Optical Properties and Applications of Cadmium Selenide (CdSe) Thin Films Prepared by Chemical Bath Deposition Technique

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ABSTRACT

Cadmium selenide (CdSe) thin films have been prepared by chemical bath deposition technique. The films deposited are highly uniform and firmly adhered to the substrate. Some of the films were annealed at 423K. The range of thickness for various films deposited is 1.805×10^{-7} – 14.310×10^{-7}m. The transmittance of the films is proportional to the wavelength of the electro magnetic radiation within the visible region and near infra-red regions. The reflectance rises to a peak value and then falls in the visible region.

The bandgap for the CdSe films is 2.25eV and the refractive index has a peak value of 2.64 in the visible regions. The brilliant orange colour of the films and their high transmittance make them suitable for use as aesthetic window glaze.

(Key words: cadmium selenide, chemical bath, optical properties, thin films, refractive index).

INTRODUCTION

Cadmium selenide is one of the II-VI semiconductor compounds. Among the group, CdSe is an important material for the development of various modern technologies of solid state devices such as solar cells, high efficiency thin film transistors, and light emitting diodes [1-2]. Other areas of successful applications include, photo-detectors, light amplifiers, lasers, photo electrochemical cells, gas sensors for the detection of oxygen, etc. [3-5]. A direct bandgap range of 1.65-1.84 eV has been reported for CdSe by various authors [1-2] and its photosensitivity gives it an edge over other II-VI semiconductor materials.

CdSe thin films have been prepared by various film deposition techniques such as physical vapour deposition, vacuum evaporation, sputtering, spray pyrolysis, electrodeposition, chemical bath or solution growth, etc. [1, 3, 7]. Among these deposition techniques, chemical bath is preferred. The choice of this technique centers largely on the fact that it possesses a number of advantages over conventional thin film deposition methods, such as low cost, low temperature, and easy coating of large surfaces. This technology is based on the controlled release of the metal ions [8]. In this paper, the preparation and optical characterization of CdSe is reported.

EXPERIMENTAL DETAIL

Chemical bath deposition technique was adopted for the preparation of the cadmium selenide thin films.

Ordinarily selenium is not soluble in water. In order to create selenium ions in the absence of sodium selenosulphate (Na_2SeSO_3), selenium powder was mixed with sodium sulphite solution and heated under reflux for a period between one and two hours.

The resulting Na_2SeSO_3 becomes the source of Se^{2-} while the source of Cd^{2+} is the cadmium chloride ($CdCl_2$). Ammonia (NH_3) was used as complexing agent.

The reaction both was made in 50ml beakers. 76mm x 26mm x 1mm commercial quality glass microscope slides were used as substrate. Preparation of substrates for use has already been reported in previous works [8].

The substrate was vertically immersed in the reaction bath such that it was not touching the walls of the beaker. Several variations of the deposition parameters (concentration, dip time, etc.) were employed to optimize and standardize the deposition process.

The reaction mechanism is of the form:

$2\ CdCl_2 + 4NH_3 \longleftrightarrow Cd(NH_3)^{2+} + CdCl_4^{2-}$

$Cd(NH_3)^{2+} \longleftrightarrow Cd^{2+} + 4NH_3$

$Na_2SeSO_3. + 2OH^- \longleftrightarrow Na_2SO_4 + H_2O + Se^{-2}$

$Cd^{2+} + Se^{-2} \longleftrightarrow CdSe \downarrow$

At the end of the dip period, the films were washed and drip-dried in the air. Some of the samples were annealed at 423K. The composition of the samples was determined by analyzing the Energy Dispersive X-ray Fluorescence (EDXRF) of the samples. The X-ray system emits Ag-K X-rays (22.1KeV).

The optical absorbance/transmittance of the films were studied in the spectral range of 340-1000nm using a Unicam Helios® gamma UV-Visible spectrophotometer. The thickness of the films was determined by gravimetric method.

RESULTS AND DISCUSSION

The colour of the CdSe film is orange. Bath concentration between 0.04 and 0.10M produced very uniform and firmly adhered films. The period of deposition is 4-24 hours.

The EDXRF of the deposited films showed energy of 11.210 keV corresponding to peak intensity of 0.377C/s for Se as shown in Table 1 and Table 2.

Table 1: Energy Dispersive X-ray Fluorescence of Blank Glass Substrate (as reference).

ELEMENT	ENERGY [KEV]	INTENSITY [c/s]	SENSITIVITY	GEOMETRY	CONCENTRAT. [FRAC]	ERROR
CD	3.130	0.065	2.25E+02	0.0022	1.30E-01	-LOD-
K	3.312	0.052	1.26E+03	0.0025	1.57E-02	-LOD-
SN	3.440	0.001	3.07E+02	0.0028	9.02E-04	-LOD-
CA	3.690	0.362	1.50E+03	0.0023	1.03E-01	4.49E-03
I	3.930	0.040	1.04E+03	0.0024	1.58E-02	-LOD-
TI	4.508	0.031	3.44E+03	0.0026	3.39E-03	-LOD-
V	4.949	0.032	5.16E+03	0.0032	1.86E-03	-LOD-
CR	5.411	0.040	6.70E+03	0.0040	1.44E-03	-LOD-
FE	6.400	0.085	1.05E+04	0.0062	1.27E-03	1.82E-04
CO	6.925	0.045	1.31E+04	0.0076	4.36E-04	-LOD-
NI	7.472	0.035	1.63E+04	0.0093	2.26E-04	-LOD-
CU	8.041	0.035	1.92E+04	0.0112	1.61E-04	1.09E-04
ZN	8.631	0.043	2.30E+04	0.0133	1.38E-04	4.34E-05
GA	9.243	0.039	2.53E+04	0.0158	9.59E-05	3.34E-05
AS	10.532	0.060	3.26E+04	0.0216	8.27E-05	3.12E-05
SE	11.210	0.047	3.67E+04	0.0250	4.97E-05	-LOD-
PB	10.540	0.051	1.91E+04	0.0217	1.21E-04	-LOD-
BR	11.907	0.042	4.54E+04	0.0287	3.15E-05	-LOD-
RB	13.375	0.045	4.94E+04	0.0369	2.40E-05	-LOD-
SR	14.142	1.037	5.37E+04	0.0414	4.55E-04	-LOD-
Y	14.933	0.198	5.81E+04	0.0461	7.24E-05	-LOD-
ZR	15.746	0.745	7.47E+04	0.0509	1.91E-04	1.10E-05
NB	16.584	0.073	8.11E+04	0.0558	1.58E-05	4.42E-06
MO	17.443	0.111	8.76E+04	0.0608	2.03E-05	4.16E-06

SAMPLE: IS6594 MATRIX: [AO(RES) = 11000] WEIGHT [g/cm^2]: 1.048 Blank

Table 2: Analysis Results for Energy Dispersive X-ray Fluorescence of Substrate with CdSe Film.

ELEMENT	ENERGY [KEV]	INTENSITY [c/s]	SENSITIVITY	GEOMETRY	CONCENTRAT. [FRAC]	ERROR
CD	3.130	0.077	2.25E+02	0.0022	1.55E-01	-LOD-
K	3.312	0.052	1.26E+03	0.0025	1.57E-02	4.65E-03
SN	3.440	0.001	3.07E+02	0.0028	9.05E-04	-LOD-
CA	3.690	0.340	1.50E+03	0.0022	1.02E-01	6.13E-03
I	3.930	0.033	1.04E+03	0.0022	1.39E-02	-LOD-
TI	4.508	0.038	3.44E+03	0.0024	4.40E-03	-LOD-
V	4.949	0.033	5.16E+03	0.0030	2.03E-03	-LOD-
CR	5.411	0.033	6.70E+03	0.0038	1.25E-03	-LOD-
FE	6.400	0.076	1.05E+04	0.0059	1.20E-03	2.47E-04
CO	6.925	0.037	1.31E+04	0.0072	3.85E-04	-LOD-
NI	7.472	0.036	1.63E+04	0.0088	2.46E-04	-LOD-
CU	8.041	0.042	1.92E+04	0.0106	2.00E-04	7.53E-05
ZN	8.631	0.038	2.30E+04	0.0126	1.29E-04	5.14E-05
GA	9.243	0.046	2.53E+04	0.0150	1.18E-04	-LOD-
AS	10.532	0.082	3.26E+04	0.0205	1.20E-04	3.80E-05
SE	11.210	0.377	3.67E+04	0.0237	4.24E-04	2.42E-05
PB	10.540	0.053	1.91E+04	0.0205	1.31E-04	-LOD-
BR	11.907	0.043	4.54E+04	0.0271	3.39E-05	-LOD-
RB	13.375	0.043	4.94E+04	0.0348	2.47E-05	-LOD-
SR	14.142	0.963	5.37E+04	0.0390	4.48E-04	1.45E-05
Y	14.933	0.163	5.81E+04	0.0434	6.30E-05	-LOD-
ZR	15.746	0.752	7.47E+04	0.0480	2.04E-04	1.44E-05
NB	16.584	0.123	8.11E+04	0.0526	2.80E-05	5.26E-06
MO	17.443	0.094	8.76E+04	0.0574	1.82E-05	4.79E-06

SAMPLE: IS6592 MATRIX: [AO(RES) = 11000] WEIGHT [g/cm^2]: 1.048 C

The intensity for cadmium could not be used to identify the element itself as a result of the effect of cadmium being the excitation source.

The thickness of the films is proportional to both the period of deposition and the concentration of the reaction bath as shown in Figures 1 and 2. At higher thickness, the colour of the film becomes dark red.

The variation of transmittance and reflectance as functions of wavelength are shown in Figure 3. The transmittance is proportional to the wavelength. Both transmittance and reflectance are almost zero in the UV-region but transmittance increases rapidly within the visible region of the spectrum. The rate of increase is more steep in the films annealed at 423K (series 2) than in the as grown ones (series 1).

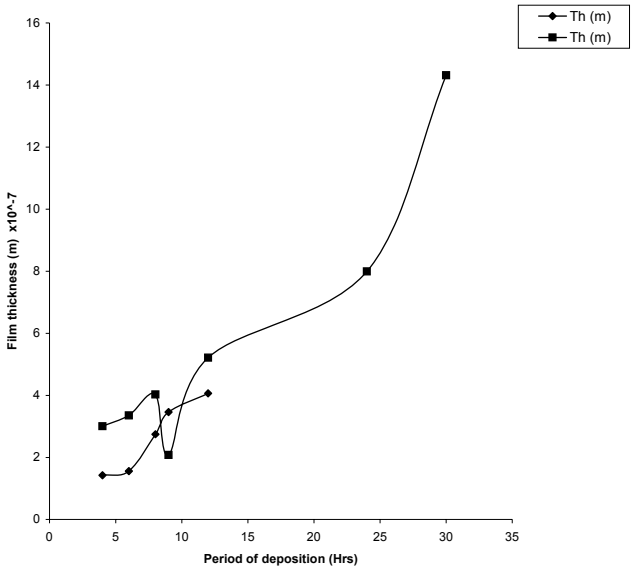

Figure 1: Variation of Film Thickness with Period of Deposition.

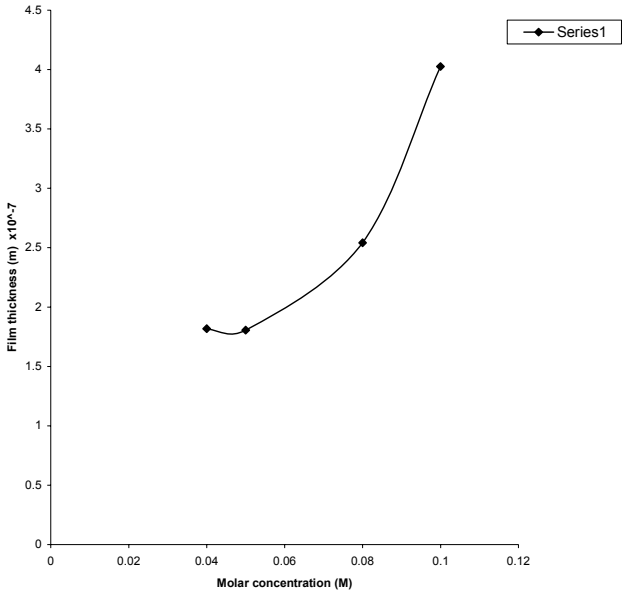

Figure 2: Variation of Film Thickness with Molar Concentration of Ions.

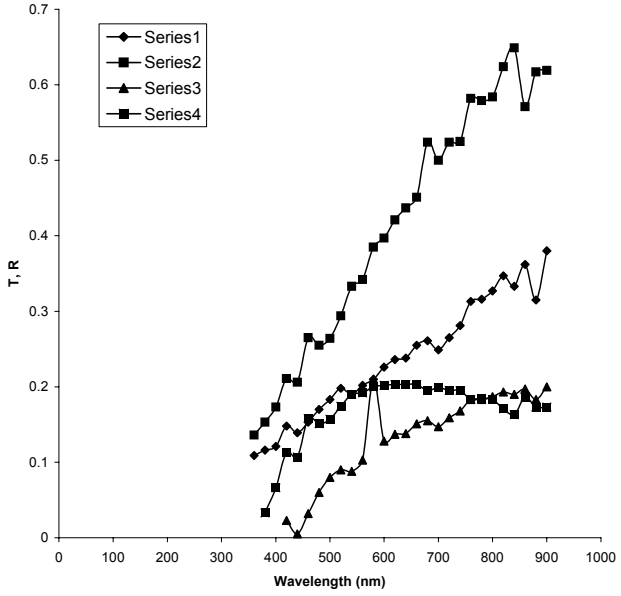

Figure 3: A Plot of Transmittance (T) and Reflectance (R) of Wavelength.

The reflectance increases slightly to a maximum value (0.203) and falls again. The very high transmittance of the films in the visible region and the brilliant colour of the films make CdSe films useful aesthetic window glaze material. The dependence of the absorption coefficient on the energy of light quanta near the fundamental edge for direct electron transition is given by:

$$\alpha = (h\nu - E_g)^{1/2} \quad \text{or}$$
$$\alpha^2 = h\nu - E_g.$$

Thus a plot of α^2 against hv gives a straight line graph. However, in the region of the absorption edge, the absorption falls to such low values that it becomes difficult to measure the path that is due to band to band transition. This is due to the fact that it is now liable to be masked by other incidental absorption or losses in specimen or experimental equipment. A plot of α^2 versus hv in the region deviates from being straight but extrapolation of the straight portion of the graph to $\alpha 2 = O$ gives the bandgap Eg of the sample [9 -11].

Figure 4 shows the plot of the graph of a sample of the film. The graph shows a bandgap of 2.25eV for the CdSe film. This value is comparable with the range found in the literature.

Figure 5 shows the variation of the refractive index of the CdSe film with wavelength of the electromagnetic spectrum. The graph shows a peak value of 2.64 for the films. This means that electromagnetic radiation is 2.64 times slower in CdSe films than in free space [8]. This peak value occurs within the visible region of the electro magnetic spectrum.

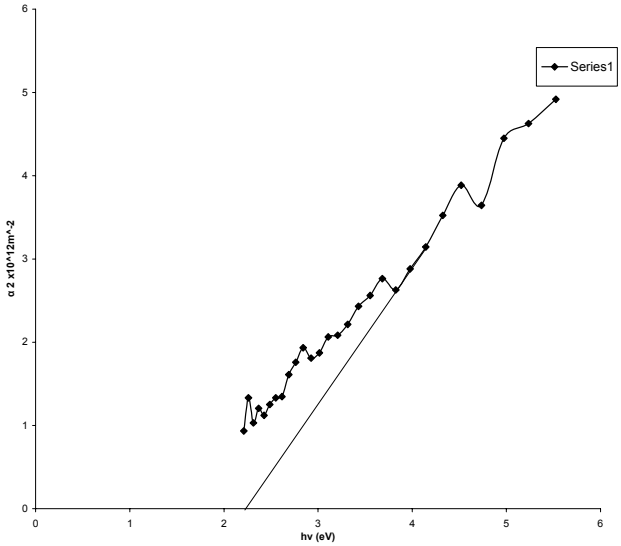

Figure 4: A Plot of α^2 as a Function of *hv*.

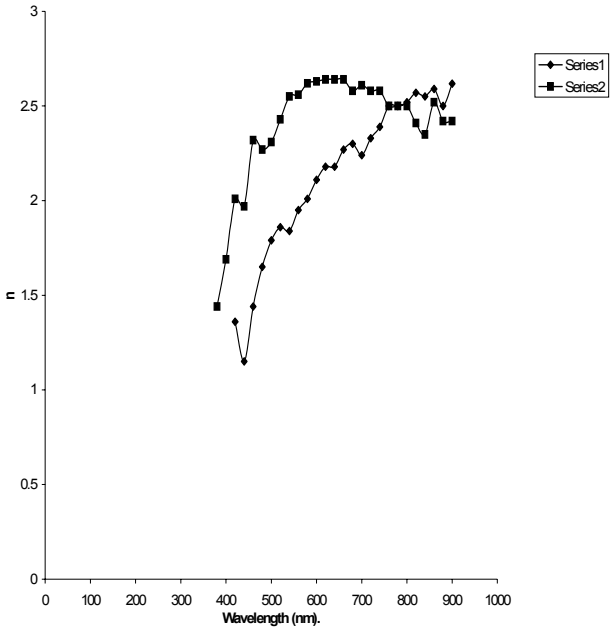

Figure 5: A Plot of Refractive Index (n) as a Function of Wavelength.

CONCLUSION

Cadmium selenide thin films have been successfully deposited using chemical bath deposition technique. Solutions of Na_2SeSO_3, $CdCl_2$ and NH_3 formed the reaction bath. Some of the films grown were annealed at 423K.

The bandgap of the CdSe films is 2.25eV, the refractive index of the films has a peak value of 2.64 within the visible region of the electromagnetic spectrum. The optical transmittance is proportional to the wavelength of electromagnetic spectrum within the visible and near infra-red region. In the visible region, the reflectance rises slightly to a peak value and falls again.

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