1991

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Publication Info


http://dx.doi.org/10.1039/JM9910100301

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Novel Chemical Preparative Route for Semiconducting MoSe\textsubscript{2} Thin Films

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Semiconducting MoSe\textsubscript{2} thin film has been prepared chemically and characterized by various physical methods.

**Keywords:** Thin film; Chemical deposition; Selenium; Molybdenum

One-dimensional linear polymers of Mo-chalcogenides have a wide range of potential applications, e.g. as electrode materials for photoelectrochemical (PEC) solar cells,\textsuperscript{1,2} solar rechargeable batteries,\textsuperscript{3,4} solid lubricants\textsuperscript{5} and superlattice structures.\textsuperscript{4} A variety of techniques, viz. chemical vapour deposition,\textsuperscript{5} molecular beam epitaxy\textsuperscript{6} and radiofrequency sputtering\textsuperscript{7} have been reported in the literature. However, these techniques are expensive and pose definite environmental hazards. Chemical deposition, which is a less expensive low-temperature deposition technique and non-polluting, offers a suitable method for the preparation of MoSe\textsubscript{2} films on any kind of large-area substrates, such as Ti, Al, Cu, stainless steel, and conducting and non-conducting glass. In this communication we report for the first time a simple chemical deposition technique that has good reproducibility and non-polluting, which dramatically enhanced the average grain size from 0.13 ± 0.01 \( \mu \text{m} \) to 0.42 ± 0.01 \( \mu \text{m} \). The as-deposited film showed a broad X-ray spectrum suggesting that it had an amorphous structure. The grain size was measured using the method described by Cottrell.\textsuperscript{8} The thermal treatment of the deposited films was done in N\textsubscript{2} atmosphere under optimal conditions; optimal conditions were found as 380 °C, 1 h, which dramatically enhanced the average grain size from 0.13 ± 0.01 \( \mu \text{m} \) to 0.42 ± 0.01 \( \mu \text{m} \). The compositional analysis by EDAX (energy-dispersive analysis by X-rays) was carried out on both the as-deposited and the annealed films. The Mo and Se contents were estimated by comparison of the intensities of 99.999% purity elemental Mo and Se and were used as standards. The as-deposited samples showed 37.8 ± 0.5\% Mo and 62.2 ± 0.8\% Se by weight (very close to the stoichiometric composition). After annealing (N\textsubscript{2} atmosphere, 380 °C for 1 h) the film composition showed 39.4 ± 0.5\% Mo and 61.6 ± 0.8\% Se. The slight drop in Se in the film may be due to its out-diffusion during annealing.

The structural parameters of the deposited film were determined by X-ray powder diffraction using nickel-filtered Cu-K\textsubscript{x} radiation \((\lambda = 1.5405 \text{ Å})\) using a Siemens D500, and are shown in Fig. 1. The annealed sample showed well defined crystallographic planes, which were identified using the standard JCPDS diffraction data file. The observed \( d \)-values are in good agreement with the JCPDS values and the structure is rhombohedral with preferred orientation (003) and lattice constants \( a = 3.289 \text{ Å} \) and \( c = 19.391 \text{ Å} \). The as-deposited film showed a broad X-ray spectrum suggesting that it had an amorphous structure. The grain size was measured using the method described by Cottrell.\textsuperscript{8} The thermal treatment of the deposited films was done in N\textsubscript{2} atmosphere under optimal conditions; optimal conditions were found as 380 °C, 1 h, which dramatically enhanced the average grain size from 0.13 ± 0.01 \( \mu \text{m} \) to 0.42 ± 0.01 \( \mu \text{m} \). The compositional analysis by EDAX (energy-dispersive analysis by X-rays) was carried out on both the as-deposited and the annealed films. The Mo and Se contents were estimated by comparison of the intensities of 99.999% purity elemental Mo and Se and were used as standards. The as-deposited samples showed 37.8 ± 0.5\% Mo and 62.2 ± 0.8\% Se by weight (very close to the stoichiometric composition). After annealing (N\textsubscript{2} atmosphere, 380 °C for 1 h) the film composition showed 39.4 ± 0.5\% Mo and 61.6 ± 0.8\% Se. The slight drop in Se in the film may be due to its out-diffusion during annealing.

\begin{align}
\text{SeSO}_3^2^- + 2\text{OH}^- & \rightarrow \text{Se}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O} \\
\text{Mo(NH}_3)_6^{2+} + \text{SeSO}_3^{2-} + \text{Se}^{2+} + 2\text{OH}^- & \rightarrow \text{MoSe}_2 + 6\text{NH}_3 + \text{SO}_4^{2-} + \text{H}_2\text{O}
\end{align}

The film thus obtained was washed thoroughly with deionized water and dried in air. The films were smooth, of thickness 0.6–0.8 \( \mu \text{m} \) and very good adherents to the glass substrates. If the solution contained >10 cm\textsuperscript{3} of hydrizade hydrate, the films showed non-uniformity and poor electrical properties; increased thickness (>0.8 \( \mu \text{m} \)) was attained within 3–4 h but

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\footnote{† Sodium selenosulphate solution \((0.45 \text{ mol dm}^{-3})\) was prepared by refluxing 8 g Se powder with 10 g sodium sulphite (anhydrous) in 150 cm\textsuperscript{3} of water for ca. 4 h. A small amount of Se, which remained undissolved, was separated through a glass filter (G 3–4). The formation of sodium selenosulphate can be explained by the reaction \( \text{2SO}_3^{2-} + \text{Se} + \text{H}_2\text{O} \rightarrow \text{SeSO}_3^{2-} + \text{SO}_4^{2-} + \text{H}_2 \).}
Fig. 2 Variation of $(\alpha h\nu)^2$ vs. incident photon energy ($h\nu$) for a typical MoSe$_2$ film on a glass substrate. (a) As-deposited and (b) with annealing (380 °C, 1 h in N$_2$ atmosphere).

close agreement with the value of 1.35 eV for polycrystalline MoSe$_2$ films. The electrical resistivity was at 300 K measured with a four-point probe and the van der Pauw technique. Conducting silver paint is used for ohmic contact. The as-grown film had a resistivity of ca. $3.8 \pm 10^3 \Omega \text{cm}$. After the thermal treatment (380 °C for 1 h in an N$_2$ atmosphere), the resistivity decreased significantly to 1.2 $\Omega \text{cm}$. This decrease in resistivity is due mainly to the formation of Se vacancies and is confirmed by EDAX analysis. This explains the n-type conductivity in this material. Room-temperature (300 K) Hall-effect measurements on the annealed samples showed that the majority of the charge carriers were electrons with a mobility of 36.4 cm$^2$ V$^{-1}$ s$^{-1}$ and a concentration of $1.4 \times 10^{17} \text{cm}^{-3}$.

The authors acknowledge Les fonds FCAR 'Aide aux jeunes chercheurs' and 'Action structurante' of the Quebec Government for their financial support. The authors are also grateful to Mr. B. Das for the computational work of determining the structural parameters.

References