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# Effect of vacuum and $H_2S$ annealing on the electrical properties of CdS thin films

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Polycrystalline CdS films were grown on to glass substrates kept at room temperature using a resistive heating technique. Films grown from the same batch were annealed in vacuum and $H_2S$ vapour at 300 and 400° C for various periods up to 2 h. D.C. conductivity studies were made on these films in the temperature range 77 to 300 K. It was found that the d.c. conductivity decreases with vacuum and $H_2S$ annealing; however, decrease is more significant in the latter films. X-ray diffraction studies were also carried out on these films.

## 1. Introduction

The study of polycrystalline II–VI compound semiconductors, particularly CdS, has drawn considerable interest in recent years because of its high potential as photoresistors and phosphors, electroluminescent layers [1], space charge limited diodes and triodes [2], heterojunction diodes [3], insulated gate TFT's [4], photovoltaic devices [5, 6] and SAW devices [7]. Low resistive films are essential for photovoltaic devices, whereas high resistive films are used for surface acoustic wave devices.

The work of Veith [8], Aitchison [9], Bramley [10], Wilson and Woods [11] and Wu and Bube [12], who studied photoconductivity, thermoelectric and photo-thermoelectric properties of these films, indicated the importance of controlling the pressure during evaporation, the substrate temperature and the impurity content of the charge. Only more recently has it been realized that the evaporation rate and source temperature, thickness of the resultant films, the nature of the substrate and its morphology, and the composition of the residual gas are equally important variables. Post evaporation treatment of a film may, of course, override the importance of some of these by changing the structure and composition of the films.

In the present work, the structure and d.c. conductivity of the films is reported. The manner in which the properties of thin films of CdS prepared from high purity material depend on post deposition annealing in vacuum and in $H_2S$ vapours is also studied. The d.c. conductivity measurements were made in the temperature range 77 to 300 K. 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 details

Polycrystalline films of CdS of size 20 mm × 4 mm and rectangular in shape, were grown from bulk CdS of evaporation grade obtained from Balzers, using tantalum masks under a vacuum of $\sim 5 \times 10^{-6}$ torr on to glass substrates kept at room temperature. The growth rate and the thickness of the films were controlled by using a quartz crystal thickness monitor. The growth rate is of $\sim 0.5\,\text{nm sec}^{-1}$. CdS powder was placed in a tungsten boat (Box shape) and covered with quartz wool to avoid spattering of the material from the boat. The thickness of the films was $\sim 0.8\,\mu\text{m}$. Electrical contacts were made by the evaporation of high purity indium on to the films under vacuum through a tantalum mask. The ohmic nature of the contacts was confirmed throughout the temperature range by their linear $I$–$V$ characteristics.

A Philips X-ray diffractometer (model no. PW 1130/00) was used in the present study to

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determine the crystalline nature of the films and to identify components and phases in the films. Cu*K*$\alpha$ radiation was employed in these experiments and the $2\theta$ spectrum from 15° to 60° was recorded for each film specimen. A diffraction spectrum of the bulk powder CdS starting material was also taken for comparison. Crystallite sizes were determined from X-ray diffraction spectra using the Scherrer formula.

The d.c. conductivity measurements were made using a 610 C Keithley Electrometer. 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 soldered to the copper block, was used to measure the temperature. The current through the films was reversed in order to eliminate errors due to thermoelectric effects. The overall error in d.c. conductivity is estimated to be about 4%.

## 3. Results and discussion

### 3.1. X-ray diffraction studies

Diffractometer spectra for all the films which illustrate different structural features are shown in Fig. 1. The powder diffraction spectrum for the CdS used for evaporation is also shown in the same figure for comparison. The spectrum of the CdS powder is seen to exhibit sharp peaks at $2\theta$ equal to 26.80°, 43.75°, 51.90° which correspond to

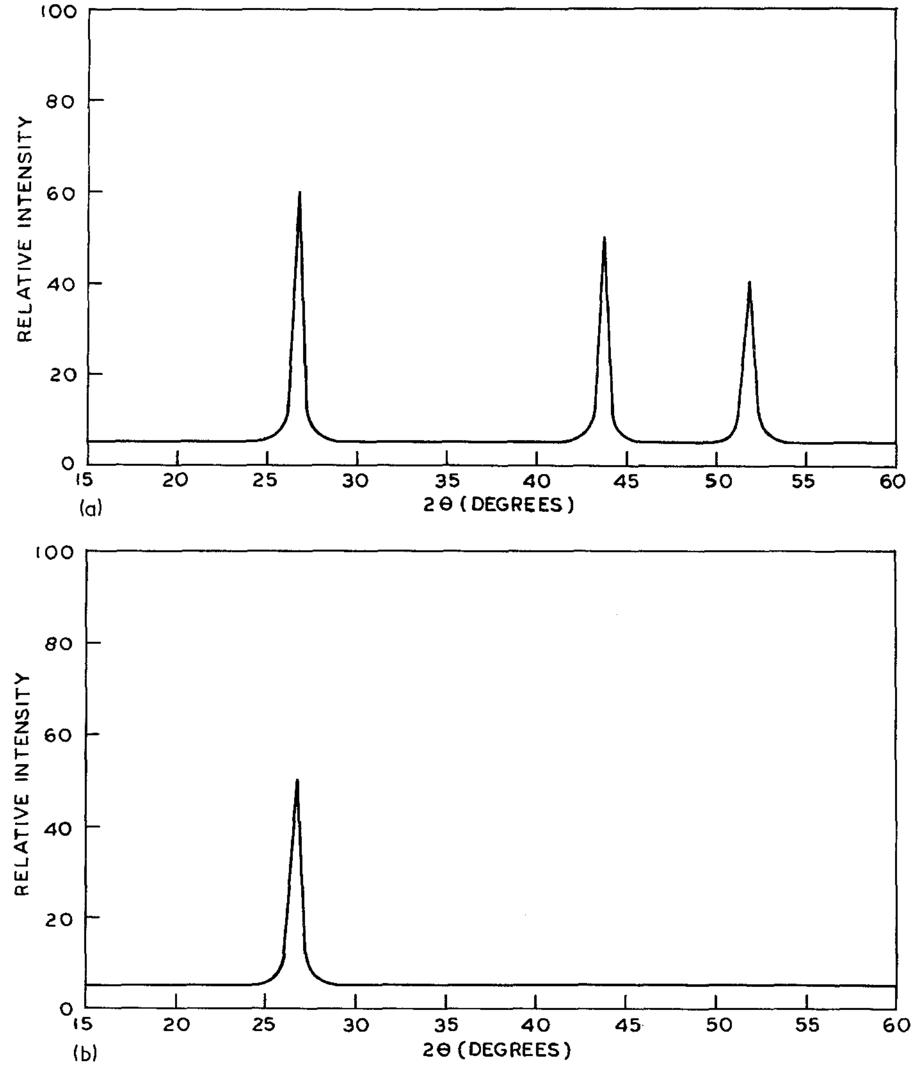
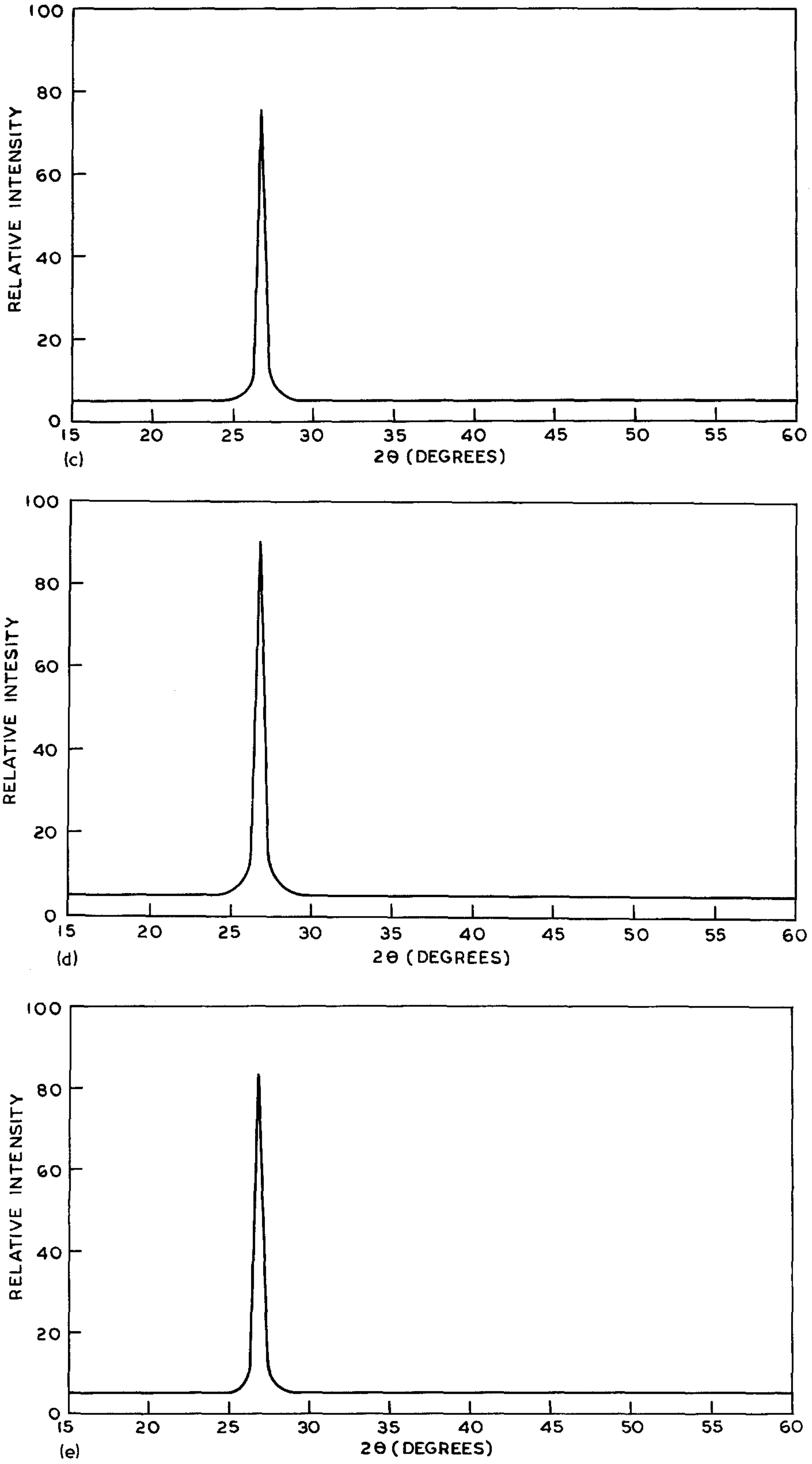


*Figure 1* X-ray diffraction spectra for CdS powder specimen and films showing principal peaks for Cu*K*$\alpha$ radiation. (a) CdS powder, (b) as-grown, (c) vacuum-annealed at 300° C for 2 h, (d) vacuum-annealed at 400° C for 2 h, (e) $H_2S$-annealed at 300° C for 2 h, (f) $H_2S$ annealed at 400° C for 2 h.



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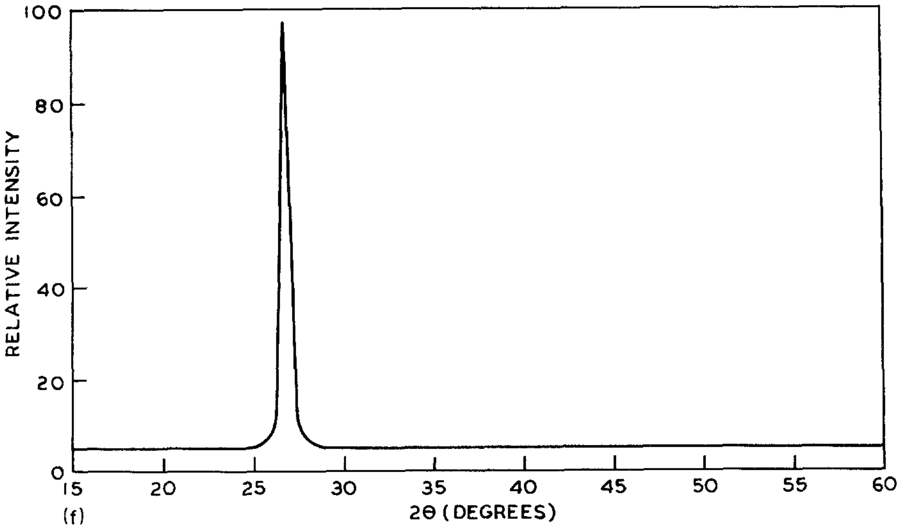

*Figure 1.* Continued

diffraction from the (0 0 2), (1 1 0), (1 1 2) planes of the hexagonal phase, respectively. Both the peak heights and peak positions are in good agreement with ASTM X-ray Powder file data (6-0314) for hexagonal CdS, whereas as-grown films on glass substrates kept at room temperature, showed a peak at $2\theta$ equal to 26.8° which corresponds to diffraction from the (0 0 2) plane. The other planes (1 1 0) and (1 1 2) are absent in the films. The films grown at room temperature are *c*-axis oriented, which has been observed previously [13, 14].

X-ray diffraction spectra obtained for the films after annealing in vacuum and in $H_2S$ vapour did not show any extra peaks; however, the peak height of the (0 0 2) plane increased with annealing time in both cases. X-ray diffraction spectra of films annealed in vacuum and $H_2S$ vapour at 300 and 400° C for 2 h are shown in Fig. 1. Films annealed for shorter durations also showed an increase in the peak height when compared to the as-grown films, which can be observed from Fig. 1.

The grain size ($l$) of these films was estimated using the Scherrer formula [15]:

$$l = \frac{\lambda}{D \cos \theta},$$

where $D$ is the full width at half maximum of the peak, $\lambda$ is the wavelength of the X-rays. The values of $l$ for all the films are shown in Tables I and II.

### 3.2. D.C. conductivity studies

As-grown CdS films were annealed in vacuum at 300 and 400° C for various periods (up to 2 h) and it was found that conductivity decreases with annealing time and the decrease in conductivity for the films annealed at 400° C is higher when compared to the films annealed at 300° C for the same period. The films grown in the same batch were annealed in $H_2S$ vapour in a furnace specially designed for this purpose. First of all, the films were kept in the furnace and argon gas was passed through the furnace for 15 min and afterwards $H_2S$ gas was allowed to pass through the furnace

TABLE I Vacuum annealed films

| Sample no. | Sample specification | $T_0$ (K) | $N(E_F)$ ($eV^{-1}$ $cm^{-3}$) | $\alpha R$ | $E_\sigma$ (meV) | $l$ (nm) |
|---|---|---|---|---|---|---|
| A | As-grown | $1.48 \times 10^6$ | $2.3 \times 10^{19}$ | 4.14 | 81.73 | 22 |
| B | 300° C, 0.5 h | $3.57 \times 10^5$ | $8.37 \times 10^{13}$ | 2.90 | 68.06 | 22.4 |
| C | 400° C, 0.5 h | $1.27 \times 10^5$ | $2.84 \times 10^{10}$ | 2.24 | 53.32 | 22.7 |
| D | 300° C, 1 h | $7.29 \times 10^4$ | $4.69 \times 10^9$ | 1.95 | 44.12 | 23 |
| E | 300° C, 2 h | $4.13 \times 10^4$ | $4.34 \times 10^8$ | 1.69 | 40.99 | 23.3 |
| F | 400° C, 1 h | $3.73 \times 10^4$ | $2.7 \times 10^7$ | 1.65 | 38.2 | 23.5 |
| G | 400° C, 2 h | $2.4 \times 10^4$ | $3.95 \times 10^5$ | 1.48 | 32.53 | 24 |

TABLE II $H_2S$ annealed films

| Sample no. | Sample specification | $T_0$ (K) | $N(E_F)$ ($eV^{-1}$ $cm^{-3}$) | $\alpha R$ | $E_\sigma$ (meV) | $l$ (nm) |
|---|---|---|---|---|---|---|
| A | *as-grown* | $1.48 \times 10^6$ | $2.30 \times 10^{19}$ | 4.14 | 81.73 | 22 |
| B | 300° C, 0.5 h | $3.5 \times 10^5$ | $6.76 \times 10^{13}$ | 2.89 | 66.32 | 22.5 |
| C | 300° C, 1 h | $6.97 \times 10^4$ | $2.72 \times 10^9$ | 1.93 | 41.96 | 23.4 |
| D | 400° C, 0.5 h | $9.78 \times 10^4$ | $2.17 \times 10^{10}$ | 2.10 | 50.76 | 22.9 |
| E | 300° C, 2 h | $3.83 \times 10^4$ | $1.72 \times 10^8$ | 1.66 | 40.62 | 24 |
| F | 400° C, 1 h | – | – | – | 34.89 | 24.4 |
| G | 400° C, 2 h | – | – | – | 30.4 | 25 |

while the temperature of the furnace was gradually increased to the required value (i.e. 300 or 400° C). Films annealed at 300° C in $H_2S$ vapour showed changes in the conductivity values which are comparable with the changes observed in the films annealed at 300° C in vacuum. On the other hand, the films annealed in $H_2S$ vapour at 400° C showed a greater decrease in conductivity when compared to the films vacuum-annealed at 400° C, for the same period.

The variation of d.c. conductivity with temperature (log $\sigma$ against $1000/T$) for different films, i.e. as-grown, vacuum-annealed and $H_2S$-annealed films, is shown in Figs. 2 and 3, respectively. It is found that the conductivity of the films decreases with annealing in vacuum as well as in $H_2S$ vapour; however, the decrease is greater in the $H_2S$-annealed films.

In the vacuum-annealed and $H_2S$-annealed films, the conductivity increases slowly with temperature in the low temperature region (77 to 200 K), while at higher temperatures, the increase in the conductivity with temperature is comparatively sharper. Owing to the low activation energy for the conduction process, the low temperature data have been analysed for the variable range hopping pro-

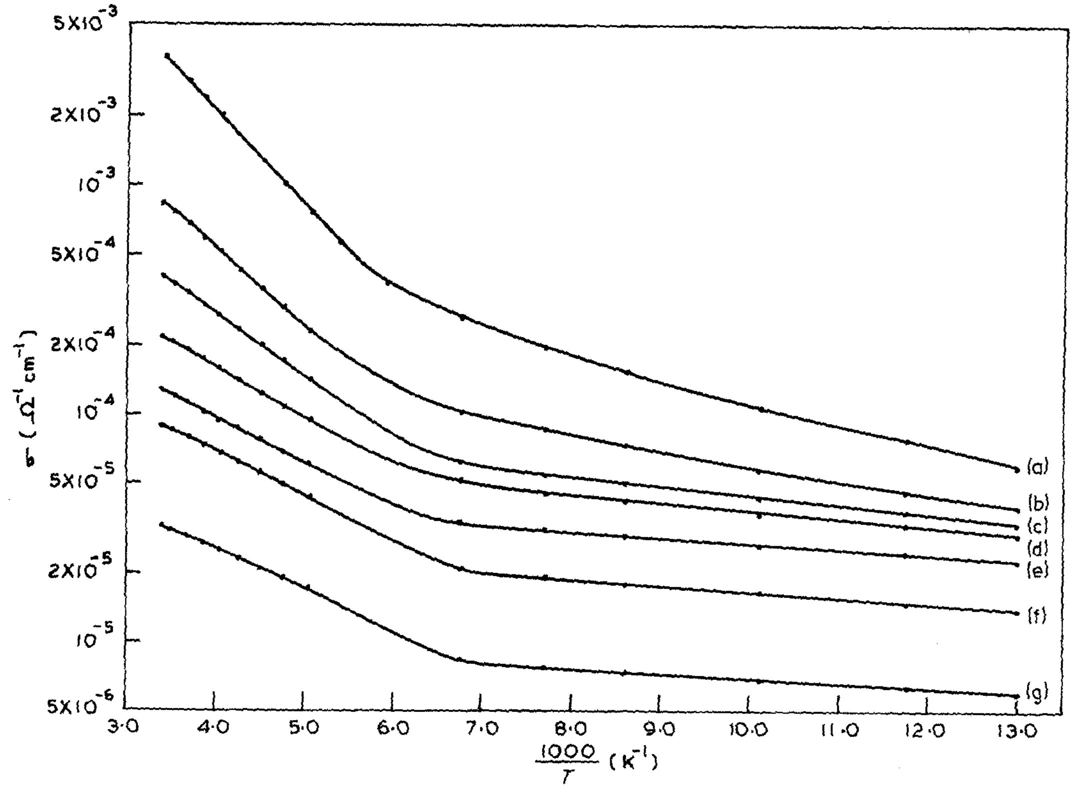

*Figure 2* Variation of d.c. conductivity ($\sigma$) with temperature (log $\sigma$ against $1000/T$) of vacuum-annealed CdS films. (a) as-grown, (b) at 300° C for 0.5 h, (c) at 400° C for 0.5 h, (d) at 300° C for 1 h, (e) at 300° C for 2 h, (f) at 400° C for 1 h, (g) at 400° C for 2 h.

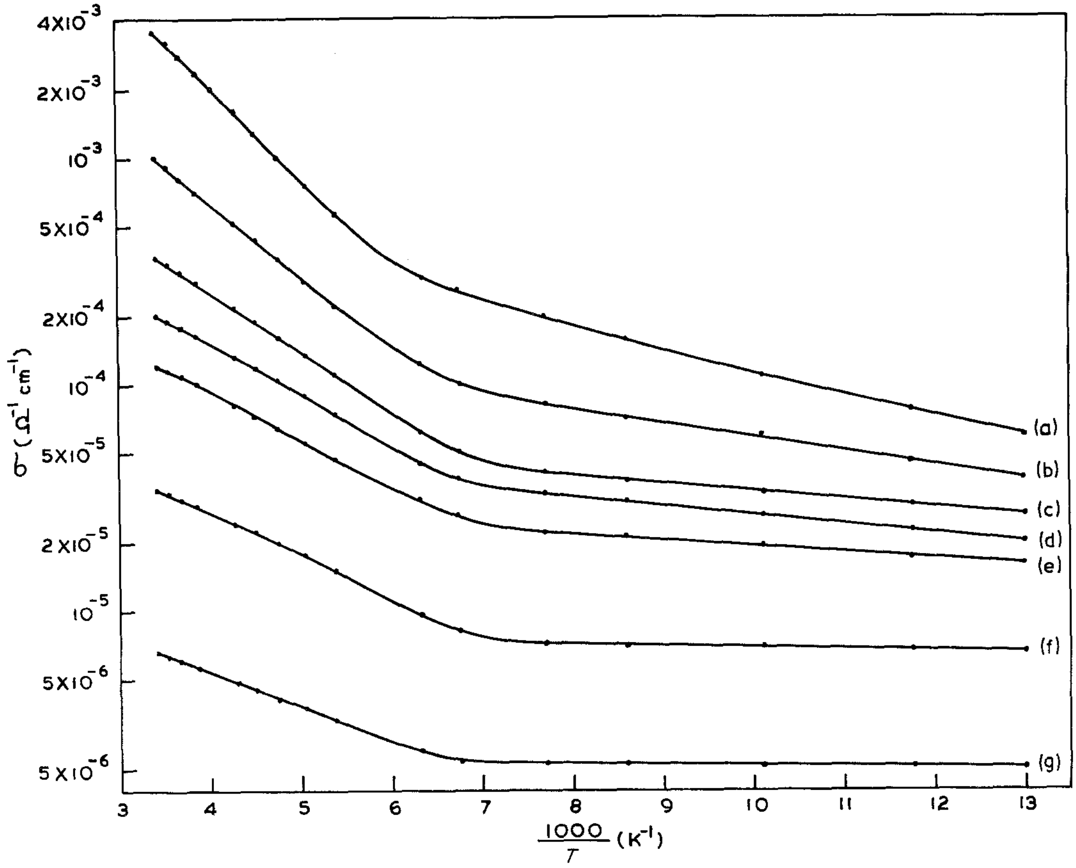

*Figure 3* Variation of d.c. conductivity ($\sigma$) with temperature (log $\sigma$ against $1000/T$) of $H_2S$-annealed films. (a) as-grown, (b) at 300° C for 0.5 h, (c) at 300° C for 1 h, (d) at 400° C for 0.5 h, (e) at 300° C for 2 h, (f) at 400° C for 1 h, (g) at 400° C for 2 h.

cess on the basis of Mott's model for disordered materials in the following manner. The data have been replotted in Figs. 4 and 5 for the vacuum-annealed and $H_2S$-annealed films, respectively, 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's expression [16]

$$\sigma_1 = \frac{\sigma_0'}{T^{1/2}} \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \quad (1)$$

where

$$\sigma_0' = 3e^2\nu_{\mathrm{ph}}\left[\frac{N(E_F)}{8\pi\alpha k}\right]^{1/2} \quad (2)$$

$$T_0 = \frac{\lambda\alpha^3}{kN(E_F)}; \quad R = \left[\frac{9}{8\pi\alpha kTN(E_F)}\right]^{1/4}, \quad (3)$$

where $N(E_F)$ is the density of states near the Fermi level, $\lambda$ is dimensionless constant ($\approx 18$), $\nu_{\mathrm{ph}}$ is a frequency factor taken here as the Debye frequency ($\approx 3.3 \times 10^{12}$ Hz), $\alpha$ is the decay constant of the wavefunction of the localized states near the Fermi level, $e$ is the electron charge, $k$ the Boltzmann constant, and $R$ the hopping distance.

Simultaneous solution of Equations 2 and 3 yields

$$N(E_F) = 5.55416 \times 10^{10}(\sigma_0')^3 T_0^{1/2}\ \mathrm{eV}^{-1}\ \mathrm{cm}^{-3} \quad (4)$$

$$\alpha = 64.303\,\sigma_0' T_0^{1/2}\ \mathrm{cm}^{-1}; \quad R = \left[\frac{41.5634}{\alpha N(E_F)}\right]^{1/4}. \quad (5)$$

In amorphous materials the variable range hopping conduction (VRH) occurs at temperatures at which the phonons do not have sufficient energy for 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 many interatomic distances away. On the other hand, in polycrystalline materials, the VRH conduction process exists in the grain

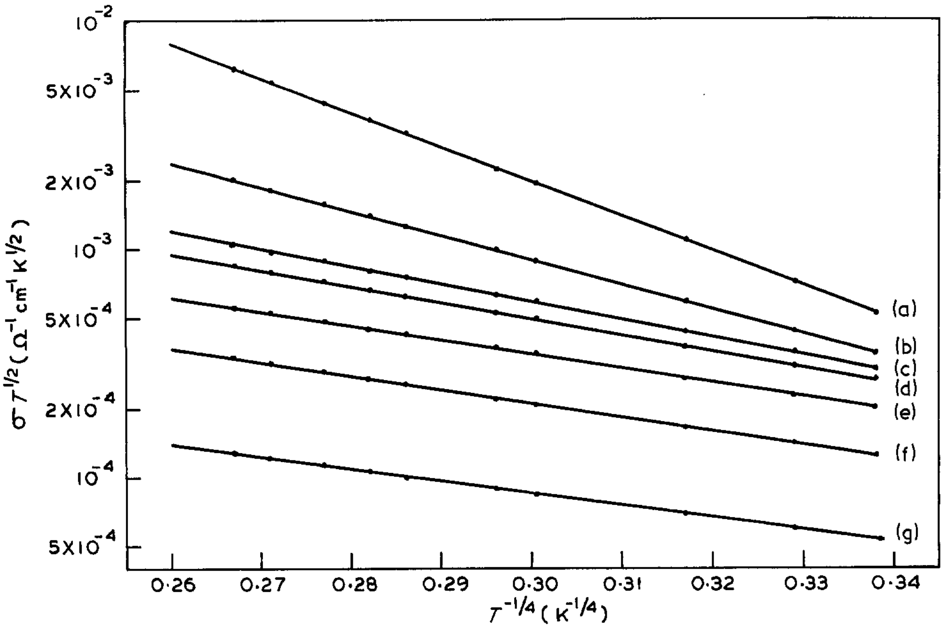

*Figure 4* Variation of log $\sigma T^{1/2}$ as a function of $T^{-1/4}$ for vacuum-annealed films. Labelling as in Fig. 2.

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. However, in this case, hopping takes place owing to the transfer of the charge carriers from a charged trap state to a neutral trap state. The temperature ranges 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 [17]

$$L_D = \left(\frac{\epsilon\epsilon_0 kT}{e^2 N}\right)^{1/2} \qquad (6)$$

where $N$ is the doping concentration and $\epsilon$ is the dielectric constant of the sample. If $l \ll L_D$, 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 $l \gg L_D$

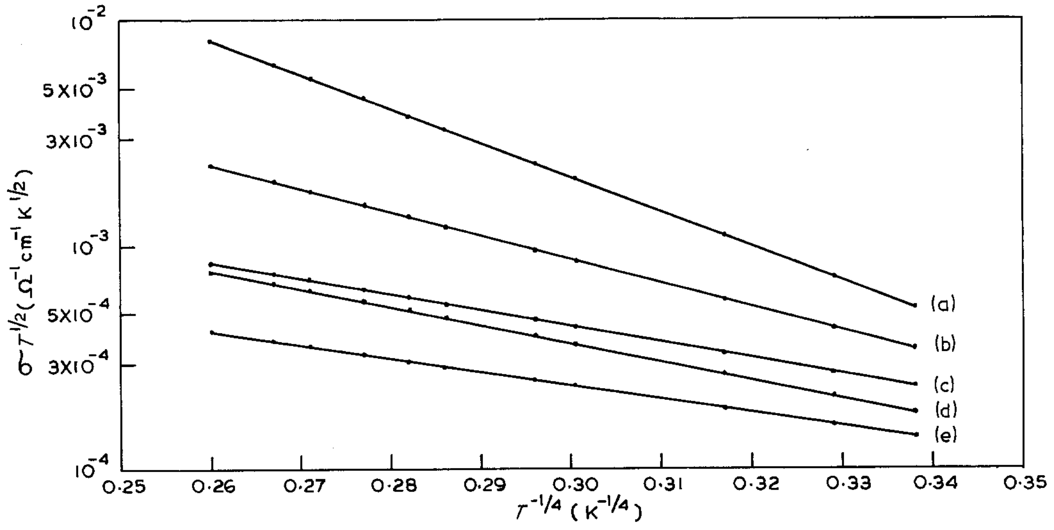

*Figure 5* Variation of log $\sigma T^{1/2}$ as a function of $T^{-1/4}$ for $H_2S$-annealed films. Labelling as in Fig. 3.

the thermionic emission process will be predominant over the VRH process even at very low temperatures. The values of $T_0$, $N(E_F)$, $\alpha R$ for the vacuum-annealed and $H_2S$-annealed films is shown in Tables I and II. From the tables one can observe the decrease in the value of $T_0$ with increase in annealing time. It may be mentioned that the values of $T_0$ are a measure of disorder in the material. Typical values of $T_0$ for amorphous materials is $\sim 10^7$ K and higher [18–20].

In the present case, calculated values of $T_0$ suggest that the disorder decreases with vacuum and $H_2S$-annealing at 300 and 400° C, however, decrease in disorder is higher in the latter films, which is also confirmed by the X-ray diffraction spectra given in Fig. 1. From this figure one can observe an increase in the peak height of CdS (0 0 2) peak with annealing time. The calculated values of $N(E_F)$ also suggest that the density of trap states near the Fermi level decreases considerably with annealing at 300 and 400° C. In the hopping conduction process the parameter $\alpha R$ represents the degree of localization of the carriers in the trap states and from Tables I and II one can observe a decrease in the value of $\alpha R$ with vacuum and $H_2S$-annealing. It can be further observed from Tables I and II, that the value of $\alpha R$ is greater than unity in all cases, which confirms Mott's theory [16]. It may be mentioned that the values of $N(E_F)$ calculated from Mott's expression given in Equation 1 are only qualitative due to the simplifying assumptions [21] made by Mott of which the most important are: energy independence of the density of states at $E_F$, neglect of the correlation effects in the tunnelling process, omission of multiphonon processes and neglect of the electron–phonon interaction. However, inspite of these assumptions one can draw a qualitative conclusion regarding the structure of the material. However, the films annealed in $H_2S$ vapour at 400° C for 1 h and 2 h showed very low value of $T_0$, i.e. $< 10^3$ K and the value of $\alpha R$ is also $< 1$. Therefore, Mott's variable range hopping conduction process cannot be applied to these films. The conduction process in the low-temperature region in these films may, therefore, be attributed to the thermally assisted tunnelling of the carriers through the grain boundaries.

The high temperature data for the as-grown as well as the vacuum- and $H_2S$-annealed films have already been plotted in Figs. 2 and 3 as $\log \sigma$ against $1000/T$. Mankarious [22] and others [23–26] extended the Petritz model and suggested that when the transport occurs by thermionic emission of the carriers over the grain boundaries, the conductivity is given by

$$\sigma_2 \sim \exp - (E_\sigma/kT)$$

where $E_\sigma$ is the conductivity activation energy.

$$E_\sigma \simeq E_n + q\phi_b$$

$E_n$ is the carrier activation energy for n-type films. The Vogler [27] and Petritz [28] models give a relation for the barrier height

$$q\phi_b = kT \ln \left(\frac{n_1}{n_2}\right),$$

where $n_1$ and $n_2$ are the carrier densities in the grain and boundary regions, respectively. The value of $E_\sigma$ calculated for all the films is shown in Tables I and II. From these tables one can observe that the value of $E_\sigma$ decreases with annealing. If we assume a constant value of $E_n$ in these films, the results suggest that decrease in $E_\sigma$ can be attributed to the decrease in $\phi_b$ which may be because of the decrease in the carrier density in the grains $n_1$, without affecting the carrier density in the boundary regions, $n_2$.

## 4. Conclusion

It is concluded that vacuum annealing and $H_2S$ annealing decreases the conductivity of CdS films and also decreases the density of states near the Fermi level; however, the decrease is greater in the $H_2S$-annealed films. The as-grown, vacuum-annealed and $H_2S$-annealed films showed a variable range hopping conduction process and the $H_2S$-annealed (at 400° C for 1 and 2 h) films showed thermally assisted tunnelling of the carriers through the grain-boundary barrier in the low-temperature region. The conduction process in the high-temperature region in all the films is due to thermionic emission of the carriers over the grain boundaries and the conductivity activation energy decreases with annealing in vacuum and as well as in $H_2S$. The grain-boundary barrier potential, $\phi_b$, also decreases with vacuum- and $H_2S$-annealing. This may be attributed to the decrease in the carrier concentration in the grains without affecting the carrier concentration in the grain-boundary regions.

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