CHAPTER - III

OPTICAL AND OPTOELECTRONIC PROPERTIES
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3.1 INTRODUCTION

Thin films of CdS find extensive applications as window layer in various heterojunction solar cells due to good optical transmittance in the visible region above 520 nm. On the other hand high optical absorbance below 520 nm wave length makes it suitable as visible radiation sensor. Good transmittance and low resistivity film is the basic requirement in the large band gap window material. On the other hand high dark resistivity and high optical absorption is the other basic requirement for preparing highly photosensitive films. To fulfil the requirement of having both high optical transmittance and high optical absorbance within the visible spectrum of radiation, CdS is the only material of suitable band gap (2.42 eV). The band gap of a thin film again depends mainly on film composition, structure and stoichiometry. By optimizing the growth conditions and bath parameters, films of required band gap can be tailored. The band gap of semiconducting thin film can be determined either by temperature dependence of conductivity or optical method. From temperature dependence of conductivity, only the value of band gap \((E_{g})\) can be obtained. The direct \((E_{gd})\) or indirect \((E_{gi})\) nature of band gap cannot be obtained. Optical absorption and transmittance method can provide both the value of band gap as well as the
direct or indirect nature of the band gap. Hence, to obtain the value of band gap of the deposited films as well as direct or indirect nature of band gap we applied spectrophotometric method to determine both. Further by observing the optical transmittance of various films deposited under different growth conditions, optimization of growth conditions was also made possible. The most suitable condition of CdS film growth to obtain intrinsic value of band gap was determined from such optical observations. In this chapter details of spectrophotometric observations along with some photoconductivity measurements are discussed.

3.2 EXPERIMENTAL

The optical absorbance and transmittance of CdS films were recorded at room temperature using two different double beam automated spectrophotometers (HITACHI – U 3210 and PERKIN - ELMER Lamda 40 UV / VIS) available at the Chemistry Department of Gauhati University. The spectrophotometers were maintained in a moisture controlled dust free air cooled room. The substrate contribution to the absorption was corrected by introducing a blank and cleaned glass substrate in the reference beam of the double beam spectrophotometer. The absorption coefficient ($\alpha$) of all the investigated samples was deduced from transmittance ($T\%$) and absorbance ($A$) and thickness ($t$). The thickness of the samples was measured by Gravimetry method (1-3) as
discussed in Chapter-II. The maximum experimental error in thickness measurement was ± 3%.

The electrical conductivity was measured with coplanar high purity silver electrodes as ohmic contact to these films. The electrodes were separated by a gap of 1 mm, 2 mm and 5 mm, printed on the film surface by conductive silver paint (conductive Pen, Micro tip, CW 2200MTP, UK). To avoid the effect of silver diffusion into the films, silver paint was applied on the film surface after annealing and before conductivity measurements. A Systronic Auto LCR-Q-TESTER (Systronic-928) bridge was used for conductivity measurements. Films were illuminated with different simulated solar radiation to observe the photoconductivity of the film.

3.3 THEORITICAL CONSIDERATIONS ON OPTICAL AND OPTO-ELECTRONIC MEASUREMENTS

3.3.1 Optical Absorption and Band gap Determination

The interactions among the atomic energy levels in a crystal lattice yield a series of allowed energy bands. The highest energy band occupied by electrons is called a valence band (VB) and the lowest unoccupied band is called conduction band (CB). The energy gap between these two bands is called band gap energy \( (E_g) \). For insulators \( E_g \) is very large (larger than about 3 eV) whereas for semiconductors it acquires an intermediate value. As mentioned earlier
II-VI semiconductors have wide variation in band gap value, as low as \( \sim 10^{-2} \text{ eV} \) (for Hg Te) and as high as \( E_g \geq 3 \text{ eV} \) (for ZnO and ZnS). For metals, the highest energy band with significant electronic occupancy is partially filled. Electrons can be excited from VB to CB by the absorption of incident radiant energy (hv) only if \( hv \geq E_g \). The absorption of light occurs when the energy of a quantum (hv) equals \( E_g \),

\[
E_g = hv = \frac{hc}{\lambda_g} = (1240/\lambda_g) \text{ eV}
\]

where \( \lambda \) (wavelength) is expressed in nm.

In the experimental observation by spectrophotometer, threshold wavelength \( \lambda_g \) is determined at the point where there is an abrupt change in the absorbance (A) versus wavelength (\( \lambda \)) curve or transmittance (T\%) versus wavelength (\( \lambda \)) curve of the thin film. Semiconductor absorb light below threshold wavelength \( \lambda_g \) and transmit light above \( \lambda_g \). For CdS \( \lambda_g = 512 \text{ nm} \), which give \( E_g = 2.42 \text{ eV} \) as generally accepted value at room temperature (\( \sim 300 \text{ K} \)) for pure bulk sample (4, 5). Within the semiconductor, the extinction of light follows the exponential law.

\[
I = I_o \exp (-\alpha \cdot t)
\]

where \( t \) is the penetration distance of light or thickness of the film, \( \alpha \) is the absorption coefficient, \( I_o \) is the incident light intensity and \( I \) is the transmitted
light intensity. Evidently equation (3.02) is the Bouguer-Lambert law with the absorption coefficient related to the concentration of absorption centres \( (N) \) and to the effective absorption cross section for one photon per unit time \( (\sigma) \).

\[
\alpha = \sigma N \quad 3.03
\]

The quantity \((\sigma N)^{-1}\) or \(\alpha^{-1}\) may be termed mean free path \(t_{ph}\) of a photon in an absorbing medium:

\[
t_{ph} = (N)^{-1} = \alpha^{-1} \quad 3.04
\]

The quantity \(\alpha\), the absorption coefficient is the probability of a photon absorption over a unit path.

The absorption coefficient \(\alpha \) (cm\(^{-1}\)) can be calculated from the absorbance \((A)\) or transmittance \((T)\) and the film thickness \((t)\) using the relation (6).

\[
\alpha = 2.3026 \left( \frac{A}{t} \right) \quad 3.05
\]

Since the transmittance \(T\) is expressed in percent and is defined as:

\[
T = 100 \left( \frac{1}{I_0} \right)
\]
The transmittance $T(\%)$ of films with various thickness could approximately be expressed by the following equation for each wavelength near the absorption edge:

$$T = 100 \exp (-\alpha t)$$ \hspace{1cm} 3.06

The interband transitions are characterized by some variations of the non-linear absorption coefficient ($\alpha$) when plotted with photon energy ($hv$). The interband absorption theory shows that near the optical absorption band edges the coefficient ($\alpha$) satisfies the relation.

$$\alpha hv = \text{constant} (hv - E_g)^n$$ \hspace{1cm} 3.07

Where $E_g$ is the energy gap. For direct transition $n = \frac{1}{2}$ and in this case $E_g$ or $E_{gd}$ is the energy of the optical direct gap. For the indirect allowed transition $n = 2$ and where $E_g$ or $E_{gi}$ now will be the energy of indirect gap. The exponential curve linearity for direct transition is

$$\alpha hv = (\text{constant})d^\frac{1}{2} (hv - E_{gd})$$ \hspace{1cm} 3.08

and for indirect transition

$$\alpha hv = (\text{constant})d^\frac{1}{2} (hv - E_{gi})$$ \hspace{1cm} 3.09

The absorption data obtained from the spectrophotometer can be fitted to equations (3.08) or (3.09). The best fit will give the nature of the band gap in the
film material. The direct transition is conditional upon the probability of two particles meeting an electron and a photon. An indirect transition involves the meeting of three particles: an electron, a photon, and a phonon. This means that the indirect transition is a less probable process than the direct. Therefore, the light absorption coefficient ($\alpha$) should be greater for the direct transitions than for the indirect ones.

### 3.3.2 Photoconduction and Absorption of Light

Photoconduction is one of nonequilibrium process that occurs in semiconductors. It consists in the appearance of a change in the conductivity of a semiconductor under the effect of some radiation (ultraviolet, visible or infrared). As a rule, when a semiconductor is irradiated its conductivity ($\sigma$) increases owing to an increase in the free carrier concentration $n$ (the mobility $\mu$ of nonequilibrium carriers is practically the same as the mobility of equilibrium carriers). The change of conductivity or photoconductivity is given by (7).

$$\Delta \sigma = \sigma_{ph} = \sigma_L - \sigma_D = q (\Delta n \mu_n + \Delta p \mu_p)$$  \hspace{1cm} 3.10

Where $\sigma_L$ is the conductivity under illumination, $\sigma_D$ is the dark conductivity, $\Delta n$ and $\Delta p$ are the change of electron and hole concentration due to intrinsic absorption of light photon, $\mu_n$ and $\mu_p$ are the mobilities of electron and hole respectively.
For an extrinsic or doped semiconductor either positive or negative nonequilibrium charge carriers prevail in the semiconductor. If the change of conductivity is considered due to ionization of donor impurities, then $\Delta n \gg \Delta p$ and as a consequence the extrinsic photoconductivity is given by:

$$\sigma_{\text{ph}(ao)} = q (\Delta n \mu_n)$$  \hspace{1cm} (3.11)

Photoconductivity processes in semiconductor thin films is not only explained by change of carrier concentration and mobility, but also by the life time of majority and minority carriers. Photoconductivity is also profoundly influenced by the trapping centres located within the band gap, through their effect on the life time of the carriers in various ways. General review in these lines may be obtained from standard monograph (7).

3.4 RESULTS AND DISCUSSION

3.4.1 Optical transmittance and Absorbance

The CdS films prepared under the optimum growth conditions showed good optical transmittance and sharp increase beyond its band edge wavelength 520 nm. Figure 3.01 shows the optical transmittance of a CdS film grown by TEA complex method without etching and annealing. The film was grown at room temperature bath (30°C) and at optimum value of pH = 11.5. Optical transmittance of nearly 70% above the band edge wavelength is observed. An
ideal non-scattering CdS film should have optical transmittance of about 80% for wavelengths above the band edge (8). The remaining 20% corresponds to reflectance and optical absorbance by other impurity atoms present on the film surface. As the film is unetched and without annealing, further 10% transmission loss occur due to poor crystalline nature and also colloidal particles present on the film surface scatter light. As the film was grown in the chemical bath with CdI₂ : TEA : TU : NH₃ mole ratio 1:3.5:1:14.4 which was found to be optimum for better growth of the film with less number of colloidal particles covering the film, only small loss of transmission in the film is expected due to particulate present on film surface. Similarly for a CdS film grown by tetraamine complex method, the optical transmittance is shown in Fig. 3.02. This film is also grown under optimum growth conditions and before etching and annealing. Same nature of transmittance is also observed for this type of film.

As mentioned in Chapter II chemical bath deposited CdS films contain some colloidal particles and some organometallic impurities and so etching of the film with dilute acetic acid is necessary for its removal. Further annealing of the films after deposition is also necessary step for improvement of crystalline nature of the film (Chapter IV). Figure 3.03 shows the optical transmittance of a CdS film prepared by TEA complex method under optimized conditions at two different time values and also after etching and annealing in air at 200°C for 2 hours. It is also seen from the optical transmittance curves that film deposited by
TEA complex method for longer interval of time (48 hr) does not produce any significant difference in the optical transmittance curve. This is probably due to attaining of a terminal thickness (0.9 μm) after some interval of time as reported by Mondal et al. (11). They have shown that CdS films prepared by TEA complex method at the initial stage of growth, the thickness increases at a fast rate. Thereafter the rate of growth decreases resulting in a terminal thickness. Therefore it can be said that both the films (curve b and curve c) are of similar nature and of nearly same thickness value. Figure 3.04 shows superimposed curve of CdS film before and after etching. As mentioned in Chapter II, chemical bath deposited CdS film contains some colloidal particles and some organometallic impurities and so etching of the film with dilute acetic acid is necessary for their removal from CdS film. Further annealing of the films after deposition is also necessary state for improvement of crystalline nature of the film (Chapter IV).

The bath composition also plays a major role on CdS film growth. In Chapter II, we discussed the effect of bath composition on film growth. The optimum value of molar concentration ratio of CdI₂ : TEA : TU : NH₃ was 1 : 3.5 : 1 : 14.4. In TEA complex method with increasing CdI₂ : TEA molar ratio (CdI₂ : TU : NH₃ remaining constant), thickness of the film decreases from 0.9 μm to 0.1 μm as shown in Table 2.2. The smaller thickness results due to high degree of complexing (TEA with Cd²⁺ ions) in the chemical bath.
Figure 3.05 shows the optical transmittance of three different films prepared with CdI$_2$ : TEA molar ratio at (a) 1 : 3.5, (b) 1 : 7.0 and (c) 1 : 10.5 respectively. The percentage of optical transmittance is lower for curve (a), because of higher thickness of the film. It is again seen that there is sharp increase in film transmittance near the band edge wavelength suggesting better quality film growth. With increasing CdI$_2$ : TEA concentrations the band edge shifts towards the shorter wavelength side. Higher percentage of transmission in curve (c) is due to very smaller thickness (0.1$\mu$m) of the deposited film. All the curves show the measurements of optical transmittance after etching and annealing of the films.

Similarly the effects of varying CdI$_2$ : TU concentration on film transmittance for three different films have been shown in Fig. 3.06. All these films were without etching to show the effect of colloidal particles adhering on the film surface. As the TU concentration in the bath increases the film surface become more particulate. High TU concentration in the chemical bath makes available more free S$^{2-}$ ions in the bath, which favour the formation of more colloidal particles of CdS in the bath and hence the film becomes more particulate in nature (8). Increasing colloidal particle on the film surface scatter more light as the surface become rough. Therefore, the optical transmittance in Fig. 3.06 is seen to decrease with increasing TU concentration.
**Fig. 3.01:** The optical transmittance of a chemically deposited CdS film under optimum growth condition (by TEA complex method) without etching and annealing.

**Fig. 3.02:** The optical transmittance of a chemically deposited CdS film under optimum growth condition (by tetraamine complex method) before etching and annealing.
Fig. 3.03: The optical transmittance of CdS film prepared by TEA complex method at 30°C and at different time values for:

a. 24 hours without annealing,
b. 24 hours, annealed at 200°C for 2 hours and after etching,
c. 48 hours, annealed at 200°C for 2 hours and after etching.
Fig. 3.04: Superimposed optical transmittance curve of CdS film prepared by TEA complex method, 
a, b, c – before etching, a', b', c' – after etching.

(a') 510.0 nm  45.67% T
(b') 502.0 nm  74.29% T
(c') 494.0 nm  71.98% T

(a) 482.0 nm  11.79% T
(b) 482.2 nm  17.80% T
(c) 491.2 nm  10.91% T
Fig. 3.05: The effect of increasing CdI₂:TEA molar ratio on film transmittance
(a) CdI₂:TEA :: 1:3.5,
(b) CdI₂:TEA :: 1:7.0,
(c) CdI₂:TEA :: 1:10.5

Fig. 3.06: The effect of increasing CdI₂:TU molar ratio in the chemical bath on optical transmittance of CdS films
(a) CdI₂ : TU :: 1 : 1, (b) CdI₂ : TU :: 1 : 2,
(c) CdI₂ : TU :: 1 : 3
Fig. 3.07: The effect of increasing Cd I₂ : NH₃ concentration on film transmittance curve
(a) CdI₂ : NH₃ :: 1 : 14.4, (b) CdI₂ : NH₃ :: 1 : 28.8

Fig. 3.08: The optical transmittance of a chemically deposited CdS film at different pH values (by TEA complex method)
(a) pH 8.0, (b) pH 9.0, (c) pH 10.0, (d) pH 11.5
Fig. 3.09: Absorption spectra of double deposited CdS film (a) after etching, (b) after etching and annealing.

Fig. 3.10: Absorption spectra of (a) Double deposited CdS film by tetraamine complex method, (b) Silver doped CdS film, before etching.
Fig. 3.11: Absorption spectra of CdS thin film
(a) Single deposition (after etching and annealing),
(b) Double deposition (after etching and annealing)
Figure 3.07 shows the effect of increasing CdI$_2$ : NH$_3$ mole ratio keeping the CdI$_2$ : TEA : TU mole ratio constant at $1 : 3.5 : 14.4$. It is clearly seen from the graph that increasing ammonia concentration decreases the optical transmittance to a large extent. At very high concentration of NH$_3$ the complex formation may be so completed that the availability of Cd$^{+2}$ ion for film formation is much less (Chapter II). With increasing ammonia, the abundance of the overgrowth on the film surface also increases thereby decreasing the optical transmittance of the film. The optical transmittance of different films prepared at different value of pH of the solution at room temperature (~ 30°C) bath by TEA complex method is shown in Fig. 3.08. The nature of the curves are seen to be similar with absorption edge near about 500 nm and corresponds to band edge wavelength 510 nm for CdS film. It is also seen from the curves that maximum transmission near 90% is seen for film grown at optimum value of pH = 11.5.

Figure 3.09 shows the absorption spectra of a double deposited CdS film grown under optimum growth conditions. Curve (a) represents the film after etching and curve (b) represents the absorption spectra of the same film after annealing in air oven at 200°C for 2 hours. It is clearly seen that annealed film has got higher absorbance. Figure 3.10 shows the absorption spectra of silver doped CdS film (curve a) and undoped CdS film (curve b). The decrease of absorbance at shorter wavelength for the silver doped CdS film may be due to increase of Ag$^+$ ion concentration in solution. It is also clearly seen from the
Fig. 3.11 that double deposited CdS thin films acquire better crystalline nature with sharp rise in optical absorption in lower wavelength side.

3.4.2 Band gap estimation of CdS film

The band gap of the deposited CdS thin films were determined from the optical transmission and absorbance data using the equation 3.07.

\[ \alpha h\nu = C_d (h\nu - E_{gd})^{1/2} \]

where \( C_d = \text{Constant} \)

Finally from equation (3.08) plotting \((\alpha h\nu)^2\) versus photon energy \(h\nu\) for various CdS films grown under different conditions of deposition direct band gap of each film was obtained by extrapolation of the curves to \(\alpha^2 = 0\). The \(\alpha^2\) value was calculated within the wave length range 365 nm to 800 nm at an interval of 15 nm. The best fit curves of \(\alpha^2\) versus \(h\nu\) for various films grown under different conditions are shown in Figs. 3.12 – 3.18. All the films were found to have average thickness value of \(\sim 0.9 \mu m\). Calculated values of band gaps for various films are shown in Table 3.1. It is seen from the table that single deposited films prepared by both TEA complex and tetraamine complex method without etching and annealing have higher values of band gap. Figure 3.12 shows the \(\alpha^2\) versus \(h\nu\) plot for a CdS film prepared by TEA complex method prepared at room temperature (31°C) bath. The film is single deposited layer
without etching and annealing. To observe the effect of etching on band gap determination, we plotted \( \alpha^2 \) versus \( h\nu \) for CdS films after etching and without annealing. Figure 3.13 shows the \( \alpha^2 \) versus \( h\nu \) plot for a representative etched CdS film prepared by TEA complex method. The film was single deposited layer and prepared at room temperature substrate. The band gap value for this type of film was also found to be higher (2.79 eV) than the expected value 2.42 eV. The higher value of band gap obtained in our films are therefore expected to be due to amorphous or microcrystalline nature of the film as discussed in Chapter IV. Finally we plotted \( \alpha^2 \) versus \( h\nu \) plot for CdS films which are found to be suitable after structural analysis having good crystalline nature and lattice parameter agreeing with bulk CdS. Figure 3.14 represents a \( \alpha^2 \) versus \( h\nu \) plot for a CdS film prepared by TEA complex method under optimum growth conditions and after etching and annealing. The film is also a double deposited layer under similar growth conditions on the previously grown film. The value of band gap for this film was found to be 2.48 eV and agrees well with that of standard value for CdS which is 2.42 eV (12, 13). Similar value of band gap in cubic (zinc blende) type of CdS films grown by chemical bath deposition (CBD) technique have been reported by Nakanishi et al. (14). They have however, reported a higher value of band gap (2.62 eV) for hexagonal (Wurtizite) structure. Our films are also found to be mainly cubic (zinc blende) type as discussed in Chapter IV.
<table>
<thead>
<tr>
<th>Complexing Method</th>
<th>Temperature of bath (°C)</th>
<th>Film thickness (Å)</th>
<th>Band gap (eV)</th>
<th>Post growth treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA</td>
<td>11.5</td>
<td>8935</td>
<td>2.80</td>
<td>Single deposition</td>
</tr>
<tr>
<td>Tetraamine</td>
<td>11.5</td>
<td>8825</td>
<td>2.79</td>
<td>Single deposition</td>
</tr>
<tr>
<td>Tetraamine</td>
<td>11.5</td>
<td>8735</td>
<td>2.45</td>
<td>Single deposition</td>
</tr>
<tr>
<td>Tetraamine</td>
<td>11.5</td>
<td>9895</td>
<td>2.35</td>
<td>Double deposition</td>
</tr>
<tr>
<td>Tetraamine</td>
<td>11.5</td>
<td>9921</td>
<td>2.45</td>
<td>Double deposition</td>
</tr>
<tr>
<td>Tetraamine</td>
<td>11.5</td>
<td>9978</td>
<td>2.45</td>
<td>Silver doped</td>
</tr>
<tr>
<td>Tetraamine</td>
<td>10.5</td>
<td>9625</td>
<td>2.35</td>
<td>Silver doped</td>
</tr>
</tbody>
</table>
Fig. 3.12: The $\alpha^2$ versus $h\nu$ plot showing the band gap energy of CdS film prepared by TEA complex method at 31°C (single deposition without etching and without annealing) $t = 8935$ Å

Fig. 3.13: The $\alpha^2$ versus $h\nu$ plot showing the band gap energy of CdS film prepared by TEA complex method at 31°C (single deposition and after etching but without annealing) $t = 8825$ Å
Fig. 3.14: The $\alpha^2$ versus $hv$ plot showing the band gap energy of CdS film prepared by TEA complex method at 31°C (double deposition, after etching and annealed at 200°C for 2 hours) $t = 9895 \text{ Å}$

Fig. 3.15: The $\alpha^2$ versus $hv$ plot showing the band gap energy of CdS film prepared by TEA complex method at 60°C (single deposition, after etching and without annealing) $t = 8735 \text{ Å}$
Fig. 3.16: The $\alpha^2$ versus $hv$ plot showing the band gap energy of CdS film prepared by TEA complex method at 60°C in two hours (double deposition, after etching and annealed at 200°C for 2 hours) $t = 9921 \text{ Å}$.

Fig. 3.17: The $\alpha^2$ versus $hv$ plot showing the band gap of silver doped CdS thin film deposited at 60°C (pH 10.5. $t = 9625 \text{ Å}$)
Fig. 3.18: The $\alpha^2$ versus $hv$ plot showing the band gap energy of silver doped CdS thin film prepared by tetraamine complex method (after etching and annealing)

$t = 99785 \text{ Å}$

Fig. 3.19: The $\alpha^2$ versus $hv$ plot showing the superimposed curve of the band gap energy of (a) Silver doped CdS thin film, (b) Undoped CdS thin film prepared by tetraamine complex method (c) Undoped CdS thin film prepared by TEA complex method
Cadmium sulphide thin films prepared by tetraamine complex method also show higher value of band gap for unetched and unannealed single deposited layer. Figure 3.15 shows the $\alpha^2$ versus $hv$ plot for a representative CdS films prepared by tetraamine complex method at 60°C bath temperature. The film is also single deposited layer and the band gap value was found to be 2.8 eV which is higher than the expected value 2.42 eV. Again for films of double deposited layer on the previously coated single layer of CdS film prepared by tetraamine complex and after etching and annealing, the observed value of band gap from $\alpha^2$ versus $hv$ plot is found to be 2.45 eV as shown in Fig. 3.16. For silver doped film also the band gap value for unetched and unannealed layer at pH 10.5 has been found to be 2.85 eV. Figure 3.17 shows $\alpha^2$ versus $hv$ plot for such type of representative silver doped film. Similarly for a silver doped CdS film deposited at pH 11.5 after etching and annealing the value of band gap has been found to be 2.35 eV as shown in Fig. 3.18. From the results discussed above it can be concluded that a double deposited CdS film on a previously coated film can have suitable value of band gap value near the bulk value 2.42 eV of cubic structure. Etching and annealing process is also necessary to obtain the desirable value of band gap. The result is applicable for films grown by both TEA complex and tetraamine complex method under optimized growth conditions. Figure 3.19 shows the superimposed $\alpha^2$ versus $hv$ plot for three different films which are (a) silver doped, (b) undoped prepared by
tetraamine complex method and (c) undoped prepared by TEA complex method respectively. All the curves are of double deposited CdS films after etching and annealing process and give band gap value near 2.42 eV. The close agreement of band gap value to the bulk value of CdS suggests that the films prepared under above conditions are stoichiometric (15). The stoichiometric nature of the films are supported by the close agreement of their cubic lattice parameter (a) with the accepted lattice parameter value determined from XRD observations (Chapter IV).

3.4.3 Some conductivity and Photoconductivity observations

The conductivity under dark and photoconductivity under simulated solar radiation was observed for few films with limited experimental facilities. For conductivity measurements Systronic Auto LCR Bridge (928) was used. The electrodes were painted on the etched surface of CdS film prior to each observations by the conducting pen mentioned earlier. It has been found difficult to prepare the silver electrode by the conducting pen as the paint dried very quickly coming in contact with air. Several films were destroyed in our attempt. The films were kept within an evacuated glass jacket. Freshly prepared films are found to be photosensitive even under room light. But films kept for few days after preparation within the desciccator are found to be weekly photosensitive or photoinsensitive. Some of the observations of dark conductivity and conductivity under illumination of solar light are shown in Table 3.2.
Table 3.2
Dark and photoconductivity observations of CdS films

<table>
<thead>
<tr>
<th>Type of film</th>
<th>Complexing method</th>
<th>Dark resistance $R_D$ (ohms)</th>
<th>Resistance under solar illumination $R_L$ (ohms)</th>
<th>$R_D / R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double deposition</td>
<td>TEA 0.1M</td>
<td>$4 \times 10^3$</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Double deposition</td>
<td>Tetraamine 85 K</td>
<td>$5.1 \times 10^3$</td>
<td></td>
<td>16.6</td>
</tr>
<tr>
<td>Single deposition</td>
<td>TEA 12.5 K</td>
<td>8.2 K</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>Single deposition</td>
<td>Tetraamine 14.6 K</td>
<td>5.1 K</td>
<td></td>
<td>2.86</td>
</tr>
</tbody>
</table>

The observations made only in presence of sunlight within the room the ratio of dark resistance ($R_D$) and light resistance ($R_L$) is not vary large. Under strong illumination of direct light quite appreciable change can be observed. Further illuminating the film with a red laser diode (1 mW) it was noticed that there was no appreciable change of dark conductivity. This is because the wavelength of red laser is 6328 Å which is above the band edge wavelength of light absorption (5200 Å). Detail analysis of photosensitivity observations could not be carried out due to our limitations in measuring instruments, making of ohmic contact to the film and further works on preparing CdS thin films as photosensor applications with fast response can be taken as further work of research.
3.5 CONCLUSIONS

Optical transmission and absorption studies performed on chemically deposited CdS films show that under different conditions of deposition film optical transmission vary between 70% to 90%. Post deposition treatment of etching and annealing is necessary to increase the optical transmission of CdS films. Films prepared under optimized growth conditions show sharp increase in transmission spectra after the band edge wavelength 500 nm. Sharp increase in absorption spectra below 500 nm is also observed. It is also seen that optical transmittance of chemically deposited CdS films depend on the concentrations of TEA, ammonia (aq) and TU along with pH value of the solution.

CBD grown CdS thin films are found to have a direct band gap near the bulk band gap value of 2.42 eV. Only the double deposited CdS films with post deposition treatment of etching and annealing have suitable value of band gap corresponding to bulk value. Single deposited unetched films without annealing treatment show somewhat higher value near 2.8 eV. This higher value of band gap is expected due to amorphous or microcrystalline nature of the film or variation of stoichiometry. The optical band gap calculated from $\alpha^2 \text{ versus } \hbar \nu$ plot of silver doped CdS film clearly shows the decrease in band gap of CdS film from 2.45 eV to 2.38 eV. However, it can be said from the Fig. 3.18 that silver doped film also have band gap value near the bulk value for etched and annealed double deposited layer.
From various experimental observations it can be concluded that to prepare good quality stoichiometric films with high optical transmission a double deposited layer with post deposition annealing combined with etching in dilute acetic acid is necessary. Films prepared under suitable optimum conditions are also found to be photosensitive under solar illumination.
REFERENCES


3. A. Goswami, "Thin Film Fundamentals", New Age Int (P) Ltd., New Delhi, p 35.


