ML MoS₂

channel. The dual sweep transfer curves obviously illustrated the hysteresis difference among these three devices. G - t_{diel}-30 nm device realized smallest hysteresis value as $\Delta V_G = 0.4 \text{ V}$ ($\Delta V_G = V_{THr} - V_{THf}$). The appearance of such small hysteresis could be explained by two reasons: one is better gate tunability as mentioned above, which could suppress trap states; the other is the operation of gate voltage in this device is smaller than the other devices, thus the hysteresis induced by the gate voltage stress could be drastically reduced.^[53] Field effect mobility change for these three devices is depicted in Figure 6g. Mobility of P - t_{diel}-60 nm device (about 12 cm²/Vs) displayed an obvious drop compared with the other two global channel devices (both value about 20 cm²/Vs). In order to minimize the overestimation of mobility value in the case of global devices (due to underestimated global channel width), we re-estimated the channel width to be 230 μm and obtained a $\mu_{FE} = 17.4 \text{ cm}^2/\text{Vs}$ (details shown in SI), which is still higher than that of patterned channel devices. Combining the modeling calculation on both global and patterned channel on/off current values (detail in SI and Figure S12), the reason for inferior mobility of patterned channel was inferred to be etching damage of the channel during the patterning process. Leakage currents are displayed in Figure 6h showing that G - t_{diel}-60 nm device has largest leakage value up to 10⁻⁷ A. This result may be because the overlap area between the global channel and top gate electrode is much larger than the patterned one. Also, the operation gate voltage is larger, thus leakage current larger than that of G - t_{diel}-30 nm device. The performance comparison of these three devices is listed in detail in Table S1. Dual sweep logarithmic transfer curves of P - t_{diel}-60 nm device is exhibited in Figure 6i with different V_{SD} (That of another two devices are shown in Figure S13). These plot helps to further verify the field effect behavior of the ML MoS₂ channel.

Thus our ML MoS₂ films have been successfully grown at the wafer scale using the two-step growth process, which allows us to achieve tunable optoelectronic properties. Significantly,

combining our process with simple TFT device construction modification, optimized ML MoS₂ transistor properties could be achieved, including field effect mobility of 10-30 cm²/Vs, maximum current on/off ratio of 10⁷, and low hysteresis of 0.4 V. Table S1 shows a comparison of the performance of our ML MoS₂ TFTs with previously reported two-step grown MoS₂ (almost all are few-layer films). It can be seen that this report is the first one to realize 2D semiconductor film with single layer continuously at 2-inch wafer scale by two-step process. The electronic properties of our optimized ML film realized the highest transistor performance among all these two-step grown MoS₂ films. We further compared our two-step grown ML MoS₂ film with wafer-scale ML films prepared through other growth methods, as displayed in Table S3. It is obvious that device performance based on our two-step prepared ML film is comparable with these methods. Thus we can see that our two-step growth process significantly improves on existing two-step growth of ML MoS₂.

3. Conclusion

We have developed a novel two-step growth process, which surmounts the long-standing challenges of achieving continuous, homogeneous, 2D ML films at the wafer scale. By using the atomically-thin epitaxial precursor MoO₂ film and well-established sulfurization process, we realized high-quality ML MoS₂ films uniformly and continuously at the wafer scale. The transistor devices based on our ML 2D MoS₂ films exhibit transport properties that exceed all previously reported two-step ML MoS₂, and is comparable to chemical vapor deposited ML MoS₂. By optimizing the parameters of the two-step process and TFT device architectures, the device performance can realize field effect mobility 10-30 cm²/Vs, on/off current ratio 10³⁻⁷, and hysteresis as low as 0.4 V. More significantly, through engineering the ML film preparation process, the material structure, electron doping level, response to laser radiation, and electric

properties could be carefully modulated. These results show great potential for our ML two-step process in various large-scale applications.

4. Experimental Section

4.1. Fabricating ML MoS₂ film by two-step process

Atomic-thin epitaxial MoO₂ film preparation: Epitaxial MoO₂ films with thickness 0.63 nm (20 laser shots) and 1.26 nm (40 laser shots) were deposited on 2-inch (001) Al₂O₃ substrates (Cryscore) by an optimized pulsed laser deposition process. The details could be found in a previous report. ^[54]

Conversion from MoO₂ to ML (BL) MoS₂ film: The precursor epitaxial MoO₂/sapphire wafer was placed in a cleaned quartz boat and loaded into the right zone of 3-zone tube furnace. It should be noticed that the precursor film should be quickly put inside the 3-zone tube furnace for conversion, since the atomically thin MoO₂ film is sensitive to oxygen and moisture. Argon was provided as the carrier gas during sulfurization; sulfur powder (Fisher scientific) was put in the left zone in the tube furnace, which is upstream side of Ar flow. The MoO₂ film relative position to the Ar flow direction is one of the most important parameters in order to realize continuous and homogeneous ML film at wafer scale. Before starting the conversion process, Ar gas should be purged several times in order to remove the oxygen in the quartz tube, then keeping the Ar gas flow at 100 sccm. The pressure inside tube should be kept at 5-10 torr. The left zone should be heated up to 150 °C in 10 min to keep constant S vapor in the Ar gas flow. The right zone was heated up to the elevated temperatures (500 to 1,000 °C) with heating rate 20 °C /min, then keeping the elevated temperatures 1 hr for the conversion process. The 3-zone furnace should be cooled down to room temperature once the process is completed.

4.2. TFT devices fabrication

The ML MoS₂ film was dry-etched to get the channel pattern. S/D and gate electrodes were deposited using Ti/Au with thickness 10/50 nm and patterned by lift-off process. HfO₂ dielectric (60 nm or 30 nm thick) was deposited by atomic layer deposition at 160 °C. Deionized water and Tetrakis (dimethylamido) hafnium (IV) precursor (Sigma-Aldrich) were used as the oxidization and Hf source. Once the device was fabricated, the annealing process was performed in quartz furnace with temperature of 200 °C in 2 hr, inner atmosphere was protected with Ar/H₂ gas at a flow rate 40/5 sccm in low pressure.

4.3. Characterization

Optical images were captured using a Nikon DS-Fi2 microscope. Raman & PL spectra and maps were characterized using Horiba Aramis Raman spectrometer (Horiba Scientific), with an excitation source of visible light of wavelengths of 473 nm and 532 nm. XPS spectra of ML MoS₂ grown at different temperatures were measured in a Kratos Axis Ultra DLD spectrometer. The thickness, continuity and homogeneity of ML or BL MoS₂ film were characterized by Atomic force microscopy (AFM) (Bruker, Dimension Icon SPM). Performances of ML MoS₂ film based transistors were measured by semiconductor device analyzer (Agilent B1500A).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Uniformity of MoS₂ films prepared by two-step process. a) Images and relevant AFM characterization (dimension: $2 \times 2 \mu\text{m}$) of BL (left), ML (middle) MoS₂ film and bare (right) sapphire substrate. Raman Characterization of b) BL c) ML MoS₂ film. d) PL spectra comparison of BL and ML MoS₂ films e) Optical image at a large scale.

Figure 2. Continuity of ML MoS₂ film prepared by two-step process. a) Photo of 2-inch wafer scale ML MoS₂. b-e) PL intensity mapping at four areas (marked in Figure 2a, color bar unit: counts). f) Optical image of concentric circle patterns. g) AFM height image of circle pattern (color bar unit: nm). h) E'_{2g} Raman peak position mapping of square pattern (color bar unit: cm⁻¹). i) Peak intensity mapping of triangular pattern (color bar unit: counts). (Resolution of PL and Raman maps: 200 nm).

Figure 3. XPS of ML MoS₂ sample grown at different temperatures a) Normalized and fitted Mo-3d (left curves), S-2p (right curves) b) Mo⁶⁺/Mo⁴⁺ ratio vs sulfurization temperatures.

Figure 4. Raman and PL of ML MoS₂ grown at different temperatures. a) Raman b) FWHM of E_{2g} and c) peak positions of E_{2g} and A_{1g} vs conversion temperatures. d) PL spectra with Lorentzian-Gaussian fitting. e) Neutral exciton (X , orange dots) and trion (X^- , dark yellow dots) peak position differences (inset: the integrated intensity ratio of I_{X^-}/I_{total}) vs conversion temperatures. f) Relation between n_{el} and I_{X^-}/I_{total} calculated by the law of mass action. g) ML MoS₂ electron density n_{el} values derived from PL spectra and electronic devices reported at recent years and this work. h) PL measurement of ML MoS₂ repeating at the same point with 9 times. i) PL peak intensity and position changes vs repeating counts, inset is repeating PL (Laser power 3.1 mW) another 10 times 1.5 hr after first round 10-times measurement. ((h, i) are based on ML MoS₂ film converted at 900 °C). j) PL measurement repeating at the same point for ML MoS₂ films converted at different temperatures.

Figure 5. Electronic performance of ML MoS₂ grown at different temperatures. a) Transfer curves of transistor performance. b) On, off current and on/off current ratio c) Subthreshold Swing (SS) (inset is subthreshold voltage and hysteresis) d) Field effect mobility (μ_{FE}) change trend vs ML film conversion temperatures.

Figure 6. Electronic performance of MoS₂ (ML fabricated at 900 °C) with different device structure. Logarithmic-scale transfer curves of device with $V_{DS} = 1$ V with a) G - t_{diel}-30 nm b) G - t_{diel}-60 nm c) P - t_{diel}-60 nm, inset are the corresponding device structures. Linear-scale transfer curves d) G - t_{diel}-30 nm e) G - t_{diel}-60 nm f) P - t_{diel}-60 nm, inset are the corresponding output curves. g) Field effect mobility change trend (μ_{FE}) vs V_{GS} h) leakage current (I_{GS}) vs V_{GS} of these three devices. i) Logarithmic-scale transfer curves at different source-drain voltages of P - t_{diel}-60 nm device.

TOC

This is the first time that the continuous and homogeneous wafer-scale ML MoS₂ film was grown by two-step process, excitonic and electronic properties of this ML film could be engineered. The electronic performance of this ML film through this method is superior among all the other two-step methods, also comparable with that from the CVD methods.

Key Words: two-step process, wafer scale, ML MoS₂, exciton, transistor.

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