Effect of substrate temperature on photoconductivity in CdS thin films

K Kunjabali Singh¹, Manoranjan Kar² & H L Das³
¹ T M College, Oinam 795 134, Manipur
² Centre for Nanotechnology, Indian Institute of Technology, Guwahati 781 039, Assam
³ Department of Physics, Gauhati University, Guwahati 781 014, Assam
E-mail: kksphystmc@yahoo.com
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Photo-electronic properties of CdS thin films (0.25µm thick) grown by thermal evaporation (TE) method on cleaned glass substrates held at different substrate temperatures \((T_s)\) in the range 300-473K have been studied under different intensities of white light, bias voltages and ambient temperatures. The grain sizes are found to increase with \(T_s\) which enhanced the photosensitivity of the films. The photosensitivity of the films has been found to increase with light intensity, \(T_s\) and bias voltage. The evaluation of dark and photo-activation energies and mobility activation energies show double photo-activation processes. The activation energies and the mobility activation energies are observed to be decreasing with increasing \(T_s\) and ambient temperature, and reveal the presence of various discrete trap distributions at different trap depths.

**Keywords**: CdS thin films, Substrate temperature, Grain size, Photoconductivity, Activation energy

1 Introduction

Cadmium sulphide thin films offer wide range of technological applications for successful fabrications of low cost high efficiency thin film solar cells¹²³, laser diodes⁴, photo-electrochemical cells⁵⁶, X-ray detectors⁷ and IR detectors⁸. Thus, study of photo-response characteristics of this material is of considerable interest for characterization of the relevant attributes. Keeping these aspects in view, more attention is being given in producing good quality CdS thin films. Work in growing CdS thin films for photoluminescence and structural properties of the films using different deposition techniques were reported earlier⁹¹⁰. Depending on the growth parameters, particularly the substrate temperature, a vacuum evaporated thin film may be either amorphous or polycrystalline in nature. A polycrystalline thin film contains a large number of inherent native defects irrespective of their deposition methods and growing conditions. These defect states which may act, either as trapping or recombination centers greatly influence the photo-conductivity process. The nature and the amount of such inherent defects depend on different deposition parameters like degree of vacuum, substrate temperature and film thickness¹¹¹². Extensive research work on CdS thin films concerning different aspects were carried out during the past few decades. In this paper, the role of grain sizes and grain boundary potential barriers in the photoconductivity process at different temperatures in vacuum evaporated CdS thin films under different ambient conditions has been studied.

2 Experimental Details

High purity (99.999%) CdS powder obtained from Koch Light Laboratory, U K, was used as the source material. A suitably cleaned Ta boat was used as the source heater. For obtaining gap-type film cell configuration and also to ensure good ohmic contacts for photoconductivity measurements, photo-grade purity Ag electrodes of 4.0×10.0 mm² size were uniformly deposited at room temperature over CdS thin films. Hind High Vacuum Unit (HINDHIVAC 12A4) was used for preparation of the films. The cell configuration was Ag-CdS-Ag with inter-electrode spacing of 7 mm. The vacuum maintained was 1.33×10⁻⁴ Pa. The thickness of the films were measured with a suitably designed multiple beam interferometer at an accuracy of ±15Å. The samples were successively mounted on a suitably designed sample mount, and then suspended vertically inside a continuously evacuated glass jacket with the help of thin enameled-copper wires under a vacuum of ~2.67Pa. A double stage rotary pump was used for this purpose. A suitable optical arrangement was made to illuminate the sample uniformly with white light, for which a tungsten halogen lamp (250W-24V) attached with a parabolic focusing mirror was used as
the light source. The block diagram of the experimental set up is shown in Fig. 1.

The intensity of light was measured with the help of a sensitive APLAB luxmeter (model 5011S). High ambient temperatures were achieved by means of a resistive heater connected to a stabilized power supply. The temperatures of the films were measured with the help of a copper-constantant thermocouple coupled with a digital micro-voltmeter. The dark currents \( I_D \) and the currents under illumination \( I_L \) were measured with the help of a high input impedance (~10^{14} \Omega) ECIL electrometer amplifier under different dc bias voltages. A number of dry cells each of e.m.f. 9 volts connected in series were used. The whole experimental set-up including the observer was housed inside a suitably grounded Faraday Cage to minimize external ground loop currents and pick up noises. The observations were, therefore, taken preferably at night to avoid the high day time noise.

3 Results and Discussion

3.1 Film structure

The study of the X-ray diffraction profiles of the vacuum deposited CdS thin films revealed polycrystalline growth with f.c.c cubic zinc sulphide structure at \( T_s \leq 423 \) K with preferential reflection along (111) plane, and hexagonal wurtzite structure at \( T_s \geq 473 \) K with prominent reflection along (002) plane. The detailed analysis of the microstructural properties of the vacuum evaporated CdS thin films is done earlier^{13}.

3.2 Photosensitivity

The variation of \( \ln I_{ph} \) vs \( \ln \Phi \) of the films grown at 300 K and elevated 473 K at different fixed bias voltages (63 and 90 volts) under illumination of white light with intensities 1100-96000 lx are shown in Fig. 2. In this figure \( \Phi \) represents the intensity of white light illumination. In these films, the photocurrent \( I_{ph} \) defined by \( I_{ph} = I_L - I_D \), is related to \( \Phi \) through the power law, \( I_{ph} \propto \Phi^x \), where the exponent \( x \) is a number which is an index of the imperfection level of the films. The values of \( x \) were evaluated from the slopes of the \( \ln I_{ph} \) vs \( \ln \Phi \) plots. It is observed that the different values of \( x \) under white light illumination were not much different from the mean value 0.52. Table 1 shows the variation of \( x \) with different applied bias in these films. It implies that bimolecular carrier recombination process

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![Fig. 1 — Schematic block diagram of experimental set-up for photoconductivity measurement](image1)

![Fig. 2 — \( \ln I_{ph} \) versus \( \ln \Phi \) plots for CdS films at different \( T_s \) under different bias](image2)

| \( T_s \) (K) | 36V  | 63V  | 90V  |
|----------------|
| 300            | 0.56 | 0.51 | 0.44 |
| 423            | 0.54 | 0.52 | 0.51 |
| 473            | 0.52 | 0.54 | 0.56 |
predominates the photoconduction mechanism in these films. Similar results were also obtained by other researchers. From Fig. 2, it was also observed that $I_{ph}$ increases with increasing $T_s$, the intensity of illumination and bias.

Photosensitivity of a material is an effective parameter to determine its photoconductivity. In the present work, the photosensitivity at a particular temperature is defined as:

$$S = \frac{I_{L} - I_{D}}{I_{D}} = \frac{I_{ph}}{I_{D}} \quad \ldots (1)$$

where $I_{ph} = (I_{L} - I_{D})$, $I_{L}$ being the current under illumination and $I_{D}$ the dark current.

The variation of photosensitivity as a function of the light intensity of the films grown at 373 and 473 K ($T_s$) at the same bias range have been shown in Fig. 3. It is observed that photosensitivity $S$ shows an increase with intensity and bias. A comparative study of the plots revealed that photosensitivity in these films improved with increasing $T_s$.

Since the same source material was used to grow the films at different $T_s$, it was, therefore, expected that the average impurity concentrations in different films was the same. Hence, keeping other growth parameters the same, by vacuum depositing thin films of the same thickness at different $T_s$, one can expect that different films will have different crystallite sizes. Therefore, at any fixed temperature and illumination level, the difference in conductivity may be attributed to the effect of crystallite or grain sizes on the phototransport processes. Figure 4 shows the variation of grain-sizes versus $T_s$ of the same film thickness. Crystallite or grain-sizes were determined from X-ray diffraction data using the Scherrer formula:

$$D_{hkl} = \frac{k\lambda}{\beta_\theta \cos \theta} \quad \ldots (2)$$

where $\theta$ is the Bragg angle, $\lambda$ the wavelength of X-rays, $\beta_\theta$ the width of the peak at half of the maximum peak intensity and $k$ the proportionality constant whose value is taken as 0.94.

Plot of Fig. 4 shows that grain-sizes are found to be increasing almost linearly with increasing $T_s$. The grain-sizes, therefore, have dominant influence on the photosensitivity in the films. Thus the photosensitivity $S$ of the films, increases with increasing grain-size. As seen from Fig. 5, up-to 229Å grain-size, the photosensitivity in the films for all the applied bias voltages increases at a slower rate, and then increases more sharply.

### 3.3 Photoconductivity

The plots of $\ln \sigma$ versus $\ln 10^3/T$ for the CdS thin films under dark and illumination of constant flux density $11 \times 10^3 \text{Ix}$ of white light shown in Fig. 6 revealed distinct double activation processes from 313-358 K (LTR) and 358-403 K (HTR). In this process where lattice scattering was predominant, the
transport mechanism in dc conductivity in the films can be expressed by the relation:

$$\sigma = \sigma_1 \exp(-\Delta E_1/kT) + \sigma_2 \exp(-\Delta E_2/kT) \quad \ldots (3)$$

where $\Delta E_1$ and $\Delta E_2$ are the corresponding activation energies at lower and higher temperatures respectively, $T$ the ambient temperature and $k$ the Boltzmann constant. The as grown CdS thin films deposited at $T_s \geq 373$ K possess good photoconductivity. A constant stable voltage 27 volts was applied across the films during photoconductivity measurements when the ambient temperatures were increased in the range 313 – 403K. The values of the observed activation energies ($\Delta E$) and the mobility activation energies ($\Delta E_\mu$) were determined from the slopes of the plots. The mobility activation energies, $\Delta E_\mu$ in low and high temperature regions of the films at 423 K were found to be 0.07 and 0.14 eV respectively, which were observed to decrease to 0.02 and 0.06 eV respectively for films at 473 K. It is observed from the curves that the conductivity increases with increasing $T_s$ and ambient temperature. The values of the observed $\Delta E$ and $\Delta E_\mu$ in dark and under illumination shifted to lower values with increasing $T_s$ (Table 2).

![Fig. 6 — $\ln\sigma$ versus $10^3/T$ of two representative films of the same thickness 0.25µm grown at 423 K ($T_s$) and 473 K ($T_s$) illuminated with 11,000 lx, bias = 27V](image)

This can be explained in terms of the grain boundary potential barriers in polycrystalline thin films. In the dark, there are barriers interposed between different crystallites of the film, which play dominant role enhancing the resistivity beyond that of the bulk material. A portion of the photogene rated carriers (appropriate charge type) neutralizes some localized charges in the depletion region in the intergrain boundary. This process results in a reduction of the grain boundary potential barrier height, $V_b$, which in turn, enhances the overall photoconductivity in the films. Similar results were also obtained in CdTe thin films by Kalita15. Various kinds of native and foreign lattice imperfections are also present in the intergrain boundaries which result in the formation of defect energy states within the band gap. These energy states can, therefore, act as effective trapping centers. Under a suitable excitation, the carriers generated were trapped and energy states became charged. Such processes cause the formation of potential barriers across the grain boundaries17. The average grain boundary potential barrier height, $V_b$ under illumination can be expressed as18:

$$V_b = q (\Delta m - \Delta n)/8\varepsilon\varepsilon_0 n \quad \ldots (4)$$

<table>
<thead>
<tr>
<th>Films $,(t = 0.25 \mu m)$</th>
<th>Substrate temperature (K)</th>
<th>Temperature range (K) in dark</th>
<th>Temperature range (K) under light</th>
<th>Activation energies $\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>(313-358)</td>
<td>0.32</td>
<td>0.32</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>(358-403)</td>
<td>0.56</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>423</td>
<td>(313-358)</td>
<td>0.23</td>
<td>0.23</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>(358-403)</td>
<td>0.49</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>(313-358)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>(358-403)</td>
<td>0.25</td>
<td>0.19</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 7 — Resistivity versus substrate temperature plots of the CdS films illuminated with 11000 lx of white light under dark and illumination

where the photogene rated carrier density \( n \) is greater than the trapped majority carrier density \( \Delta m \) (\( \Delta n \) is the density of trapped minority carriers, \( \epsilon, \epsilon_0 \) are the dielectric constants of the films and free space respectively, \( q \) the carrier charge), the height of potential barrier \( V_b \) gets reduced, thereby enhancing the photoconductivity, particularly in high temperature regions\(^19,20\). It is also observed from the experimental data that the values of \( \Delta E \) and \( \Delta E_n \) in the high and low temperature regions in the films grown at 473 K (\( T_s \)) are comparatively lower than their corresponding values at 423 K (\( T_s \)) and other lower temperatures. This indicates the presence of various trap distributions at different trap depths. Figure 7 represents the variations of dark and photo-resistivity (\( \rho \)) vs substrate temperatures (\( T_s \)) of the films. It is observed that CdS thin films grown at room temperature possess high resistive values (~10\(^6\) \( \Omega \)\(^{-m} \)), and the resistivity decreases exponentially with increasing \( T_s \), thereby enhancing photoconductivity of the films. These experimental observations, therefore, suggest that the thermally evaporated CdS thin films grown at \( T_s \), 473 K are highly photosensitive.

4 Conclusions

Thermal evaporation is one of the best methods for CdS thin film deposition. The deposited CdS thin films are found to be highly resistive, which decreases with increasing \( T_s \). The substrate temperature, intensity of illumination and bias influenced the enhancement of photocurrent in the films. The crystallite sizes grown in the films have attributed to increase photosensitivity and other phototransport mechanism in the films. The conductivity of the films was observed with two types of activation processes in the temperature range 300-403 K, which reveals the presence of various discrete traps at different trap depths.

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