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Electrical properties of vacuum annealed CdS films

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Cadmium sulphide (CdS) films were evaporated in vacuum on glass substrates maintained at room temperature. These films were later annealed in vacuum at temperatures in the range 30 to 300° C. The variation of d.c. electrical conductivity was studied in the temperature range 100 to 300 K. While the conductivity data in the range 100 to 150 K were observed to follow Mott's variable range hopping process, the conductivity in the high-temperature region (150 to 300 K) could be explained by Seto's model.

1. Introduction

In recent years, polycrystalline II–VI compound semiconductors such as CdS have received considerable attention owing to their high potential as electroluminescent layers [1], heterojunction diodes [2], photovoltaic devices [3, 4] and SAW devices [5]. The earlier studies on photoconductivity, thermoelectric power and photothermoelectric properties of CdS films [6–10] indicated the importance of controlling the pressure during evaporation, the substrate temperature and the impurity content of the charge. The evaporation rate and the source temperature, thickness of the resultant films, the nature of the substrate and its morphology and composition of the residual gas are also equally important variables. Post-evaporation treatment of a film may override the importance of some of these by changing the structure and composition of the films. In a recent report [11], it was concluded that conductivity of CdS films decreases with vacuum and H_2S annealing, but the films were annealed at temperatures higher than 300° C. In the present work, the structure and d.c. conductivity of CdS films evaporated using the powder prepared in our laboratory are reported. The films were annealed in vacuum at temperatures in the range 100 to 300° C. The d.c. conductivity measurements were made in the temperature range 100 to 300 K. The low-temperature data have been analysed on the basis of Mott's variable range hopping conduction process and the high-temperature data have been examined for the thermionic emission of the carriers over the grain boundaries.

2. Experimental methods

The polycrystalline CdS powder used as source in the preparation of films was synthesized by adopting the following procedure. 1.5 M thiourea solution was added to a 10% cadmium acetate solution, previously complexed with sufficient quantity of ammonia. The pH of the resultant solution was raised to 10 by adding liquor ammonia (AR/BDH) and refluxed at 80° C for 2.5 h. The colloidal suspension of the CdS powder thus obtained was left overnight in contact with the mother liquor and filtered the next day, washed until free from alkali and dried at 110° C for 6 h.

The powder prepared as above was characterized by X-ray diffraction and was found to be single-phase CdS. The CdS powder (5 g) was compacted into pellets by applying a pressure of 1 ton cm^{-2} at room temperature. This pellet was used as the source using a tungsten filament under a vacuum of $\sim 10^{-5}$ torr on to glass substrates kept at room temperature. For the sake of comparison, commercial CdS powder was compacted into a pellet and was also used as a source for preparation of films. The thickness of the films was $\sim 1.5\,\mu$m. Electrical contacts were made by the evaporation of high-impurity indium on to the films under vacuum. The ohmic nature of the contacts was confirmed throughout the temperature range by their linear I–V characteristics.

X-ray diffraction studies were made on the films to determine the crystalline nature of the films and to identify components and phases in the films. A diffraction spectrum of the powder of bulk CdS starting material was also taken for comparison.

The d.c. conductivity measurements were made using standard apparatus reported elsewhere [12]. The sample was mounted on a copper block with electrical insulation, which was kept in a Dewar flask containing liquid nitrogen. A copper-constantan thermocouple was used to measure the temperature. The current through the films was reversed in order to eliminate errors due to thermoelectric effects.

3. Results and discussion

Films prepared using laboratory-prepared CdS and commercial material exhibited identical behaviour. The results of X-ray diffraction of films prepared using the laboratory-prepared CdS are presented in Table I. CdS powder was observed to exhibit sharp peaks at 2θ equal to 26.8°, 43.8°, 51.9° which correspond to

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TABLE I X-ray diffraction data for CdS films

Sample	Intensity for different 2θ values		
	26.8°	43.8°	51.9°
CdS powder	80	60	70
As-grown film	5	–	10
Annealed at 100° C	10	–	10
Annealed at 250° C	15	–	10
Annealed at 300° C	20	–	10

different planes of hexagonal phase. The peak positions and peak heights are in good agreement with the ASTM X-ray powder file data for the hexagonal CdS. The as-grown films of CdS exhibited peaks at $2\theta = 26.8°$ and 51.9°, which correspond to diffraction from (0 0 2) and (1 1 2) planes. The diffraction spectra of the films annealed in vacuum at different temperatures showed an increase in peak height corresponding to the (0 0 2) plane.

As-grown CdS films were annealed in vacuum at different temperatures in the range 100 to 300° C for about 1 h. Films annealed at 300° C in vacuum showed a large decrease in conductivity compared to the films annealed at temperatures lower than 300° C for the same period. The variations of d.c. conductivity with temperature (log σ against $1000/T$) for different films vacuum annealed at different temperatures, is shown in Fig. 1.

The conductivity of these films increases slowly with temperature in the low-temperature region (100 to 155 K), while at higher temperatures, the increase in the conductivity with temperature is comparatively sharper. Because of the low activation energy associated with the low-temperature data, they have been analysed for the variable range hopping process on the basis of Mott's model for disordered materials in the following manner. The data were replotted in Fig. 2 as log $\sigma T^{1/2}$ against $T^{-1/4}$ and from the linearity of this plot it is found that the results are in accordance with Mott and Davis' expression [13],

$$\sigma = \frac{\sigma_0}{T} \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \tag{1}$$

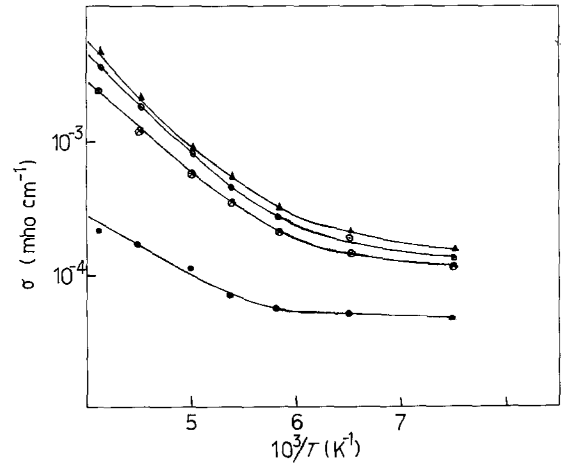

Figure 1 Variation of d.c. conductivity (σ) with temperature of vacuum annealed CdS films: (a) as-grown, (b) 100° C, (c) 250° C, (d) 300° C for 1 h.

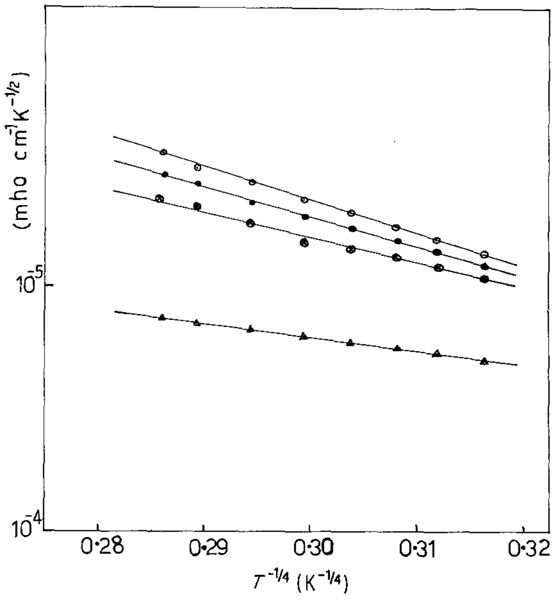

Figure 2 Variation of log $\sigma T^{1/2}$ with $T^{-1/4}$ for vacuum-annealed films. The labelling scheme is as in Fig. 1.

where

$$\sigma_0 = 3e^2\nu_{\text{ph}}\left[\frac{N(E_F)}{8\pi\alpha K}\right]^{1/2} \tag{2}$$

$$T_0 = \frac{\lambda\alpha^3}{KN(E_F)} \tag{3}$$

$$N(E_F) = 5.554 \times 10^{10}(\sigma_0)^3 T_0^{1/2}\ \text{eV}^{-1}\,\text{cm}^{-3} \tag{4}$$

$$\alpha = 64.303\ \sigma_0 T_0^{1/2}\,\text{cm}^{-1} \tag{5}$$

and

$$R = [41.5634/\alpha N(E_F)]^{1/4} \tag{6}$$

where $N(E_F)$ is the density of states near the Fermi level, λ is a dimensionless constant (~ 18), ν_{ph} is a frequency factor, α is the decay constant of the wavefunction of the localized states near the Fermi level, e is the electron charge, K is the Boltzmann constant, and R is the hopping distance.

In amorphous materials, the variable range hopping conduction (VRH) occurs at temperatures at which the phonons do not have sufficient energy to transfer to a nearest neighbour atom and the charge carrier hops from a neutral atom to another neutral atom situated at the same energy level which can be positioned many interatomic distances away. On the other hand, in polycrystalline materials, the VRH conduction process exists in the grain boundaries at temperatures at which the carriers do not have sufficient energy to cross the potential barrier and to transfer themselves into the grain by the process of thermionic emission. Hopping, however, in this case takes place due to the transfer of the charge carriers from a charged trap state to a neutral trap state. The temperature range over which the VRH process is predominant in polycrystalline materials depends on the relative size of the grain with respect to the Debye length (L_D) which is defined as [14]

$$L_D = \left(\frac{\varepsilon\varepsilon_0 KT}{e^2 N}\right)^{1/2} \tag{7}$$

where N is the doping concentration and ε is the

TABLE II Mott's parameters

Sample	T_0 (K)	$N(E_F)$ (eV^{-1} cm^3)	R (cm)	E_σ (eV)
As-grown	2.5×10^7	8.42×10^{18}	0.84×10^{-6}	0.27
100° C	1.03×19^7	6.03×10^{18}	10^{-6}	0.24
250° C	1.44×10^6	5.8×10^{18}	1.2×10^{-6}	0.21
300° C	4.09×10^3	5.4×10^3	6×10^2	0.12

dielectric constant of the sample. If $1 \ll L_D$ practically the entire grain is depleted and the VRH process will be effective over a considerably wide range of temperature. On the other hand, if $1 \gg L_D$ the thermionic emission process will be predominant over the VRH even at very low temperatures. The values of T_0, $N(E_F)$, and R for the vacuum-annealed films are shown in Table II. From Table II one can observe a decrease in the value of T_0 with increase of annealing temperature. The value of T_0 is a measure of disorder in the material. Typical values of T_0 for amorphous materials are $\sim 10^7$ K and higher [15–17]. The values to T_0 decreases with vacuum annealing, resulting in a decrease in disorder. The calculated values of $N(E_f)$ also suggest that the density of trap states near the Fermi level decreases considerably on annealing at 300° C for 1 h.

The high-temperature data for the as-grown as well as vacuum-annealed films are shown in Fig. 3. It has been shown by Seto [18] that when transport occurs by the thermionic emission over the grain boundaries the conductivity is given by

$$\sigma = \frac{e^2 l \eta_{av}}{(2\pi m^* KT)^{1/2}} \exp\,[E_\sigma/KT] \qquad (8)$$

where η_{av} is the average free carrier concentration, l is the average grain size of the sample, m^* is the density of states effective mass of holes, and E_σ defines the activation energy for the grain-boundary limited conductivity. The values of E_σ for all the films are indicated in Table II. It is observed E_σ decreases with annealing. If we assume a constant value of $(E_V - E_F)$ in these films, the results suggest that a decrese in E_σ can be attributed to the decrease in ϕ_b which may be because of the decrease in the carrier density in the grains, without affecting the carrier density in the boundary regions.

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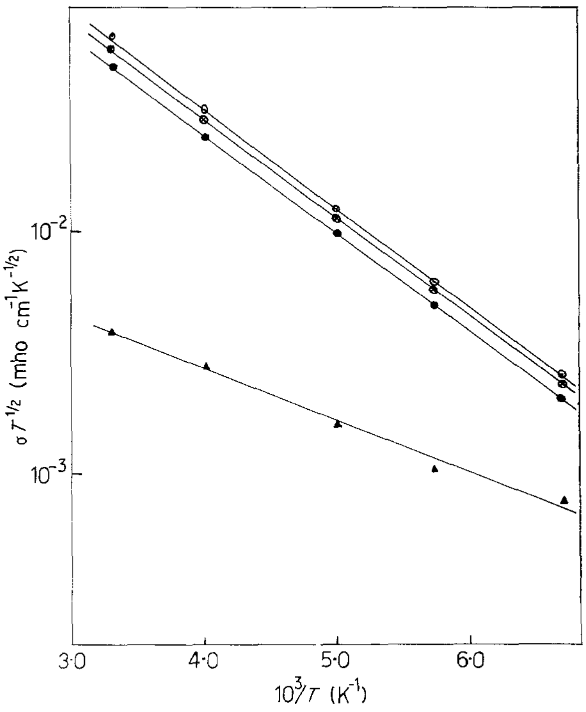

Figure 3 Variation of log $\sigma T^{1/2}$ with $1000/T$ for vacuum-annealed films.

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