Synthesis and Characterization of MoS$_2$ Thin Films Deposited by automatic CBD Method

Authors

S.B.Sargar$^1$, D.J.Sathe$^2$, P.A.Chate$^3$, Z.D.Sandi$^4$, S.V.Kite$^5$

$^1,4$Dept. of Chemistry, VTU Research Resource Centre, VTU (M.S.) India.
$^2,5$ Dept. of Chemistry, KIT’s College of Engineering, Kolhapur (M.S.) India.
$^3$ Dept. of Chemistry, JSM College, Alibag-Raigad, (M.S.) India.
E-mails: sbsargar@gmail.com, djsathe77@gmail.com

ABSTRACT

The films were characterized by X-ray diffraction, scanning electron microscope, compositional studies, and electrical measurements. Nanocrystalline Molybdenum disulphide thin films have been deposited at room temperature on non-conducting glass substrates by modifying Chemical Bath Deposition (Automatic-CBD) technique. Ammonium molybdate and sodium thiosulphate were used as basic precursors. The X-ray diffraction analysis shows that the film samples are in layer-hexagonal crystal structure with composition Molybdenum disulfide. Specific electrical conductivity was found to be in the order of $10^{-5}$ to $10^{-3}$ ($\Omega$ cm)$^{-1}$. The average crystallite size of the films is found to be 284 Å. EDAX analysis shows that the films are nearly stoichiometries of the Mo:S. It is observed from scanning electron microscopy (SEM) that the substrates are well-covered with the deposited Molybdenum disulfide layers without cracks and pinholes.

Keywords: Nanostructure; SEM; Chemical synthesis; Electrical properties; Growth Mechanism

1. INTRODUCTION

It consists of weakly coupled sandwich layers X-Mo-X in which a Mo-atom layer is enclosed within two chalcogen layers (X = S, Se, Te)[1-3]. The molybdenum dichalcogenides (MX$_2$; M = Mo, and X= S, Se and Te) belong to the large family of layered transition metal dichalcogenides whose crystal structure results from the stacking of sheets of hexagonally packed atoms.

MoS$_2$ has been fabricated into sensors, transistors and integrated circuits. [4-9]. There are numbers of the methods engaged for the synthesis of Molybdenum disulfide thin film like chemical vapor deposition, electrodeposition, spray pyrolysis, physical vapor deposition, and chemical methods [10-17]. However, chemical bath deposition method is an alternative, low-cost method which can operate at low processing temperature and provides large-area deposition.

In this paper, we report that a synthesize the nanocrystalline molybdenum disulfide thin film by a chemical route at room temperature using ammonium molybdate and sodium thiosulphate were used as basic precursors and tartaric acid as a complexing agent. The film was studied for structural, morphological, compositional and electrical measurement.

2. EXPERIMENTAL DETAILS

Ammonium Molybdate, tartaric acid, hydrazine hydrate, ammonia and sodium thiosulphate were obtained from Thermo Fisher Scientific Ltd., India. All the solutions were prepared in double distilled water. The substrates used for depositing the films were non-conducting glass slides of the size 75 × 25 × 2 mm (Bombay Trading Co., New Delhi), and good quality polished stainless steel strips. The films deposited on
the glass substrates were used for characterization of the films. All the chemicals used were of analytical grade.

The deposition of molybdenum disulfide thin films was made in a reactive bath. The solution obtained by mixing of 10 mL (0.25 M) ammonium molybdate \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O}\), 12 mL (1M) tartaric acid \((\text{C}_4\text{H}_6\text{O}_6.\text{H}_2\text{O})\), 9 mL (15 %) and hydrazine hydrate \((\text{NH}_2.\text{NH}_2.\text{H}_2\text{O})\), in a beaker. To this mixture, 20 mL (0.25 N) sodium thiosulphate \((\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O})\) was added and the total volume of the reaction mixture was made to 100 ml by adding double distilled water. The solution was stirred vigorously before dipping glass substrates, which were kept vertically slightly tilted in the reactive bath. The temperature of the reactive bath was maintained at 298 K, speed of rotation of substrates adjusted between 65-70 rpm, timing for deposition 2 hrs and string speed of precursor is 30 rpm set on the Automatic Chemical Bath Unit (A-CBD unit). After completion commanded experimental time the automatic-Chemical Bath Unit stops. Then the slides were removed and washed several times with double-distilled water. The deposited substrate was dried naturally, preserved in dark desiccators over anhydrous CaCl₂ and subjected to various characterizations. Automatic Chemical Bath Unit (A-CBD unit) and deposited materials in the form of thin film are shown Fig.1 a & b.

![Fig.1 (a) Automatic Chemical Bath Unit (A-CBD unit) & (b) As a deposited MoS₂ of thin film.](image)

3. RESULTS AND DISCUSSION

3.1 Growth Mechanism

Initially, reaction mixture can prepare by mixing ammonium molybdate. Slow increase in temperature decomposes moderately stable sodium thiosulphate to yield \(\text{S}^-\), while hydrazine hydrate reduce \(\text{M}^{6+}\) to \(\text{M}^{4+}\) in basic medium. The dissociation of \(\text{M-tartaric acid}\) complex at higher temperature liberates \(\text{M}^{4+}\) ions that react with \(\text{S}^-\) ion to get faint yellow color thin film. Tartaric acid as a complexing agent, which controls the metal ion concentration in the reaction vessel. Hydrazine hydrate acts as a reducing agent and it also serves complementary complex to help increase compactness and adherence of the film. The growth mechanism can be described from the following reactions:

\[
\text{Mo}^{6+} + 3 \text{(tartaric ion)} \rightarrow [\text{Mo-(tartarate)}]_3
\]

\[
[\text{Mo-(tartarate)}]_3 + 2\text{NH}_2-\text{NH}_2 \rightarrow \text{Mo}^{4+} + 3 \text{tartaric acid} + 2\text{N}_2 \uparrow
\]

\[
\text{S}_2\text{O}_3 + \text{H}^+ \rightarrow 2\text{S}^{2-} + \text{H}_2\text{O}
\]

\[
\text{Mo}^{4+} + 2\text{S}^{2-} \rightarrow \text{MoS}_2
\]

In chemical bath deposition method, the ionic product exceeds or become equal to the solubility product, precipitation take place and ions combine on the substrate and in the solution to form nuclei followed by growth process. The film deposition takes place by recombination of ions on the glass surface via nucleation followed by growth. In the growth process, no film formation occurs within first 50 min. This is the
induction period required to from nucleation centers on the substrates. The presence of induction period suggests ion-by-ion growth mechanism instead of cluster-by-cluster. Speed of rotation 65–70 rpm was selected to deposit molybdenum disulphide thin films. The films obtained are uniform, well adherent to substrate. The thickness of thin film was calculated by the gravimetric method and found to be 0.6 μm

3.2 Structural Characterization

Structural studies of MoS$_2$ thin film were characterized by using a Phillips PW-1710 X-ray diffractometer. The XRD pattern of Molybdenum disulfide thin film is shown in Fig 2.

![XRD pattern of MoS$_2$ thin film](image)

**Fig 2.** The XRD pattern of Molybdenum disulfide thin film.

XRD pattern shows a hump between 14$^0$-36$^0$ due to the amorphous glass substrate. The presence of a large number of peaks indicates that the films are polycrystalline in nature. The observed ‘d’ values of depositing samples were in full accord with the standard ‘d’ values taken from JCPDS diffraction file No.73-1508. Comparison of observed ‘d’ with standard ‘d’ values confirms that chemically deposited film shows a single phase compound with typical lines belonging to the hexagonal structure in accordance with the literature-reported data [6].

The lattice parameters of the hexagonal phase were calculated by using the relation:

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

‘a’ and ‘c’ values are in good agreement with the earlier reported value [7]. The average crystallite size was calculated using Scherrer formula.

$$D = \frac{k \lambda}{\beta \cos \theta}$$

where $D$ is the crystallite size (Å), $\lambda$ is the X-ray wavelength (Å), $\beta$ is the full width at half maximum (rad), $\theta$ is the Bragg’s diffraction angle and $k$ is constant (0.94). The average crystallite size was calculated by resolving the highest intensity peak, i.e., (600) plane. Comparison of observed ‘d’ with standard ‘d’ values, lattice cell parameters, and the average crystallite size of the thin film are listed in the table 1.
Table 1: Crystallographic data of the thin film.

<table>
<thead>
<tr>
<th>Film</th>
<th>d' Values (Å)</th>
<th>Average crystallite size (Å)</th>
<th>Lattice Cell parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
<td>Standard</td>
<td></td>
</tr>
<tr>
<td>MoS₂</td>
<td>3.4618</td>
<td>3.5507</td>
<td>300</td>
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<td></td>
<td>1.4745</td>
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<td></td>
<td>2.3148</td>
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<td></td>
<td>2.7890</td>
<td>1.7759</td>
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<tr>
<td></td>
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<td>1.4771</td>
<td>620</td>
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<tr>
<td></td>
<td>2.2265</td>
<td>1.2264</td>
<td>801</td>
</tr>
</tbody>
</table>

3.3 Surface Morphology

The surface morphology of molybdenum disulfide thin film used to be additionally studied by means of scanning electron microscopy (SEM). The SEM micrograph of Molybdenum disulfide thin film is provided in Fig.3. It's found from scanning electron microscopy (SEM) that the substrates are well-covered with the deposited Molybdenum disulfide layers without cracks and pinholes. The spherical grains are obvious to be blended with the adjoining as soon as. This sort of morphology is ordinary of layered constitution. The average grain size used to be calculated by way of utilizing Contrell’s system.

The mean grain size measurement as calculated from SEM used to be observed to be in accord with these received from Scherer’s components in XRD.

![SEM micrograph of Molybdenum disulfide thin film.](image)

3.4 Compositional Studies

Figure 4 shows the EDAX patterns for the typical Molybdenum disulfide thin film sample. The stoichiometry of the grown crystals was once analyzed with the aid of EDAX and it was found that the progress crystals possess nearly excellent stoichiometry with the chemical formulation Molybdenum disulfide (Mo: S.). No impurities had been reward within the limit of sensitivity.

![EDAX patterns for the typical Molybdenum disulfide thin film sample.](image)
3.5 Electrical Properties
The electrical transport properties play a key section in deciding the character as good as applications of the semiconductor instruments. These properties are in most cases influenced by using their structural traits, purity, nature and the awareness of the impurities. The electrical conductivity dimension used to be applied within the temperature variety 300-525 K utilising a two-probe method. At room temperature, the specific conductance was found to be in the order of $10^{-5}$ - $10^{-3}$ (Ω cm)$^{-1}$, which agrees well with the earlier reported value [6, 18]. It is observed that the conductivity of the film increases with increase in temperature. This indicates the semiconducting behavior of the thin film.

A plot of log (conductivity) versus inverse temperature (1,000/T) is indicated in the Fig.5. There are two distinct linear regions, suggesting the presence of two-conduction mechanism, the low-temperature intrinsic and high-temperature extrinsic. It suggesting that, MoS$_2$ thin films shows hoping conduction behaviors.

![Fig.5 A plot of log (conductivity) versus inverse temperature (1,000/T)](image)

CONCLUSIONS
A molybdenum disulfide thin film deposited on glass substrates at room temperature. The deposited molybdenum disulfide thin films are practically stoichiometries, with crystalline nature, hexagonal structure. The spherical grains are noticeable to be blended with the adjoining once. This type of morphology is typical of layered structure. MoS$_2$ thin films indicate hoping conduction behaviors.

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REFERENCES