



Electrochemical deposition of bulk MoS₂ thin films for photovoltaic applications



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ABSTRACT

Layered transition metal dichalcogenides (TMDs) materials have shown high potential in many optoelectronic and photovoltaic applications due to their intriguing semiconducting properties. Most noticeably, the layered molybdenum disulfide (MoS₂) has drawn much attention because of its unique layer-dependent band gap tunability and high electron mobility. A facile non-vacuum electrodeposition approach is used to deposit bulk MoS₂ films onto FTO substrate immersed in an aqueous precursor solution of molybdenum and sulfur. The as-deposited and post-treated films are studied using X-ray diffraction, electron microscopy equipped with energy-dispersive x-ray spectroscopy, light absorption measurement, and X-ray photoelectron spectroscopy. Although the obtained gap energy values, 1.3–1.4 eV, of bulk MoS₂ are indirect, the measured light absorption characteristic is high, especially above 1.7 eV. Also, electrochemical impedance spectroscopy studies of the films show that carrier concentration is higher than 10¹⁵ cm⁻³.

1. Introduction

Recently, the layered transition metal dichalcogenides (TMDs) and their applications for optoelectronics and photovoltaics have drawn considerable attention. Among the considered applications are hydrogen evolution reaction [1–4], solar cells [5–9], energy storage [10–12], field-effect transistors [13,14], gas sensors [15,16], and photodetectors [17]. Molybdenum disulfide (MoS₂) is a TMD which is widely studied due to its intriguing physical properties, such as band gap tunability with a transition from direct bandgap energy value of 1.8 eV for monolayer MoS₂ [13,18] to an indirect bandgap of 1.2 eV for bulk MoS₂ films [18,19]. It is a layered material such that S-Mo-S atoms are covalently bonded and arranged in a closely packed hexagonal crystal structure, where adjacent layers are held together by weak van der Waals force. In room temperature, the reported electron mobility is high and ranged between 200 and 500 cm² V⁻¹s⁻¹ [13,18,20]. The layer-dependent optical transitions from indirect to direct bandgaps, high electron mobilities, and inherent flexibility [21,22], make the MoS₂ very promising for many optoelectronic applications.

Various physical and chemical deposition approaches, such as chemical vapor deposition (CVD) [5,14,18,23–26], chemical exfoliation [7,27,28], electrodeposition [29–31], dip-coating [8,26], spin-coating [9], hydrothermal [12], sputtering [3,4], pulsed laser deposition [32], spray-pyrolysis [33], etc., were explored to grow atomically thin and

bulk MoS₂ films. Yet, the mostly used approach is CVD route where solid precursors of molybdenum (Mo) and sulfur (S) are vaporized under high temperatures and co-deposited onto a suitable substrate. However, this route requires high temperature exceeding 800 °C [34], [5,35]. The chemically exfoliated two-dimensional (2D) MoS₂ films significantly differ from its bulk counterpart, both structurally and electronically due to multiple coordination of Mo [27,36]. In addition, depositing a large area well-crystalline MoS₂ films are yet to be realized using CVD. Therefore, to avoid harsh chemical and thermal treatments steps, involved in most of the physical deposition-based techniques, an alternative solution-based non-vacuum method which ensures deposition of the bulk MoS₂ material onto large substrates using environmentally benign earth-abundant precursor materials is timely needed.

For photovoltaics, an atomically thin MoS₂ film is not enough as it absorbs only a fraction, approximately 5–10%, of the visible light in the solar spectrum, resulting in low solar energy conversion efficiency [5,8,37]. Yet, the efficiency of solar cells can be much improved by enhancing the light harvesting efficiency of the photoactive MoS₂ layer in solar cells. Therefore, a high-quality bulk MoS₂ films are deposited onto fluorine-doped tin oxide (FTO) substrates. In this work, we present a newly developed growth method based on a non-vacuum and facile solution-based environmentally benign electrodeposition approach which is believed to result in a high deposition yield with low usage of

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precursor materials. Unlike any physical/chemical vapor deposition approaches, *i.e.*, sputtering, evaporation, CVD, *etc.*, where only a fraction of the target materials is deposited onto substrates, the utilized precursors solution in an electrodeposition approach can be repeatedly re-used to deposit the MoS₂ films onto flexible/rigid conducting substrates until the Mo and S precursors are consumed. Herein, we report the deposition, post-treatment, *i.e.*, annealing and sulfurization of the as-deposited films in an argon environment and characterization of the electrodeposited bulk MoS₂ films. A combination of structural, morphological, topological, optical, and compositional analyses confirm an excellent structural quality of the bulk MoS₂ films. The high absorbance of the obtained films makes them suitable for the development of efficient solar cells.

2. Experimental

2.1. Electrodeposition of bulk MoS₂ films at a constant potential

First, the cleaning of the FTO-coated glass substrate was found to be critical because its surface characteristics affected adhesion properties of the bulk MoS₂ films onto it. Therefore, the FTO substrates were sequentially cleaned several times by using aqueous soap solution, a mixture of water and ethanol, and finally deionized (DI) water for 10 min each. Following this cleaning process, the FTO substrates were dried under a stream of N₂ gas prior to electrodeposition of MoS₂ films. An electrochemical cell consisted of a platinum mesh counter electrode, a FTO substrate as working electrode. A saturated calomel electrode (SCE) was used as reference electrode to deposit the bulk MoS₂ films. The SCE electrode was chemically in contact with the working electrolyte solution through a salt bridge system (Luggin capillary) to avoid any contamination. The uncompensated solution resistance was minimized by placing the Luggin capillary as close as possible to the working electrode (FTO), during electrodeposition. The precursor materials of the MoS₂ were dissolved in DI water to prepare a stock solution of 2 mM ammonium tetrathiomolybdate ((NH₄)₂MoS₄, trace metal basis, 99.97% Sigma Aldrich), and 0.1 M potassium chloride (KCl, 99% ACS reagent, Sigma Aldrich). The aqueous precursor solution was observed to be light brown in colour.

As the reaction kinetics becomes faster with increasing temperature [38], a much more uniform and thicker bulk MoS₂ film was obtained when the temperature of the precursor solution was increased from room temperature (25 °C) to 40 °C. The thickness of the films were measured to be approximately 250 nm and 90 nm for the films deposited at 40 °C and room temperature (25 °C), respectively, confirmed by the SEM. The uniformity of the films was measured by roughness factor measured by AFM measurements as shown in Fig. S2 (Supporting Information). In addition, an intermittent magnetic stirring of precursor solution during electrodeposition led to a uniform and robust MoS₂ film onto the FTO substrate. The wetting-characteristic of a substrate is known to be governed by precursor solution, which is crucial for enhancing deposition yield and obtaining a uniform crack-free MoS₂ film. Cyclic voltammograms (CV) were recorded prior to each deposition to determine the oxidation and reduction potentials of the working solution, specifically electrochemical behavior of Mo and S precursor species on the FTO substrates. The applied potential window for the MoS₂ deposition was chosen from the CV analysis, which was then applied, *i.e.*, at −1.2 V vs. SCE for 60 min. A potentiostat (Biologic, SP-300) was used to apply the electrode potential. Under such an applied potential, the MoS₄^{2−} ions in the precursor solution could transform into MoS₂ onto electrically conducting FTO electrode. The colour of the transparent FTO electrodes was changed to dark brown, indicating the formation of MoS₂.

Controlled experiments at room temperature were also conducted to compare the films with those deposited at a temperature of 40 °C. The thickness of the bulk MoS₂ films deposited at 40 °C were found to be approximately 250 nm thick measured by SEM and TEM (Fig. 3 and

Fig. 4), whereas the film deposited at room temperature measured by a surface profilometer was observed to be approximately 90 nm thick (Fig. S1, supporting information), ~3 times thinner than the films deposited at 40 °C. The increased temperature resulted comparatively uniform and thick as compared to those deposited at room temperature (25 °C). This enhanced deposition yield could be realized from faster kinetics of electrolyte species with increasing temperature of the electrodeposition. The as-deposited MoS₂ films were then rinsed with DI water and ethanol to remove traces of residual precursors and finally dried in a vacuum furnace at 25 °C. Based on our observation, the adhered as-deposited MoS₂ films were smooth and uniform onto the FTO substrates. A delamination issue of the MoS₂ films from FTO substrates was resolved by sequentially cleaning the FTO substrates with a soap solution followed by a water-ethanol mix-solvent, and finally in DI water for 10 min each. It is worth to note that the final sonication of FTO in DI water was crucial to obtain robust MoS₂ films where the MoS₂ films showed enhanced adhesion properties with FTO substrate.

2.2. Post-treatment of the MoS₂ films for crystal growth

The as-deposited amorphous-like MoS₂ films were annealed in a quartz tube furnace (MTI, OTF-1200 ×) at 500 °C under argon atmosphere to allow their grain growth. At first, traces of oxygen in the quartz tube was removed by purging with argon several times before being heated to 120 °C and kept for 15 min to remove any residual DI water and ethanol. Then the temperature of the furnace was ramped to 500 °C at a heating rate of 10 °C/minute and held for 60 min followed by natural cooling to room temperature. To get rid of traces of oxygen and enhance semiconducting properties of the bulk MoS₂ films, the films were also sulfurized in a quartz tube furnace (MTI, OTF-1200 ×) under the argon atmosphere. A 65 cm long quartz tube with a stable heating zone of 44 cm was utilized to sulfurize the samples. The temperature at the location of sample was observed to be approximately 1 °C lower than the set point temperature. In a typical procedure, elemental S powder of 200 mg was taken into a ceramic crucible while the as-deposited MoS₂ films were kept 20 cm apart in the downstream. After purging the quartz tube several times with argon gas, at first the films were heated to 120 °C and kept for 5 min to remove any source of carbon contaminants followed by finally sulfurized at 500 °C for 60 min where the sulfur vapor (S^{2−}) species were incorporated into the non-stoichiometric host-lattice of as-deposited bulk MoS₂ films and also to replace oxygen with S^{2−} into the host lattice of MoO₃ impure phase. Then the quartz furnace was naturally cooled down to room temperature in presence of constant flow of argon gas.

2.3. Materials characterization

Crystal structure of as-deposited and post-treated films was characterized by X-ray diffraction (XRD) technique with a Rigaku Miniflex 600 diffractometer using Cu Kα1 radiation source (λ = 0.1541 nm). The surface topography was acquired by atomic force microscopy (AFM, Bruker CAFM), which offers measurement of high-resolution topographical features of the MoS₂ films. Light absorption spectra were collected using a UV-Vis-NIR spectrophotometer (JASCO, V-650) having single monochromator with low stray light at room temperature. The morphology, thickness, and chemical composition of the films were measured by a field emission scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (EDS) elemental analysis facility (FESEM, JEOL JSM-7200F). The FESEM measurement was conducted without depositing a thin gold layer. A transmission electron microscope (TEM, FEI Talos) was utilized for detail cross-sectional analyses and EDS mapping of the films. A thin layer of gold was deposited onto the MoS₂ films for the TEM cross-sectional measurement and EDS mapping. The average thickness of the film deposited at room temperature was measured by a surface profiler (Bruker Dektak XT). The chemical states of Mo and S elements in the MoS₂ films were

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