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Novel Chemical Preparative Route for Semiconducting $MoSe_2$ Thin Films

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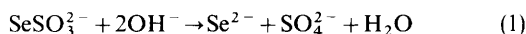
Semiconducting $MoSe_2$ thin film has been prepared chemically and characterized by various physical methods.

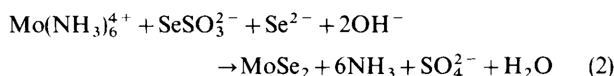
Keywords: *Thin film*; *Chemical deposition*; *Selenium*; *Molybdenum*

One-dimensional linear polymers of Mo-chalcogenides have a wide range of potential applications, *e.g.* as electrode materials for photoelectrochemical (PEC) solar cells,[1] solar rechargeable batteries,[1,2] solid lubricants[3] and superlattice structures.[4] A variety of techniques, *viz.* chemical vapour deposition,[5] molecular beam epitaxy[6] and radiofrequency sputtering[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 $MoSe_2$ 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 controllability. Investigations have also been carried out to determine the structural, optical and electrical properties of the resulting films.

The deposition of the photoactive $MoSe_2$ thin films is based on the reaction of hexaammine molybdenum(VI) ions and sodium selenosulphate with hydrazine hydrate as the reducing agent. The bath preparation was carried out by mixing together 20 cm^3 of 0.1 mol dm^{-3} Mo^{VI} solution, 7.4 cm^3 of 25% NH_3, 10 cm^3 of hydrazine hydrate (80%) and 25 cm^3 of 0.45 mol dm^{-3} sodium selenosulphate.† The mixed solution was magnetically stirred during the reaction. Before the ordinary glass substrate was used for chemical deposition it was cleaned with chromic acid and acetone to remove any residual impurities, rinsed with deionized water and dried. The cleaned substrates were placed vertically to the plating solution in a beaker. The deposition temperature was maintained at 40 ± 2 °C. After 8 h the slides were covered with dense yellow–brown $MoSe_2$ films. The following standard chemical reactions are involved in the mechanism



$$SeSO_3^{2-} + 2OH^- \rightarrow Se^{2-} + SO_4^{2-} + H_2O \quad (1)$$



$$Mo(NH_3)_6^{4+} + SeSO_3^{2-} + Se^{2-} + 2OH^- \rightarrow MoSe_2 + 6NH_3 + SO_4^{2-} + H_2O \quad (2)$$

The film thus obtained was washed thoroughly with deionized water and dried in air. The films were smooth, of thickness 0.6–0.8 μm and very good adherents to the glass substrates. If the solution contained >10 cm^3 of hydrazine hydrate, the films showed non-uniformity and poor electrical properties; increased thickness (>0.8 μm) was attained within 3–4 h but the films were more brittle. Excess amounts of NH_4OH slowed the rate of deposition of $MoSe_2$ but increased its adherence to the glass substrates.

The structural parameters of the deposited film were determined by X-ray powder diffraction using nickel-filtered Cu-Kα radiation ($\lambda = 1.5405$ 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 $a = 3.289$ Å and $c = 19.391$ Å.[8] 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.[9] The thermal treatment of the deposited films was done in N_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 μm to 0.42 ± 0.01 μm. 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_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.

Fig. 2 shows the optical absorption $(\alpha h\nu)^2$ *vs.* incident photon energy ($h\nu$) curves for (*a*) untreated (300 K) and (*b*) thermally treated $MoSe_2$ films. An identical glass slide was used as the reference and the values of optical absorption coefficient (α) were not corrected for the reflectance of the film surface. The bandgap (E_g) changed from 1.48 to 1.36 eV. The decrease in E_g after heat treatment is mainly due to an increase in the effective grain size. The latter value of E_g is in

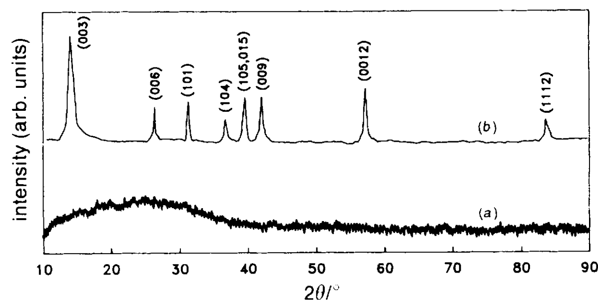


Fig. 1 X-Ray diffraction pattern of $MoSe_2$ thin film (*a*) as-deposited and (*b*) with annealing at 380 °C for 1 h in N_2 atmosphere

† Sodium selenosulphate solution (0.45 mol dm^{-3}) was prepared by refluxing 8 g Se powder with 10 g sodium sulphite (anhydrous) in 150 cm^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 $2SO_3^{2-} + Se + H_2O \rightarrow SeSO_3^{2-} + SO_4^{2-} + H_2$.

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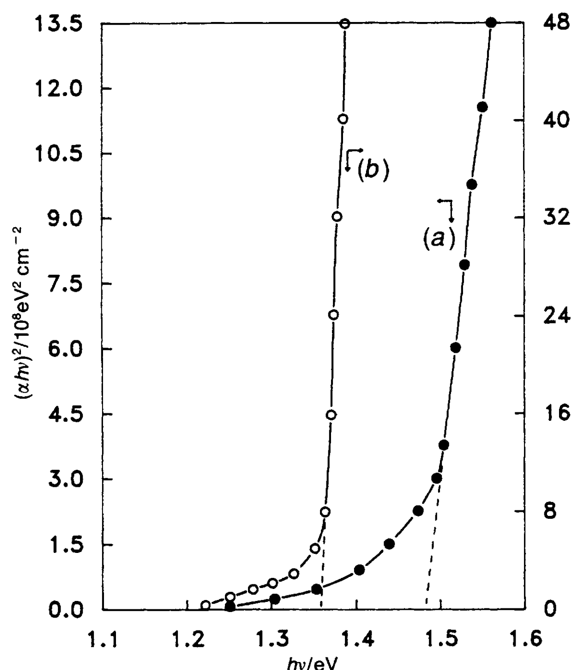

Fig. 2 Variation of $(\alpha h\nu)^2$ *vs.* incident photon energy ($h\nu$) for a typical $MoSe_2$ film on a glass substrate. (*a*) As-deposited and (*b*) with annealing (380 °C, 1 h in N_2 atmosphere)

close agreement with the value of 1.35 eV for polycrystalline $MoSe_2$ films.[10] 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 ± 10^3 Ω cm. After the thermal treatment (380 °C for 1 h in an N_2 atmosphere), the resistivity decreased significantly to 1.2 Ω 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 1.4×10^{17} cm^{-3}.

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References

1 H. Tributsch and J. C. Bennet, *J. Electroanal. Chem.*, 1977, **81**, 97; H. Tributsch, *Ber. Bunsenges. Phys. Chem.*, 1977, **81**, 361; *J. Electrochem. Soc.*, 1978, **125**, 1086; *Solar Energy Mater.*, 1979, **1**, 705; *Struct. Bonding (Berlin)*, 1982, **49**, 128.
2 A. J. Jacobson, R. R. Chianelli, S. M. Rich and M. S. Whittingham, *Mater. Res. Bull.*, 1979, **14**, 1437.
3 K. Reichelt and G. Mair, *J. Appl. Phys.*, 1978, **49**, 1245.
4 K. Ueno, K. Saiki, T. Shimada and A. Koma, *J. Vac. Sci. Technol.*, 1990, **A8**, 68.
5 D. M. Schleich, H. S. Chang, Y. I. Barberio and K. J. Hanson, *J. Electrochem. Soc.*, 1989, **136**, 3274.
6 K. Saiki, K. Ueno, T. Shimada and A. Koma, *J. Crystal Growth*, 1989, **95**, 603.
7 J. R. Lince, *J. Mater. Res.*, 1990, **5**, 218.
8 Powder Diffraction File, 1987, JCPDS.
9 A. Cottrell, in *An Introduction to Metallurgy*, Arnold, London, 1975, p. 173.
10 H. Tributsch, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 169.

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