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Demonstration of Direction Dependent Conduction through MoS₂ Films Prepared by Tunable Mass Transport Fabrication

Daniele Chiappe,^{a,*} Massimo Mongillo,^a Inge Asselberghs,^a Salim El Kazzi,^{a,*} Matty Caymax,^a Kathy Barla,^a Stefan De Gendt,^{a,b,**} Iuliana Radu,^a and Cedric Huyghebaert^a

^aImec, Kapeldreef 75, 3001 Leuven, Belgium

^bDepartment of Chemistry, University of Leuven, 3001 Leuven, Belgium

This work focuses on the synthesis of MoS₂ films grown by sulfurization of pre-deposited ultra-thin Mo films in the presence of a sulfur-containing gaseous precursor. The growth of high-quality TMDs requires careful control of specific thermodynamic and kinetic parameters. A deep understanding of mass transport mechanisms is achieved through a systematic investigation of the structural properties of MoS₂ films grown using different sulfurization conditions. Mass transport smoothing is used to reduce surface roughness and fabricate MoS₂ films in conformal contact with the underlying substrate. Oriented MoS₂ films are obtained by combining kinetically controlled sulfurization conditions and the use of single crystal templates. Good uniformity and excellent conformity of layers over large area has enabled the synthesis of patterned MoS₂ films which show anisotropic conduction properties. © The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, <http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0091611jss] All rights reserved.

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Two dimensional (2D) TMD materials, due to their unique physical properties, represent an interesting alternative to conventional semiconductors. They consist of molecular layers stacked together via weak van der Waals (vdW) forces.¹ The big interest toward 2D TMD for transistor applications arises from their ultra-thin body nature and low dielectric constants.² As a consequence, this class of materials potentially provides a superior scalability option compared to conventional materials. Another important quality of vdW materials is that ideally their surfaces are chemically saturated and have no dangling bonds. This additional feature makes 2D TMD ideal building blocks for the realization of artificial heterojunctions with designed band alignment.³

To enable the transition from the laboratory level, where most work is done on exfoliated flakes, to the industrial full-wafer scale, a large area deposition technique becomes indispensable. However, synthesis of large area, high quality TMD films using industry-compatible processes remains a major challenge and requires the development of highly controllable growth processes. Large area TMD layers can be grown using various techniques including chemical vapor deposition (CVD),^{4–6} atomic layer deposition (ALD)⁷ and molecular beam epitaxy (MBE) processes.⁸ An interesting low cost approach that is capable of providing large-area sheets of TMDs with controllable thicknesses is chalcogenidation of ultrathin transition metal films.^{9,10} This method is simple, fast, easily upscalable, and can be used to synthesize a large variety of TMDs, including TMD heterostructures.^{11,12} However, the huge potential of this versatile technique is limited by the fact that chalcogenidation processes normally result in the formation of nano-crystalline highly defective films. To significantly improve material quality it is necessary to gain a deeper understanding of mass transport effects taking place during the chemical conversion process. In this work we propose a mass transport study based on roughness analysis of MoS₂ films grown by sulfurization of pre-deposited ultra-thin Mo films. The following results demonstrate that MoS₂ films with improved conformity and texture quality can be obtained by carefully controlling the sulfurization conditions.

Materials and Methods

Material growth.—0.7 nm thick Mo films are thermally evaporated on SiO₂/Si or c-plane sapphire substrates under high vacuum conditions (10^{−6} mbar) at a deposition rate of 0.01 nm/s. Then the samples are extracted from the deposition chamber and loaded (with air-break) into a lamp-based annealing system. The reactor is pumped to a base pressure of 10^{−2} mbar before starting the annealing process in a pure H₂S atmosphere at a pressure of 10 mbar. A similar reactor is used for post-sulfurization annealing treatments at 1000°C under H₂S/N₂ flow (P_{tot} = 130 mbar, H₂S/N₂: 0.1/10 slm).

Physical/chemical characterization.—The structural properties of MoS₂ films are investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). AFM images are taken in tapping mode in ambient conditions.

Raman spectra are collected in a confocal Raman microscopic system (exciting laser wavelength 532 nm with a power of ~2 mW on the sample surface). The laser radiation is focused onto the MoS₂ sheets using a 100× objective lens with a spot-size around 1 μm. Raman spectra (performed at room temperature) are resolved by a spectrometer and acquired by an EMCCD detector.

Chemical composition is determined by X-ray photoelectron spectroscopy. The energy calibrations are made against the C1s peak to compensate for charging effects during analysis.

Device fabrication.—Large area MoS₂ films are etched into stripes by combining optical lithography and Ar/O₂ plasma treatments. An additional lithography step follows to create the openings needed for the source and drain contacts. A metal layer is deposited on top of the entire surface and then lifted-off leaving the fully-formed source and drain contacts (Mo/Au) in place. Eventually the devices are encapsulated in amorphous Al₂O₃ (30 nm) deposited by ALD. The top gate electrodes (Pd) are lastly fabricated on top of the dielectric layer. The electrical measurements are performed under ambient conditions.

Results and Discussion

A schematic description of the experimental approach is shown in Figure 1a. First an ultra-thin Mo film is deposited by thermal evaporation on a dielectric substrate. Eventually the Mo film is converted into MoS₂ by annealing in H₂S at high temperatures, ranging from

*Electrochemical Society Member.

**Electrochemical Society Fellow.

^zE-mail: daniele.chiappe@imec.be

Figure 1. Synthesis of large area MoS₂ films by sulfurization. a) Schematic illustration of the synthesis process. b) Large area 4ML-MoS₂ films grown on sapphire and SiO₂. c) XPS spectrum of the Mo 3d and S 2s core level peaks for the MoS₂ film deposited on SiO₂ at 800°C. d) The corresponding Raman spectrum.

800°C to 1000°C. Importantly the thickness of the pristine Mo layer determines the thickness of the resulting MoS₂ film.

Full conversion of Mo into MoS₂ after sulfurization at 800°C is confirmed by X-ray photoemission (XPS) and Raman spectroscopy. A typical XPS spectrum is shown in Figure 1c. The Mo3d doublet consists of two peaks at around 229.7 and 233 eV that correspond to Mo₄₊ 3d_{5/2} and Mo₄₊ 3d_{3/2} components of 2H-MoS₂, respectively. The corresponding Raman spectrum shown in Figure 1d exhibits two characteristic features, at 408 and 383 cm⁻¹, corresponding to the well-known A_{1g} and E_{2g} vibrational modes. As widely reported in the literature,¹³ the two Raman modes tend to approach each other as the number of layer decreases. In this case their frequency distance is about 25 cm⁻¹ which is consistent with the formation of a MoS₂ film with thickness corresponding to 4MLs, as confirmed by independent cross-TEM analysis.

A representative AFM image is shown in Figure 2a. The characteristic polycrystalline structure consists of interconnected lamella with lateral sizes ranging from 20 nm to 50 nm. In-plane TEM analysis (Figure 2b) allow to appreciate the hexagonal lattice as well as the presence of highly defective regions in correspondence to the domain boundaries. This observation leads to the conclusion that grain boundaries are the main source of a high density of defects which will inevitably affect the electrical and optoelectronic functionality of the 2D material.¹¹

To further improve quality of synthetic MoS₂ films grown by sulfurization, it is of fundamental importance to gain a deeper understanding of mass transport effects taking place during the chemical conversion process of Mo and learn how they can be controlled by tuning the sulfurization conditions.

A comparative roughness analysis based on AFM characterizations is proposed as investigative approach to explore mass transport effects at the nanoscale. The Mo films are grown on sapphire and eventually sulfurized at the same temperature (800°C) using different H₂S pressure conditions. A first MoS₂ film, labelled as sample A, is sulfurized using a H₂S pressure of 100 mbar under static vacuum conditions. A second MoS₂ film, sample B, is prepared following a similar procedure but in this case the H₂S pressure is reduced to 10 mbar. The most popular parameter characterizing the morphology of surfaces is the rms roughness σ , which represents the root mean square

Figure 2. Structural properties of polycrystalline MoS₂ films grown by sulfurization. a) AFM topographic images of a MoS₂ thin film grown on SiO₂ at 800°C. b) The corresponding in-plane TEM analysis. The image shows disordered regions (circled in yellow), indicating abundant uncontrollable defects in a typical MoS₂ sheet. A zoomed-in TEM image is shown in the inset.

height of a surface around its mean value. A more complete description of surface morphology is provided by the power spectral density (PSD) of the surface topography, which performs a decomposition of the surface profile into its spatial wavelengths and allows comparison of roughness measurements over different spatial frequency ranges.¹⁴ The PSD spectrum for sample A (black trace) is shown in Figure 3. It is possible to distinguish two characteristic spectral regions, a flat region ($\lambda > \lambda^*$) which is dominated by stochastic roughness components and a decaying trend for length-scales smaller than the so called lateral correlation length λ^* . In this region of the spectrum smoothing mechanisms are active and lead to selective suppression of surface roughness. For $\lambda < \lambda^*$ the PSD function follows a power law behavior of the type $g(\lambda) \sim \lambda^n$ where the coefficient n can be related to a specific mass diffusion process.^{15,16} The lateral correlation length λ^* ($\lambda^* \approx 30$ nm, for sample A) gives an estimation of the range of influence of mass transport effects. The same analysis is proposed for sample B (Figure 3, red trace). The corresponding PSD spectrum evidences a more effective suppression of the roughness components with smoothing mechanisms extending now to the sub-micron range (active over the whole spectral range). This observation demonstrates that pressure conditions during sulfurization can impact the structural properties of the resulting MoS₂ film. It is worth noting that, chemical conversion of Mo into MoS₂ leads to volume expansion and, consequently, to mechanical stress (compressive strain) which inevitably generate corrugations (Figure 4a). This mechanical stress can be minimized by reducing the sulfurization rate, as done for sample B. In this case, the system has more time to release mechanical stress, thus resulting in improved conformity of the MoS₂ planes with the underlying substrate surface (Figure 4b).

Electron diffraction pattern combined with AFM analysis (Figure 5) demonstrate that polycrystalline MoS₂ films with improved texture quality and excellent flatness can be obtained by combining optimized pressure conditions (as described in the previous paragraph) with annealing processes in H₂S at higher temperature (1000°C).¹¹ It is worth noting that sapphire templates tend to develop a vicinal surface when

Figure 3. Line averaged 1D-PSD spectra calculated from $2 \times 2 \text{ mm}^2$ AFM topographies for MoS_2 films grown on sapphire under different pressure and temperature conditions. The gray dotted trace represents a typical PSD spectrum obtained from a clean c-plane sapphire substrate.

annealed at high temperatures.¹⁷ This consists of periodic terraces oriented along the $[10\bar{1}0]$ direction with average width in the range of 100 nm and step height equivalent to one single atomic step (0.22 nm). As shown in Figure 5, the MoS_2 ad-layer replicates this characteristic periodic pattern, thus confirming the formation of molecular planes in conformal contact with the underlying sapphire substrate, as confirmed by TEM and spectral analysis of the surface roughness. It is worth observing that the corresponding PSD spectrum (Figure 3 – purple line) is now in good overlap with that obtained from the underlying substrate surface (Figure 3 – gray dotted line).

Figure 5. AFM topography of a MoS_2 film grown on sapphire by annealing in $\text{H}_2\text{S}/\text{N}_2$ at 1000°C . In the insets, a cross-sectional TEM image and the RHEED pattern of the corresponding MoS_2 film.

It is now interesting to investigate the electrical transport properties of MoS_2 films grown on sapphire substrates. To this purpose, top-gated field effect transistors are fabricated by optical lithography, as described in the Experimental section. The MoS_2 channels are oriented along two characteristic directions, i.e. longitudinal (LO) and transverse (TO) to the terraces, as sketched in Figure 6a. The corresponding transfer characteristics I_d - V_{tg} plotted in Figure 6b show anisotropic electrical conduction. The observed anisotropy reflects the characteristic pattern, in particular the ON-current values are amplified by a factor ~ 100 for the LO devices. The corresponding sheet resistance values extracted from transfer length method (TLM) analysis (Figure 6c) are $3500 \text{ M}\Omega/\text{sq.}$ and $120 \text{ M}\Omega/\text{sq.}$ for the MoS_2 channels with transverse and longitudinal orientation, respectively. This behavior can be reasonably ascribed to two concomitant effects: on one hand the periodic corrugations introduce direction-dependent scattering mechanisms¹⁸ which are obviously amplified for electrons flowing perpendicular to the terraces due to, for instance, to the

Figure 6. Device fabrication and electrical characterization. a) Schematic description of top-gated MoS_2 devices. The active channels are oriented along different directions with respect to the periodic pattern, i.e. orthogonal (TO) and longitudinal (LO) with respect to the main crystallographic axis of the underlying sapphire substrate. b) Transfer characteristics of MoS_2 transistors oriented along the two characteristic directions. c) Total device resistance plotted against channel length, for MoS_2 devices oriented along the two characteristic directions.

Figure 4. Cross-sectional TEM images and Raman spectra of a 4 ML MoS_2 films grown on sapphire under different H_2S pressure conditions, i.e. a) 10 mbar and b) 100 mbar.

enhancement of non-specular scattering at the interface; on the other hand, the substrate-induced curvatures introduce mechanical stress in the MoS₂ sheet which might generate local distortion of the electronic band structure.^{19,20} The anisotropy of the electronic structure results in anisotropic effective mass tensors which reflect the characteristic geometry of the surface pattern.

Conclusions

In conclusion we investigated tunable mass transport effects to control the structural properties of large area MoS₂ films grown by sulfurization in H₂S. Optimized kinetic conditions are found to promote the formation of smooth MoS₂ films in conformal contact with the substrate. Good uniformity and excellent conformity of layers over large area has enabled the synthesis of MoS₂ films with controlled anisotropic morphology dictated by the underlying substrate. The periodic corrugations are observed to introduce direction-dependent conduction properties. This observation sheds a light on the crucial role played by interface roughness and mechanical stress in determining the transport properties of 2D TMDs and open an avenue of optimizing MoS₂ films for electronic and optoelectronic applications by surface patterning.

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