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ELECTRICAL PROPERTIES OF SINTERED CdS_xSe_{1-x} FILMS

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CdS_xSe_{1-x} films of different composition were prepared by the slurry coating technique on titanium substrates. Powders of different composition synthesized in the laboratory were used for the film preparation. The films were sintered in argon atmosphere for 20 min in the temperature range 450 - 550°C. X-ray diffraction pattern of the films exhibited hexagonal structure. The optical bandgap estimated from the reflectance measurements was in the range of 1.72 eV – 2.44 eV. Hot probe measurements indicated the films to exhibit n-type conductivity. Indium ohmic contact was vacuum evaporated on the sides of the films for in plane resistivity measurements and on the top of the film surface for cross plane resistivity measurements. Surface morphology of then films as well as the powders was studied by atomic force microscopy.

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1.Introduction

The II-VI binary semiconducting compounds, belonging to the cadmium chalcogenide family (CdS, CdTe, CdSe), are considered to be very important materials for a wide spectrum of optoelectronic applications as having specific physical properties such as direct band-gap widths, high absorption coefficients in the visible and infrared part of the solar spectrum, good electrical properties (e.g. carrier mobility and lifetime) and increased capability in obtaining adjustable n- or p-type conductivity by doping. Particularly, the visible and near infrared, direct band-gaps of CdSe (1.75 eV and CdS (2.44 eV) respectively, make them candidates for the conversion of low energy light into electricity. Moreover, homogeneous alloys formed over the entire composition range by combination of these compounds allow the production of very interesting ternary CdS_xSe_{1-x} (0 I< x< 1) systems.

Earlier publications on preparation of CdSe, CdS and CdSSe powders were mostly based on sintering technique at high temperatures. Moreover, different compositions of CdSe and CdS in CdS_xSe_{1-x} powders were prepared by the fusion of CdS and CdSe in argon atmosphere at high temperature. The films prepared by the material obtained by sintering method show a mixture of cubic and hexagonal phases and the desired uniformity in distribution of CdS and CdSe was not achieved throughout the samples. Very few reports on the preparation of II-VI material by low temperature synthesis are available in the literature. In this investigation, a novel procedure has been developed by a low temperature wet chemical method for the preparation of CdSSe powders. By using the prepared powders, thin films were prepared by the screen printing technique. Earlier reports have screen printed CdSSe films from a mixture of CdS and CdSe powders[1,2]. To our knowledge this is the first report on screen-printing CdS_xSe_{1-x} films using the synthesized CdS_xSe_{1-x} powders. The electrical, optical, structural and morphological properties of the films have been studied in this work.

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2.Experimntal

CdS_xSe_{1-x} powders were prepared by the reaction of aqueous solutions of cadmium acetate, sodium seleno sulphate and thiourea under optimum conditions of pH ~10, obtained by the addition of ammonium hydroxide.

40 g of cadmium acetate was dissolved in 200 ml of triple distilled water, 25 g of thiourea was dissolved in 250 ml of triple distilled water by gentle heating, seleno sulphate solution was prepared by dissolving 30 g of selenium in a sodium sulphite solution (prepared by dissolving 235 g of sodium sulphite in 500 ml triple distilled water). The cadmium acetate solution was taken in a three litre flask fitted with grounded joints, and 150 ml of fresh ammonia was added when a clear solution of cadmium ammonia complex was obtained. To this clear solution different quantities of selenosulphate and thiourea solutions were taken in 100 ml of ammonia and added to the complex and refluxed on a heating mantle provided with facility for magnetically stirring the contents for a few hours. 30 ml of ammonia was added at intervals of 30 minutes. The colour of the precipitate changed from orange colour to shiny bright black colour as the composition of the powder changed from sulphur rich to selenium rich side. The precipitate was kept for about 15 hours and filtered through a Whatman 42 filter paper using Buchner funnel with vacuum suction arrangement. The powders were then washed with hot sodium sulphite to remove traces of selenium, and washed with hot acetic acid to remove traces of cadmium oxide. Further washing was continued until the pH of the filtrate was found to be neutral. Purified ethanol was employed for final washing to remove moisture. The powders were dried in vacuum oven. The powders were then annealed at 300°C in argon atmosphere for 30 minutes to remove any traces of excess selenium. The powders were then stored in vacuum desiccator.

The powders were screen printed on titanium substrates. The films were sintered in argon atmosphere. Films were prepared by adding 10% of cadmium chloride and after thoroughly grinding in an agate mortar in the presence of iso-propanol. The mixture was made into a paste by adding propylene carbonate. The paste was then screen printed on to titanium substrates. The printed films were dried in air at 120°C for a few hours. They were then sintered in argon atmosphere at different temperatures in the range 450 - 550°C for 20 minutes. The films were characterized by x-ray diffraction studies using a PANalytical Xpert X-ray diffractometer with CuK_α radiation. Reflectance measurements were made with U3400 Hitachi spectrophotometer. Thickness of the films estimated by gravimtery was in the range of 10 – 12 micrometers.

3.Results and discussion

The XRD pattern of the powders of different compositions is shown in Fig.1. The peaks corresponding to (100), (002), (101), (102), (110), (103) and (112) reflections were observed in all cases. The peaks were observed to shift to higher 2θ values as the ‘x’ value increased from 0 to 1. All the samples exhibited hexagonal structure and the lattice parameters ‘a’ and ‘c’ were calculated using the standard relation,

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2}$$

‘a’ and ‘c’ values for CdSe and CdS are taken from the ASTM data. The variation of lattice constants of cadmium sulpho selenide solid solutions with composition is shown in Table.I. A linear variation of the lattice constants with composition indicates that Vegard’s law is obeyed [3]. Similar variation has been observed for sintered pellets [4], flash evaporated layers [5], single crystals [6] and sprayed layers [7].

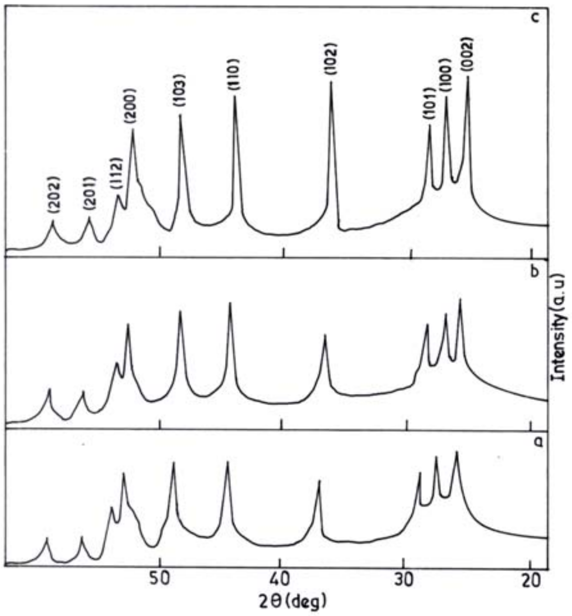


Fig.1. X-ray diffraction pattern of CdS_xSe_{1-x} films of different composition(a) x = 0.1 (b) x = 0.3 (c) x = 0.7

Table. 1. Lattice Parameters of CdS_xSe_{1-x} films

Composition (x)	**Lattice Constants**	
	a(Å)	**c(Å)**
0	4.304	7.044
0.1	4.292	6.952
0.2	4.281	6.901
0.4	4.244	6.832
0.6	4.211	6.801
0.8	4.188	6.783
1.0	4.147	6.754

Composition analysis was done by EDAX study and the composition of the powders is indicated in the Table.II. From the table, it is observed that the composition of the starting material and that of the films are nearly the same.

For the determination of band gap, we plotted a graph between the square of hν $\ln\{(R_{max} - R_{min})/(R - R_{min})\}$ and hν. The plots were linear and the extrapolation of the straight line to hν axis gave the band gap value of the films, which is very close to the values reported in other studies[1,8].Optical data analysis indicates that direct allowed transitions occur in these films. In case of cadmium salts, the maximum of valence band and the minimum of conduction band lie at the same value of electron wave vector k in

Table. 2. Composition of CdS_xSe_{1-x} films.

Starting Composition	EDAX Analysis
$CdS_{0.9}Se_{0.1}$	$CdS_{0.89}Se_{0.11}$
$CdS_{0.8}Se_{0.2}$	$CdS_{0.80}Se_{0.20}$
$CdS_{0.6}Se_{0.4}$	$CdS_{0.58}Se_{0.42}$
$CdS_{0.4}Se_{0.6}$	$CdS_{0.39}Se_{0.61}$
$CdS_{0.2}Se_{0.8}$	$CdS_{0.19}Se_{0.81}$

E_{2k} band diagram and hence the transitions are of direct type. As given above, the absorption coefficient of the film material is proportional to $\ln\{(R_{max} - R_{min})/(R - R_{min})\}$. The absorption coefficient was of the order of 10^4 cm^{-1}. The variation of band gap with composition is shown in Fig.2. The band gap increases from 1.68 eV to 2.41 eV as the value of 'x' increases.

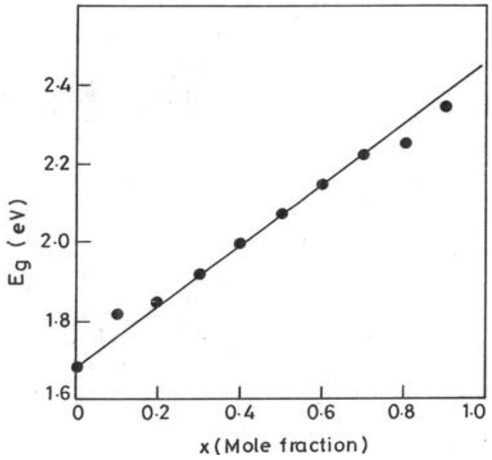
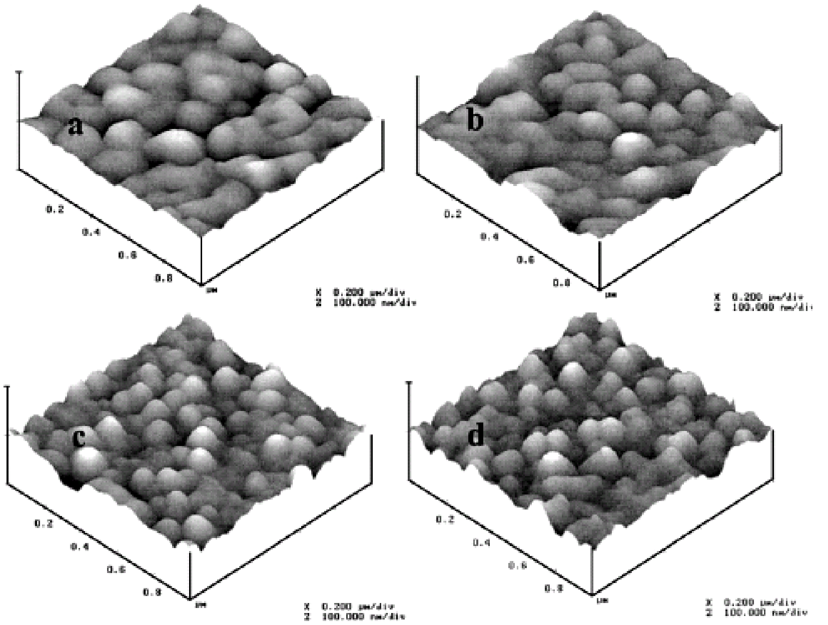


Fig. 2. Variation of band gap with composition.

Surface morphology of the films was determined for the films of different composition heat-treated at 550°C are shown in Fig.3. The evolution of the microstructure of the CdS_xSe_{1-x} thin films, deposited on titanium substrates, as a function of Se content, indicated grains rounded in shape, while the average grain size was slightly reduced with higher Se content. In addition, overall observation of the thin films indicates a good microstructure with no discontinuities in terms of pinholes and micro-cracks. The surface roughness and average grain size of the thin films measured by AFM showed values between 7.7 nm - 3.8 nm and 250 nm - 120 nm as the selenium concentration increases.



x – 0.200µm/ div
z – 100 nm/div

Fig.3. Surface topography of CdS_xSe_{1-x} films (a) x = 0.9 (b) x = 0.6 (c) x = 0.3 (d) x = 0.1.

The in-plane resistivities of CdS_xSe_{1-x} films of different composition vary from 100 ohm cm – 240 ohm cm at room temperature as the CdS content in the films increase. The transverse resistivities of the films, however, are approximately two orders higher than the in-plane resistivities. The resistivity anisotropy can be attributed to the good orientated growth of films. In the plane of the CdS_xSe_{1-x} films, the perfect lattice structure results in low in plane resistivity [9]. On the other hand, along the orientation perpendicular to the substrate, a one dimension lattice forms by a two-dimension laminated structure stacking in the CdS_xSe_{1-x} films, forming a lot of grain boundaries.

Table.3. Variation of In plane and cross plane resistivity with composition of CdS_xSe_{1-x} films.

Composition(x)	**In plane resistivity**	**Cross plane resistivity**
	(ohm cm)	**(ohm cm)**
0	100	10^4
0.2	130	1.2×10^4
0.4	152	1.8×10^4
0.6	170	5.2×10^4
0.8	195	8.1×10^4
1.0	240	9.8×10^4

which results in high transverse resistivity. Similar results were observed for CdS films[10]. Usually, the transverse resistivity, like the resistivity of bulk, decreases with increase in the amount of excess Cd^{2+}, internal micro-strain and defect such as appoint defect [9]. On the other hand, the in-plane resistivity depends on the degree of orientated growth of the films [9]. Table-III shows the values of in plane and cross plane resistivities of the films of different composition.

4. Conclusions

The results of this study clearly indicate that CdS_xSe_{1-x} films of different composition with In plane resistivity in the range of 100 – 240 ohm.cm and the values of the cross plane resistivity raises in the range of 10^4 - 9.8×10^4 ohm cm as the concentration of CdS increases. The grain size increases from 120 – 250 nm and the surface roughness increases from 3.8 – 7.7nm as the CdSe concentration in the films increase. The band gap increases from 1.68 eV to 2.41 eV as the CdS increases.

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