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Comparative Study of Cadmium Sulfide Thin Films at Room and Low Temperatures Fabricated by Closed Space Sublimation Technique

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Abstract: Cadmium sulfide (CdS)thin films wereprepared under vacuum onto glass slides by closedspace sublimation technique. X-ray diffraction was used to identify and confirm the orientation andhexagonal wurtzitecrystalline structureof CdS thin films. Optical analysis from UV-VIS-NIR ranges was used to calculate the thickness of thefilmsby taking transmission spectrum using spectrophotometer. After annealing, these thin film samples were electrically characterized using Hall measurements at room and liquid nitrogen temperature (77K), by applying currents of 1 nA, 10 nA and 50 nA. Resistivity, mobility and carrier concentrations werecalculated and effects of temperature, current and film thickness were studied. Resistivity in the range of $10^3 - 10^5$ (Ω.cm) (room temperature) and $10^3 - 10^{15}$ (Ω.cm) (liquid nitrogen temperature) has been demonstrated. Similarly, high carrier concentrationvalues in the range of 10^{13} - 10^{16} (cm^{-3}) have been demonstrated. With the increase in thickness and current, CdS thin film samples demonstrated a decrease in resistivity and a consequent increase in mobility.Correspondingly, a decrease in resistivity wasfound at room temperature (compared to low temperature), implying that CdSacts as insulator at low temperature.Overalla semiconductor behavior was exhibited and results confirmed these CdS thin film samples to beexceptionalfor use as window layer inCdTe/CdShetero-junction solar cells fabrication.

Key words: Carrier concentration · CdS thin films · Closed space sublimation · Low temperature · Mobility resistivity

INTRODUCTION

Cadmium sulfide (CdS) is a semiconductor with direct bandgap; 2.42 eV at 300 K. It exists in the form of cubic and hexagonal polymorphs. Hexagonal is a yellowish crystal and can be classified as the only real ore of cadmium.Thin films of CdS are of considerable interest for their efficient use as window material in the fabrication of solar cells and other optoelectronic devices [1-6]. Concerning solar cell applications, the film sheet resistance in particular should be relatively low in case of low series resistance and high fill factor of resultant effective solar cells [7]. Thereupon, the control of resistivity in case of cadmium sulfide thin films is very crucial [8]. Electrical resistivity and carrier concentration can be classified astwo major aspects concerned directly with the suitability of CdS thin films as window material in CdS/CdTe hetero-junction solar cells.Physical properties of CdS thin films have been reported by several workers previously. However, the effects of temperature, current and thickness variance on electrical resistivity, mobility and carrier concentrations remain to be distinctly elaborated.

Some of the highlighted techniques that can be used to deposit CdS thin films include chemical bath deposition, thermal evaporation, electro-chemical deposition, spray pyrolysis, laser ablation, electron beam evaporation and closed space sublimation (CSS) technique etc. [9-20]. CSS technique is used as a common method for the preparation of thin films of different

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materials and produces optimal results for solar cells. In principle, it allows the film to grow at a fairly high substrate temperature (500-600°C) under vacuum [21]. The high efficiency thin film solar cells are produced with cadmium sulfide being the n-partner [22].

This paper deals with electrical characterization (using Hall Effect Measurement system, at low and room temperature) of four CdSthin filmsamples deposited using CSS technique. A steady and uniform trend of resistivity and mobility and high carrier concentration values in the range of 10^{13} – 10^{16}(cm^{-3}) have been demonstrated, at both room and low temperature(77K), which are truly beneficial for CdS thin films to be used insolar cellsfabrication.

MATRIALS AND METHODS

CDs powder (99.99% pure)by Aldrich was used for thin films preparationby closed space sublimation technique onto corning glass substrates. A graphite boat holding cadmium sulfide was heated by a 1000W halogen lamp, connected to the main power with K-type thermocouple through temperature controller. The substrate was kept ~ 5 mm from the source material and was heated by a 500W halogen lamp. Temperature was controlled by keeping the thermocouple over the substrate. Substrate and source temperatures were 400°C and 550°C respectively. Chamber evacuation (~ 10^{-5} mbar) was carried out with the help of rotary anddiffusion pump. The deposition time was varied ranging from 1 - 5 minutes at a source temperature of 550°C, after the substrate and source lamps were switched off allowingthe temperature to cool down to 100°C before the chamber could be opened. Thin films were annealed at a constant temperature of 400°C for 30 minutes (under vacuum). Above mentioned equipment and technique were used to prepare CdS thin film samples 1-4.

Film structure was analyzed by PANalytical spectrometer model X'PERT PRO with Cu Kα line (λ= 1.54 Å) radiation. Transmission spectra amid 250-2000 nm recorded by Perkin Elmer LAMDA 950 spectrophotometer was used to calculate film thickness [23].

The electrical measurements at room and low temperature (77K) were taken with the help of Van der Pouw technique by means of Ecopia HMS 3000 Hall Measurement System. Characterization setup comprised of a magnetic box (magnetic flux density input system) having a magnet of 0.37T and a PCB holder, having gold

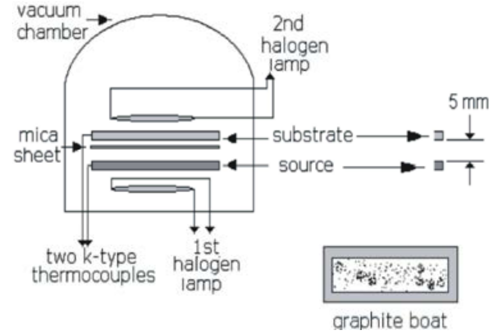

Fig. 1: CSS arrangement used for CdS thin films preparation

contact pins. The sample of CdSthin film was connected to the gold pins in such a way that the pins were placed on the four corners of the sample. This is also known as the four probe method. Figure 1 depicts the CSS arrangement used forthe preparation ofCdSthin film samples.

RESULTS AND DISCUSSION

Structural Analysis: The structural analysis of cadmium sulfide thin filmswas performed by X-ray diffraction (XRD) with a wavelength 1.5406 Å. XRD analysis of CdS thin film samplewith thickness 390 nm and bandgap 2.25 eV is shown in Figure2. XRD pattern clearly exhibits polycrystalline behavior of the film having hexagonal wurtzite structure. A strong peak with 2θ value about 26.507° corresponds to the (002) crystalline plane of CdScan be observed. A weak peak at θ = 47.84° corresponding to (103) plane is also observed in the XRD pattern.These peaks in this XRD could be indexed to hexagonal structure of CdS and the 2è value is consistent with the value in standard card (JCPDS 00-041-1049). Cadmiumsulfide thin film sample had hexagonal structure with effective parameters a = b = 4.1409A°, c = 6.7198A°. The films obtained were pinhole free, adherent, uniform and smooth.

Optical Analysis: Thickness measurements of CdSthin filmsamples wereperformed by taking transmission spectrum using spectrophotometer. Optical spectra of CdS thin film sample exhibited high transmission from 60% to 80% in infrared and visible region, with a steep edge at about 500 nm wavelength, as shown in Figure3. Thickness of the four CdS thin film samples deposited on glass substrates were found to be 220 nm, 320 nm, 390 nm and

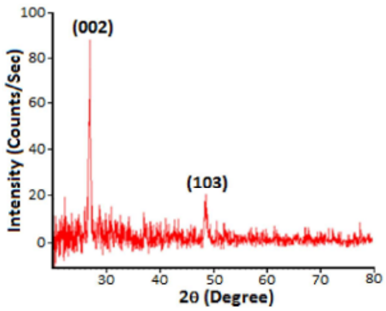

Fig. 2: XRD trace of CdSthin film sample 3.

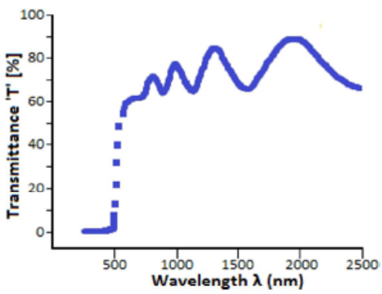

Fig. 3: Transmittancecurve ofCdSthin film sample 3.

850 nm. Refractive index and thickness of thin films can be calculated by the Swanepoel model [24]. The refractive index 'n'is given as:

$$n = \frac{[N + (N^2 - 4s^2)^{\frac{1}{2}}]}{2} \quad (1)$$

where, 's' is refractive index of the substrate, 'N' is number of oscillations, given as:

$$N = 1 + s^2 + 4s(\frac{T_{\max} - T_{\min}}{T_{\max} * T_{\min}}) \quad (2)$$

Thickness of the film can be calculated with the help of following equation:

$$d = \frac{\lambda_{\max}\lambda_{\min}}{4n(\lambda_{\max} - \lambda_{\min})} \quad (3)$$

where,'d' is the thickness, 'λ_{min}' is the minima and 'λ_{max}' is the maximavalue of the wavelength taken from the transmission curve.Bandgap was calculated as 2.25 eV and refractive index values were found to be 2.48, 2.36, 2.25 and 2.14 respectively, which are very close to the ideal value of CdS refractive index (2.529). Table 1 shows the calculated thickness and refractive index of CdSthin film samples.

Electrical Properties at Room and Lowtemperature: Electrical properties of CdSthin films such as resistivity, mobilityand carrier concentrations are reported here. Hall measurementsystem was used in correspondence [25]. Currents of 1 nA, 10 nA and 50 nAwere applied to each sample at room and low temperature (77K) andresistivity, mobility and carrier concentrations were analyzed at each current value. Decrease in resistivity with increase in thickness and applied current was observed, owing to the relationship:

$$\rho = \frac{RxLxW}{T} \quad (4)$$

where, 'ρ' represents the resistivity, 'R' equals the resistance, 'L' equals length of the film, 'W' equals width of the film and 'T' equals the thickness of the CDs thin films. An increase in mobility was also witnessed with the increase in film thickness. In addition, an increasing trend of carrier concentrations was witnessed with the increase of film thickness and current. The overall decrease in resistivity with the increase of film thickness can be attributed to the increasing number of sulfur vacancies existing in the samples.

Average values of resistivity and mobility were calculated for each sample.By taking average resistivity of CdS thin film samples at room temperature (4.31E+04Ω.cm, 7.97E+03Ω.cm, 4.34E+03Ω.cm, 2.28E+03Ω.cm) and low temperature(2.30E+14Ω.cm,1.94E+04Ω.cm,1.14E+04Ω.cm, 2.84E+03Ω.cm), it was clearly observed that, with the increase of film thickness, resistivity decreases. Consequently by taking averagemobility of CdS thin film samples at room temperature (80.37cm^2/V.s, 214.42cm^2/V.s, 359.80cm^2/V.s, 3798.49cm^2/V.s) and low temperature (214.01cm^2/V.s, 639.63cm^2/V.s, 864.00cm^2/V.s, 3068.00cm^2/V.s), an increase in mobility with increasing film thickness was observed. By comparing the average resistivity values of room and low temperature, a lower resistivity trend at room temperaturewas observed, thereby implying that these CdS thin films act as insulator at low temperature and overall follow semiconductor behavior.

Table 2, 3 and 4 show the calculated resistivity, mobility and carrier concentrations with varying current at room temperature. Table 5, 6 and 7 show the calculated resistivity, mobility and carrier concentrations with varying current at low temperature. Plots of average values of resistivity and mobility as a function of film thickness are shown in Figure 3 and 4 for room and low temperature respectively.

Table 1: Calculated thickness and refractive index of CdSthin film samples

Sample no.	Thickness '*d*' (nm)	Refractive Index '*n*'
1	220	2.48
2	320	2.36
3	390	2.25
4	850	2.14

Table 2: Calculated resistivity, mobility and carrier concentrations of CdSthin film samples characterized at 1 nA at room temperature

Sample no.	Thickness (nm)	Current (nA)	Resistivity (Ω.cm)	Mobility (cm^2/V.s)	Carrier Conc. (cm^{-3})
1	220	1	1.21E+05	171.50	3.64E+13
2	320	1	1.86E+04	558.85	3.38E+14
3	390	1	1.18E+04	678.40	7.93E+14
4	850	1	6.00E+03	10960.00	8.94E+14

Table 3: Calculated resistivity, mobility and carrier concentrations of CdSthin film samples characterized at 10 nA at room temperature.

Sample no.	Thickness (nm)	Current (nA)	Resistivity (Ω.cm)	Mobility (cm^2/V.s)	Carrier Conc. (cm^{-3})
1	220	10	0.69E+04	34.80	6.94E+14
2	320	10	0.45E+04	42.20	4.00E+15
3	390	10	0.45E+03	200.50	1.51E+16
4	850	10	1.13E+03	217.73	8.34E+16

Table 4: Calculated resistivity, mobility and carrier concentrations of CdSthin film samples characterized at 50 nA at room temperature.

Sample no.	Thickness (nm)	Current (nA)	Resistivity (Ω.cm)	Mobility (cm^2/V.s)	Carrier Conc. (cm^{-3})
1	220	50	0.15E+04	34.80	6.94E+14
2	320	50	0.82E+03	42.20	4.00E+15
3	390	50	0.78E+03	200.50	1.51E+16
4	850	50	0.72E+03	217.73	8.34E+16

Table 5: Calculated resistivity, mobility and carrier concentrations of CdSthin film samples characterized at 1 nA at low temperature (77K).

Sample no.	Thickness (nm)	Current (nA)	Resistivity (Ω.cm)	Mobility (cm^2/V.s)	Carrier Conc. (cm^{-3})
1	220	1	1.36E+05	316.00	2.03E+13
2	320	1	4.91E+04	940.00	1.75E+14
3	390	1	2.71E+04	1320.00	4.33E+14
4	850	1	4.37E+03	7020.00	1.45E+15

Table 6: Calculated resistivity, mobility and carrier concentrations of CdSthin film samples characterized at 10 nA at low temperature (77K)

Sample no.	Thickness (nm)	Current (nA)	Resistivity (Ω.cm)	Mobility (cm^2/V.s)	Carrier Conc. (cm^{-3})
1	220	10	0.69E+15	315.00	1.37E+15
2	320	10	4.68E+03	939.00	1.60E+15
3	390	10	3.57E+03	1090.00	1.42E+16
4	850	10	2.74E+03	1660.00	4.93E+16

Table 7: Calculated resistivity, mobility and carrier concentrations of CdSthin film samples characterized at 50 nA at low temperature (77K)

Sample no.	Thickness (nm)	Current (nA)	Resistivity (Ω.cm)	Mobility (cm^2/V.s)	Carrier Conc. (cm^{-3})
1	220	50	1.13E+04	11.20	8.43E+15
2	320	50	4.42E+03	39.90	1.73E+16
3	390	50	3.53E+03	182.00	3.28E+16
4	850	50	1.41E+03	524.00	9.35E+16

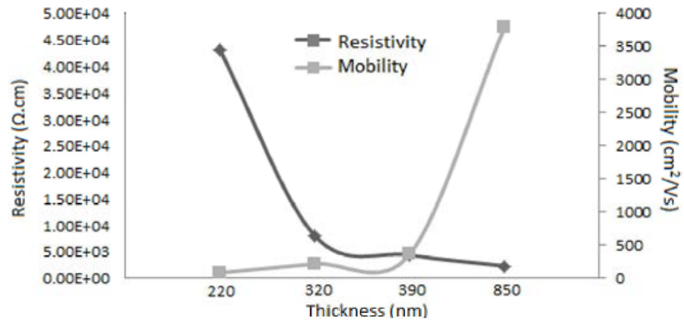

Fig. 3: Thickness vs. Resistivity and Mobility at Room Temperature

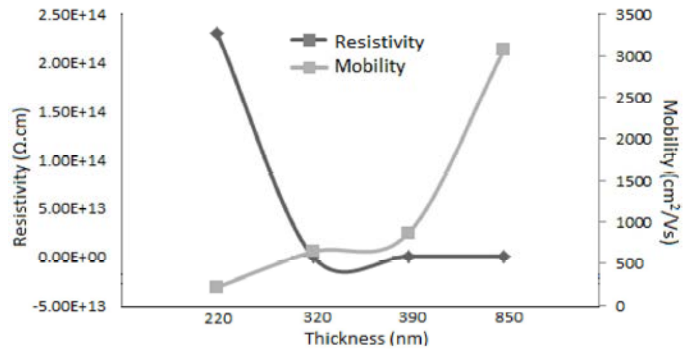

Fig. 4: Thickness vs. Resistivity and Mobility at Low Temperature

CONCLUSIONS

CdSthin films were prepared successfully using closed space sublimation technique. XRD analysis confirmed the polycrystalline hexagonal wurtzite structure of the filmswith preferred orientation of (002) diffraction plane. Optical spectra of CdS thin film sample exhibited high transmission from 60% to 80% in infrared and visible region. Thickness of the samples was obtained as 220 - 850 nm, with a bandgap of 2.25 eV and refractive index values in the range of 2.14 - 2.48. By giving current variations in Hall Effect measurement system, non-linear behavior of CDs is seen at room and low temperature. The resistivity of CdS thin film samples was demonstrated to decrease with increase of film thickness and applied current. Similarly mobility was seen to increase with increase of film thickness and current.It must be noted that high carrier concentration values in the range of $10^{13} - 10^{16}$ (cm^{-3}) have been demonstrated, outlining the fact that high concentration of carriers are available for conduction. CdS thin films showed lower resistivity at room temperature, confirming insulator behavior at low temperature and semiconductor behavior in general. Resistivity, mobility and carrier concentrations results exhibited remarkable electrical properties and signified the suitability of these films as window layersfor CdTe/CdShetero-junctionsolar cells.

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