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Effect of Cd/S molar ratio on the optical and electrical properties of spray deposited CdS thin films

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***ABSTRACT* - Cadmium sulphide thin films were deposited from the solutions containing precursor materials with different Cd/S molar ratios on glass substrates by spray pyrolysis. The grown CdS thin film show hexagonal structures as indicated by powder XRD studies. Surface morphology and elemental composition in the films were obtained from FESEM and EDX measurements, respectively. The optical properties of CdS films were less influenced by Cd/S molar ratio in the solution where as resistivity is found to be sensitive to precursor molar ratio. Transmittance of the films was found to be above 80%. The lowest resistivity of 1.04×10^2 Ω-cm were obtained for the films deposited from solution with Cd/S molar ratio equal to 0.5. The properties of the CdS thin films grown with Cd/S molar ratio equal to 0.5 appears suitable for window layer in heterojunction thin film solar cells.**

***Index Terms* – CdS, Heterojunction structure, spray pyrolysis, stoichiometry**

1. INTRODUCTION

Cadmium sulphide (CdS) belongs to direct bandgap II-VI binary chalcogenide semiconductor. CdS is frequently used as n-type window layer in a variety of heterojunction thin film solar cells such as CdS/CdTe, CdS/$CuInS_2$, CdS/$CuInGaSe_2$ etc. This is because CdS has wide bandgap of 2.42eV, high photoconductivity, high electron affinity, stability and n-type conductivity [1]. The basic requirements of the films for solar cell applications are high optical transparency with optimum bandgap which matches the solar spectrum, low electrical resistivity and better crystallinity for the films deposited at room temperature. However, a higher electrical resistivity of as deposited films (of order of 10^4 – 10^5 ohm-cm) puts a limitation on their application in the solar cells. A large number of research studies are going on in order to reduce the resistivity of as deposited CdS films. Most commonly used method is to dope the CdS films with suitable impurities. Several metals Al, Hg, Cu have been used to dope to CdS. Shadia *et al*. [2] studied on the effect of indium doping on electrical properties of spray deposited CdS thin films and achieved to decrease in resistivity of CdS thin films to an order of 10^2ohm-cm. J.C. Orlianges *et al.* [3] have showed the decrease in resistivity of CdS thin films as a function of carbon doping by pulsed laser deposition method. Optoelectronic properties of CdS thin films can also be improved by annealing the as deposited films in presence of $CdCl_2$ [4, 5].

Various methods such as vacuum evaporation, sputtering, electrodeposition, chemical bath deposition, spray pyrolysis, close spaced sublimation etc. are used to deposit CdS thin films. In the present study, the CdS thin films with different Cd/S ratio were deposited by spray pyrolysis. Spray pyrolysis is a low cost and simple growth method. It is possible to obtain uniform films with good adherence and having uniform stoichiometry with least expense from this technique. It was found that the electrical resistivity of the CdS thin films vary with the variation in the Cd and S composition in the films [6].

II. EXPERIMENTAL DETAILS

For the growth of CdS thin films, 0.15M of $CdCl_2$ and 0.15M of NH_2CSNH_2 solutions were prepared in DI water. These solutions were mixed in required quantity to obtain the spray solution with different Cd/S molar ratio. The solutions were mixed thoroughly and sprayed on to the glass substrates kept at 400^0C at a spray rate of 10ml/minute. The films were allowed to cool naturally to a room temperature. The structural properties of as deposited films were characterized by X-ray powder diffractometer (Rigaku miniflex 600) using Cu Kα radiation (λ = 1.54178 Å). FESEM images are taken using Hitachi SU6600 to study surface morphology. Chemical composition in the films was analysed from energy dispersive X-ray spectra. Thickness of the films was measured by an Ellipsometer (Holmarc opto mechatronics) using DPSS laser (532 nm) beam. Optical absorption and transmittance spectra of the films were recorded using Schimadzu 1800 UV-VIS spectrophotometer. Resistivity of the films was measured by van der Pauw method using PC controlled Keithley 236 source measure unit. Silver paste was used to make electrical contacts to the films.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD spectra of as deposited CdS thin films, shows different fundamental peaks identified as (100), (002), (101), (102), (110), (103), (112), (004), (202) which indicates that this is a hexagonal wurtzite type crystal structure (JCPDS data 00-041-1049). The (101) peak intensity dominates for CdS thin films grown from solutions with Cd/S ratio = 0.5. It was observed that the intensity of (002) peak increases and that of (101) peak decreases with increase of Cd/S molar ratio in the spray solution. This shows the stoichiometry dependent orientation of crystallites in the

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CdS thin film. Thickness of the films was obtained using a Holmarc Opto mechatronics Ellipsometer. All the films have thickness in the order of around 200 nm. Optical absorption and transmittance spectra of the films were recorded in the wavelength range from 400 nm to 1000 nm. All the films show high transmittance in the visible spectral region, shown in Fig. 2. The relatively high transmittance and sharp fall in transmittance around the absorption edge indicates the low surface roughness and homogeneity of the film [7], which was supported by the FESEM images as shown in Fig. 3. The elemental compositions of the films obtained from EDS are given in Table. 1. The films deposited from the solution with Cd/S molar ratio = 0.5 and 0.75 shows the transmittance greater than 80% in the visible and near infra-red regions. The decrease in the transmission of CdS films with the increase of Cd/S molar ratio is attributed due to the decrease in the sulphur concentration in the film [7, 8]. From the thickness of the film d, optical absorbance A, the absorption coefficient can be calculated using the Lambert law as following:

$$\ln (I_o/I) = 2.303A = \alpha d \quad (1)$$

where I_o and I are the intensity of incident and transmitted light respectively. The bandgap E_g of the semiconductor films can be obtained by analyzing the absorption spectra with the expression for the optical absorbance, i.e. by using the Tauc relation for optical absorbance,

$$\alpha h\upsilon = A (h\upsilon - E_g)^n \quad (2)$$

where A is a constant, hυ is the energy of light and the exponent n characterizes the nature of band transition, n = ½ for direct band gap semiconductor material. The graph of $(\alpha h\nu)^2$ versus hν were plotted as shown in the Fig 4. The extrapolation of linear region of the curve to the energy axis gives the band gap values. The band gap energies obtained from absorption measurements are given in the Table 1. The bandgap of the CdS thin film decreased from 2.463 eV to 2.418 eV with increase in the Cd/S molar ratio in the solution from 0.5 to 2 and it again increases for further increase in the molar ratio. This may be due to the variation in the crystallite size in the films with the variation in the Cd/S molar ratio in the solution. The room temperature resistivity of the films was measured by van der Pauw method using Keithley 236 source measure unit and are given in Table. 1. It was observed that the resistivity increases with increase of Cd/S molar ratio in the solution. The CdS thin films deposited from the solution containing the precursor elements with molar ratio of 0.5 and 0.75 have low resistivity of the order of 10^2 ohm-cm which is 2 to 3 orders smaller than the resistivity of the films obtained from higher molar ratios. Above results show that the resistivity of CdS thin films can be controlled by varying the elemental composition in the film. Similar results were published by J. Santos *et al*. for the CdS films deposited by chemical bath deposition method from the solution with S/Cd molar ratio of 2 [6]. The optical and electrical properties of the CdS films with Cd/S ratio around 0.5 are suitable for the use of these films as a window layer in the heterojunction thin film solar cells [9].

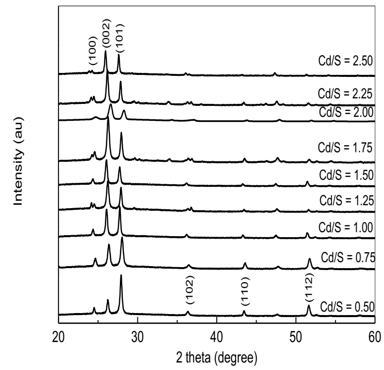

FIG.1. XRD spectra of CdS thin films

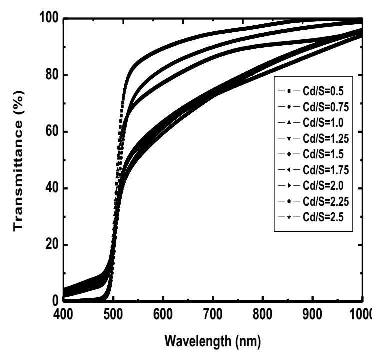

FIG. 2 Transmittance spectra of CdS thin films

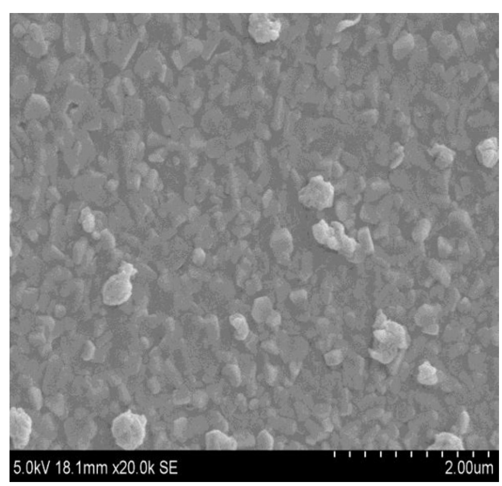

FIG. 3a SEM image of CdS film from the solution with Cd/S molar ratio equal to 0.5.

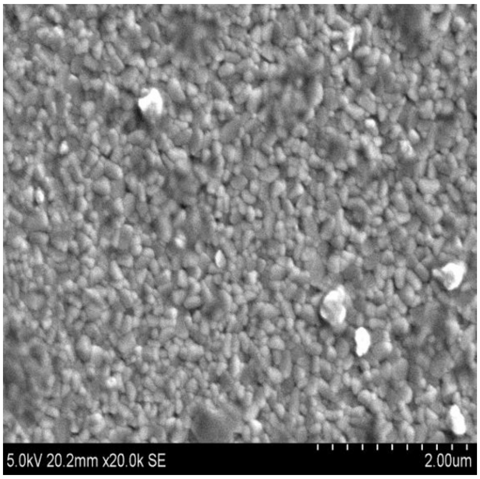

FIG. 3b SEM image of CdS film from the solution with Cd/S molar ratio equal to 1.5.

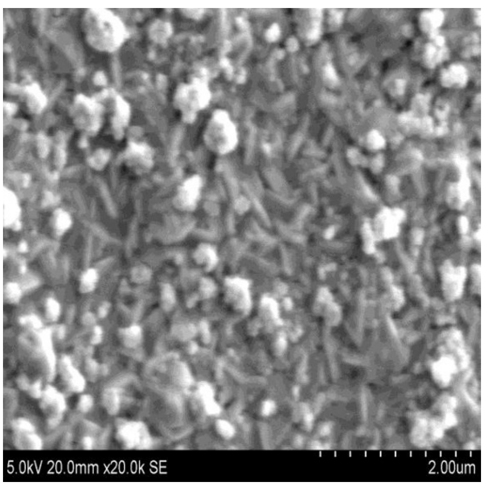

FIG. 3c SEM image of CdS film from the solution with Cd/S molar ratio equal to 2.25.

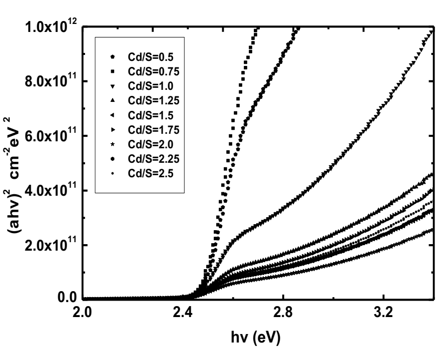

FIG. 4 $(\alpha h\upsilon)^2$ versus $h\upsilon$ of CdS thin films

Table 1 Elemental composition, bandgap and resistivity of CdS thin films

Cd:S in the solution	Cd:S in the film	Energy gap Eg (eV)	Resistivity x 10^5 Ω-cm
0.5	0.73:1	2.455	0.00104
0.75	0.96:1	2.444	0.00254
1.0	1.01:1	2.438	0.036
1.25	1.18:1	2.433	0.09
1.5	1.44:1	2.427	0.217
1.75	1.61:1	2.422	6.84
2.0	1.93:1	2.411	2.56
2.25	2.10:1	2.424	3.68
2.5	2.25:1	2.431	5.89

IV. CONCLUSIONS

Cadmium sulphide thin films with variation in stoichiometry were deposited by spray pyrolysis method. The crystallites in the films show the composition dependant orientation as can be seen from the XRD spectra. CdS thin films obtained from the solution with the Cd to S molar ratio equal to 0.5 have high transmittance in the visible region of the optical spectra and have resistivity equal to 1.04×10^2 Ω-cm. The optical and electrical property of these films meets the condition required for their application in solar cells as absorber layers.

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