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Chemically Deposited Semiconducting Molybdenum Sulfide Thin Films

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We report the morphological, structural, optical, and electrical properties of molybdenum sulfide thin films deposited for the first time on a glass substrate by a simple chemical method using molybdenum (VI) ions, ammonia, hydrazine hydrate, and thioacetamide. © 1990 Academic Press, Inc.

The transition metal dichalcogenides, originally studied by Tributsch and others (*1–8*), have now gained tremendous interest as electrode material for photoelectrochemical (PEC) solar cells and solar rechargeable batteries. These compounds have a typical layered structure in which the transition metal is sandwiched between layers of the chalcogenide, to form stacks held together by relatively weak van der Waals forces. For the use of layered semiconductors as an electrode material, it is of crucial importance to develop polycrystalline material having high photoactivity and reliability. Various authors have attempted to achieve this important goal but the results are still unsatisfactory (*9–11*). Recently the chemical deposition method which is very simple and inexpensive has attracted much attention. Other than Cd-chalcogenides, this method has also been used to deposit various metal sulfides and selenides (*12–15*). The present communication describes the authors' successful attempt at the deposition of highly photoactive MoS_2 thin films by a simple chemical route with good reproducibility and controllability.

MoO_3 (3.6 g; BDH, AR grade) was dissolved in 15 ml of 25% NH_3 solution and stirred for a few minutes in a 100-ml beaker. The volume was adjusted to 250 ml with deionized water. Fifteen milliliters of the above-mentioned Mo(VI) solution (0.1 *M*) was mixed with 7.4 ml of NH_3 solution (25%) and 10.2 ml of hydrazine hydrate (80%; BDH, AR). The mixed solution was stirred by a magnetic stirrer to homogenize the solution. The reduction was carried out by 30 ml of 0.1 *M* thioacetamide (98%; E.

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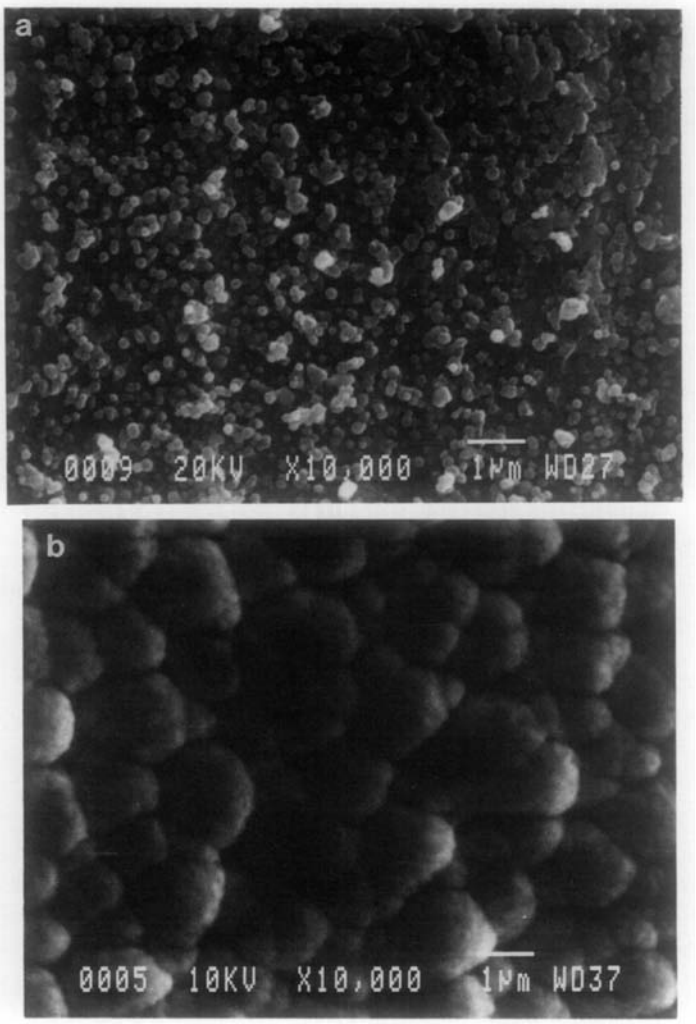

FIG. 1. Scanning electron microscope pictures of chemically deposited MoS_2 films, (a) deposited and (b) annealed at 225°C for 1 hr in N_2 atmosphere.

Merck, Darmstadt, West Germany) and the resulting solution was diluted to 100 ml with deionized water. It was stirred for a few minutes and then commercial quality microscope glass slides previously cleaned with soap solution and chromic acid were dipped vertically in the solution. It was then kept within a thermostatic bath at 80 ± 2°C. After about 10–12 hr the glass slides were covered by light to deep brown, adherent and uniform films of 0.25–0.30 μm thickness. They were then taken out, washed with water, and dried in air. When the solution contained >10.2 ml hydrazine hydrate, the films showed nonuniformity and poor electrical properties. Moreover within 5–6 hr it can generate >0.3-μm-thicker film with more brittleness. It was also observed that a slight excess of NH_4OH slows down the rate of formation

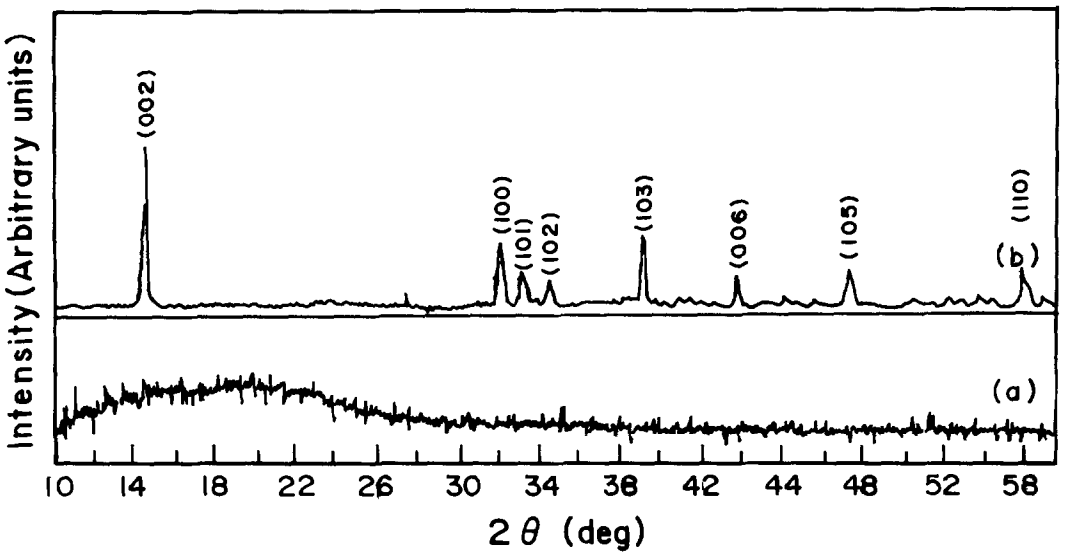

FIG. 2. X-ray diffractograph of MoS_2 film scrapped off the glass substrates, (a) without annealing and (b) with annealing at 225°C for 1 hr in N_2 atmosphere.

of MoS_2 but also increases the adherence of it on the glass substrates.

Figure 1 shows the SEM (JEOL, JSM-840) micrograph of a MoS_2 film on a glass substrate. In this micrograph a homogeneous, uniform surface without cracks or holes is observed. Thermal treatment in N_2 atmosphere (225°C, 1 hr) enhanced the grain size from 0.13 ± 0.02 to 1.16 ± 0.02 μm. The film composition determined by EDAX (energy-dispersive analysis by X-rays) analysis and was found to be 55.8% Mo and 41.5% S in weight which is very close to the stoichiometric composition.

The structural parameters of the film deposited were determined by an X-ray powder diffraction technique using SIEMENS, D500. The results are shown in Fig. 2. The films on the glass substrates were scrapped for this purpose. The annealed samples showed well-defined crystallographic planes and these were identified in the recordings (*16*); the structural features fit into the hexagonal, with the preferred orientation (002) and lattice constants $a = 3.16273$ and $c = 12.29754$ Å. The deposited samples showed a broad X-ray spectrum suggesting that they have amorphous structures.

Figure 3 shows the optical absorption $(\alpha h\nu)^2$ vs incident photon energy $(h\nu)$ curves for thermally treated (curve a) and untreated (curve b) MoS_2 film at 300 K. The band gap changes from 1.80 to 1.74 eV after thermal treatment. The decrease in E_g after heat treatment parallels the same behavior shown previously for CdS and CdSe thin films (*17–19*). This behavior is explained by increase in effective grain size by annealing. The latter value agrees closely with the 1.72 eV for polycrystalline MoS_2 films (*20*).

The electrical resistivity has been measured by a four-point probe using the Van der Pauw technique. Conducting silver paint is used for ohmic contact. The grown sample had a high resistivity of about $2.8 \times 10^2\ \Omega \cdot$ cm. After the thermal treatment (225°C for 1 hr in N_2 atmosphere), the resistivity decreased to 0.35–4.0 $\Omega \cdot$ cm. Hall effect measurements showed that the majority charge carriers were predominantly

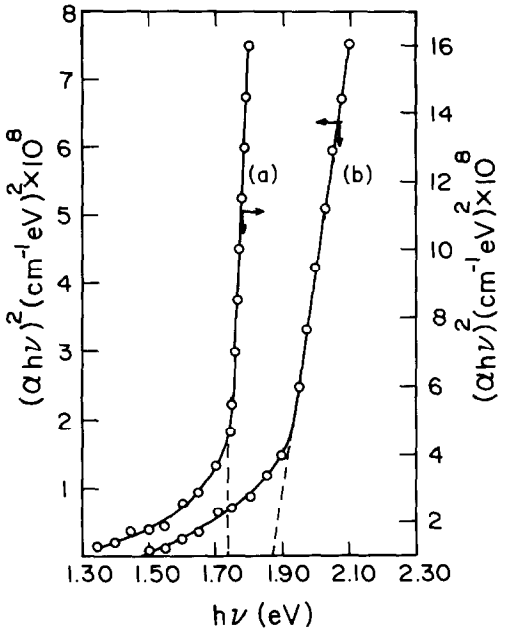

FIG. 3. Variation of $(\alpha h\nu)^2$ vs incident photon energy ($h\nu$) for a typical MoS_2 film on a glass substrate, (a) with annealing (225°C, 1 hr in N_2 atmosphere) and (b) without annealing.

electrons with mobility 16.2 $cm^2/V \cdot sec$ and concentration 1.73×10^{17} cm^{-3}.

In conclusion, a chemical method has been developed for the deposition of polycrystalline MoS_2 thin films on glass substrates. The resistivity of the films grown is very high for solar cell and other optoelectronic device applications. However, this resistivity can be reduced by thermal treatments in a N_2 atmosphere.

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