Preparations and Photochemical uses of Cadmium Selenide Thin Films

Dr.C P Sawant[*] Prof.Ashok . D Jadhav[**]

[*] G .T. P.College.Nandurbar
[**] K. T. H. M. College, Nasik – 422 002

Abstract- A systematic study has done to investigate the thin films of chemically deposited CdSe and Tl doped thin films. The deposition has been carried out in an alkaline medium at 70 ^{0}C for about 90 minutes. Characterization of thin films were done using X-ray diffraction (XRD), scanning electron microscope (SEM) optical absorption, electrical conductivity and thermoelectric techniques. These study reveals that films are polycrystalline in nature with cubic structure. The electrical conductivity of the order of 10^{-5} $(\Omega$ cm$)^{-1}$ and an optical energy gap of 1.55 eV to 2.01 eV with a direct allowed type of transitions have been noticed. The thermoelectric power measurements shows n-type conduction mechanism for pure CdSe and doped CdSe thin films.

Index Terms- A Chemical Bath Deposition. B CdSe Thin Films C Tl doped CdSe Thin films D Optical Properties

I. INTRODUCTION

Cadmium Selenide has studied extensively because of its use in photoelectron chemical solar energy conversion and optoelectronic applications [1-3]. Cadmium selenide single crystals have been shown to exhibit a conversion efficiency as high as 8 –12% in polysulphide solution, whereas crystalline cadmium selenide exhibits a lower efficiency [4-6]. The n-type cadmium selenide semiconductor (band gap 1.75 eV) has become quite interesting and important because of its major contribution to solar cells, photo detection, optoelectronics, light amplifiers, electrophotography, light emitting diodes and in the preparation of electronic elements based on existence of metal insulator – semiconductor structure. Most research so far has focused extensively on determining major features of electrical, optical and structural properties of CdSe compound[7,8]. However, doping effect on properties of CdSe thin films is still insufficient in previously reported literature. In this paper the attempt is made to dope Tl into CdSe thin films by simple chemical deposition techniques. This technique is economically viable, yields reproducible and more consistent characteristics than the other sophisticated techniques. Previously we have reported deposition of HgSe, CdHgS etc. compounds by this technique [9-11].

II. EXPERIMENTAL

Cadmium selenide thin films have been obtained onto glass substrate by chemical deposition method. For deposition 10 ml (1 M) CdSO$_4$ solution was taken in a beaker and 5 ml of triethanolamine (TEA) was added to form a stable complex. To this mixture 3 ml of NaOH (1 N) and about 20 ml (14 N) aqueous ammonia was added so as to adjust the pH of the reaction mixture equal to10.5 $\pm$ 0.1. The reaction mixture was then made upto 180 ml by adding a doubled distilled water.

Sodium selenosulphite (0.22 N) was obtained by refluxing selenium powder (5.0 gms) with anhydrous sodium sulphite (12.0 gms) in a 200 ml distilled water for about 9 hours. The beaker containing reaction mixture was then kept in oil bath whose temperature was controlled upto 60^{0}C. The glass substrate (micro slides of size 75 x 25 x 2 mm) was first cleaned with chromic acid and then degreased with acetone. For getting Tl doped CdSe films the Thallium Sulphate solution (0.01 M) was added directly to a reaction mixture in order to achieve 0.01 to 2.0 mole % doping concentrations. Throughly cleaned substrates were attached vertically perpendicular to each other and rotated in reaction mixture with 70 $\pm$ 2 r.p.m. speed. Sodium selenosulphite was then added slowly in the reaction mixture at a controlled rate by exterior arrangement. The deposition was carried out for 90 minutes. To obtain good samples, the conditions were optimized (pH = 10.6, temp 60 ^{0}C, time 90 min). After 90 minutes thin film samples were removed and washed 5 to 6 times with distilled water. The films were dried and preserved in a dark dessicator Uniformity of the film was examined by the measurement of thickness using weight difference density consideration method . The X-ray diffractogram was recorded using a Philips p.w. 1710 X-ray diffractrometer (XRD) with CuKα line in 2θ range from 10 – 100^0. The optical absorption spectra were obtained in the wavelength range from 350 to 900 nm by using Hitachi – 330 (Japan) Double Beam Spectrophotometer; at room temperature. A study of surface morphology of sample was done under scanning electron microscope, steroscan S 120, 250 M. K. III Cambridge,(UK).
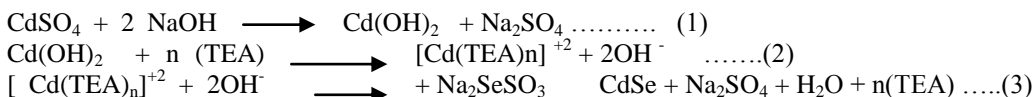
A two probe point method was employed to measure the electrical conductivity of the sample in dark. The range of working temperature was from 350 to 500 K.
The film composition was determined using a Perkin Elmer 3030 Atomic Absorption Spectrophotometer.

III. RESULTS AND DISCUSSIONS

3.1 Film growth.

To prepare a cadmium selenide thin film of maximum thickness of around 0.5 μm, the conditions are optimized. At about 60 ^{0}C temperature and time of 90 min the rate of

deposition is maximum. The kinetics of the film formation can be explained from the following reactions.

$$CdSO_4 + 2\ NaOH \longrightarrow Cd(OH)_2 + Na_2SO_4 \ldots\ldots (1)$$
$$Cd(OH)_2 + n\ (TEA) \longrightarrow [Cd(TEA)n]^{+2} + 2OH^- \ldots\ldots(2)$$
$$[\ Cd(TEA)_n]^{+2} + 2OH^- \longrightarrow + Na_2SeSO_3 \quad CdSe + Na_2SO_4 + H_2O + n(TEA) \ldots..(3)$$

The film formation is dependent on the initial nucleation step. The $Cd(OH)_2$ present on the substrate surface acts as the nucleation centre for the subsequent growth of CdSe film. The films are thin, uniform and orange red in colour, These are also highly adherent, smooth and reflecting. In the same way Thallium doped cadmium selenide thin films are obtained by adding various concentrations of Thallium sulphate solution. These films of Thallium doped cadmium selenide are some what distinct than the pure CdSe. They are more reflecting and orange reddish in colour. The thickness of the film was measured by a weight difference density method[12]. The thickness of pure CdSe thin film was found to be about 0.445

3.2 Structural Properties

The X-ray diffractogram of sample is displayed in Fig. 1. The no. of peaks increased upon increasing concentration of Tl. This clearly indicates that Tl becomes incorporated in lattice of CdSe[13]. The structural investigations showed polycrystalline natures in cubic lattice for CdSe as well as T1 doped thin films. At our experimental conditions CdSe films is found to be cubic nature having the lattice parameters a = 6.070 A (ASTM value is 6.077 A) which is in well agreement with ASTM (Card No. 19-119) data. As T1 doping concentration increases, the crystalinity of film is also increasing upto 0.07 mole% and thereafter the material tending towards amorphous nature. In order to evaluate the grain size, X-ray diffractogram and the following relation is used.

$$d = 0.9\ \lambda\ /\ Bcos\theta \ \text{-----------------------}(1)$$

where λ wavelength = 1.5406 A, B is the angular width at half maximum intensity and θ is Bragg's angle. The grain size for various film structure are cited in Table No. 1 It is observed that the film with 0.07 % T1 doping concentration showed higher sized grains. The partial support of the above observations were given by scanning electron micrographs of cadmium selenide and Thallium doped cadmium Selenide [Fig. No. 2] The cell size evaluated from XRD pattern is also shown in Table No. 1. We observe a decrease in cell parameter upto 5.998 A for 0.07 mole % Tl concentration, thereafter it rises.

The decrease in cell parameter can be attributed to distortion of lattice as Tl being intersticially situated in the vacancies. Thallium is known to have lesser ionic redii than Cd ion therefore, CdSe lattice doped with substitutional Tl atoms may shrink and become distorted. In sample with 0.07 mole % Tl doping, it can be considered that almost all of the intersticial sites were occupied by Tl atoms, further increase in doping concentration simply dope Tl intersticially into the film.

The intersticial Tl atoms may be considered to act as donars,. For heavily doped film the lattice do not become distored. The similar type of behaviour is explained for other material by Mizuhashi(14).

From figure 2 it is clear that the grains of spherical size are uniformly distributed on the glass substrate. As the concentration of T1 increases upto 0.07 mol %, not only the grain size of film increases but also the compactness increases. For higher concentrations the few grains are aggregated and few scattered throughout the surface.

3.3 Optical properties :

The optical absorbance was measured for these samples. The absorption co-efficient was determined and found to be in order of 10^4 - 10^5 cm^{-1} for pure CdSe as well as T1 doped films (fig. 3). The energy band gap was estimated from the variation of $(\alpha h\nu)^2$ versus hν (fig.4). The energy gap of 1.75 eV is of pure CdSe thin films and as the concentration of T1 increases the energy gap decreases upto 1.55 eV for 0.07 mole % and thereafter increases upto 2.01 eV (for 2 mole % Tl.). Such variation of Eg with T1 doping is shown in fig. 5. For higher doping concentrations the energy gap is more or less the same, we may attribute the decrease in band gap to the improved grain structure of the film owing to segregation of the impurity atoms along the grain boundaries. (15,21). The linear dependence of $(\alpha h\nu)^2$ on hν indicates the presence of direct allowed type optical transition.

As suggested by values of absorption co-efficient (α) and straight line nature of the $(\alpha h\nu)^2$ Vs hν, especially on high energy side, the mode of optical transition in these films have also been confirmed by computing ln ($\alpha h\nu$) versus ln(hν-Eg) curve. For direct allowed type of transitions, this variation should yield a straight line with slope equal to 0.5 (16) The slope determined for all these films are cited in Table no. 1 The values of m nearly equal to 0.5 confirming the direct type of transition.

3.4 Electrical properties:

The electrical conductivity of good quality sample was measured in the temperature range of 350 to 500 K. The observed electrical conductivity at 458 K was calculated in terms of specific conductivity for all the samples and found in the range of 10^{-5} to 10^{-6} $(\Omega - cm)^{-1}$. The low value of conductivity can be due to small grain size, grain boundary discontinuity effect, lack of stoichiometry and an increased amount of disorder during growth process (17-23). The variation of electrical conductivity with 1/T is shown in fig. 6. The activation energy of an electrical conduction has been determined and found to be 0.82 eV for pure CdSe film. Activation energy decreases as doping concentration is increased upto 0.07 mole % and then increases for higher concentration of thallium doping. Slight increase in conductivity with Tl doping concentration can be considered due to improvement in the grain size that reduces the height of the grain boundry potential, thereby increasing the carrier concentration, mobility and electrical conductivity. The fact that the conductivity did not vary much can be understood by considering the poor donar action of substitutional Tl atoms in

the sample. From the thermoelectric power measurements[24] pure and doped CdSe shows n-type semi conductivity.

IV. CONCLUSIONS

Pure CdSe and Tl doped CdSe thin films were obtained by simple chemical deposition technique. The films are polycrystalline in nature with cubic structure. The optical study shows the energy gap decreased down to 1.55 as the Tl concentration increases upto 0.07%. There after it increases and saturate. The increase in grain size can also be seen from Scanning Electron Microscopic photographs. Similar observation were obtained for electrical conductivity. Pure as well as Tl doped CdSe film shows n-type conduction. Small amount of Thallium doping concentration changes the properties as desired for device application.

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AUTHORS

First Author – Dr.C P Sawant , G .T. P.College.Nandurbar

Second Author – Prof.Ashok . D Jadhav, K. T. H. M. College, Nasik – 422 002., C No. +919604093574 email: ashokjadhav14@rediffmail.com

Figure Caption

Fig. 1 : XRD pattern of CdSe thin film.

Fig. 2: S. E. M. Photographs of Pure CdSe and doped CdSe thin films.

Fig.3.:The variation of absorption coefficient Vs wavelength of CdSe thin film and Tl doped thin films.

Fig. 4 : The variation of $(\alpha h\nu)^2$ Vs $h\nu$ for various Tl doped thin films.

Fig. 5 : Variation of Band Gap (Eg) with [Tl].

Fig. 6 : Log σ Vs $10^3/T$ for various films.

Table No. 1 : Composition dependent parameters of Tl doped CdSe thin films.

Sr. No.	Doping conc. (mole %) in CdSe		band gaps (eV)	Conductivity in $(\Omega$ cm$)^{-1}$ at temperature 223K	Grain size (in $\oplus$)	Lattice parameter. $\oplus$	Power factor m
	In Bath	In Film					
1	0	0	1.75	7×10^{-6}	131	6.070	0.54
2	0.02	0.018	1.63	9×10^{-6}	151	6.062	0.62
3	0.05	0.048	1.58	1×10^{-5}	160	6.04	0.6
4	0.07	0.065	1.55	2.1×10^{-5}	177	6.01	0.66
5	0.2	0.18	1.85	3.5×10^{-5}	171	5.998	0.49
6	0.5	0.48	1.95	4.0×10^{-5}	--	6.11	0.47
7	2.0	1.8	2.01	6.0×10^{-5}	--	6.13	0.61

Fig.-1 : XRD patterns of pure and Tl(III) CdSe thin fim.

Fig.-2 : SEM photographs of pure CdSe and doped CdSe thin films.
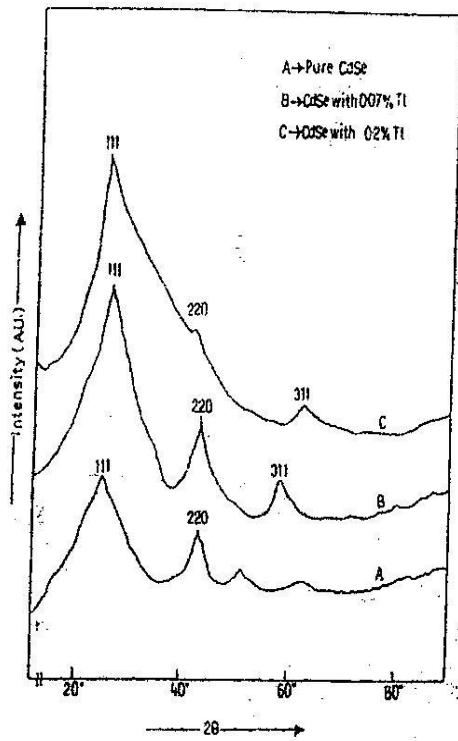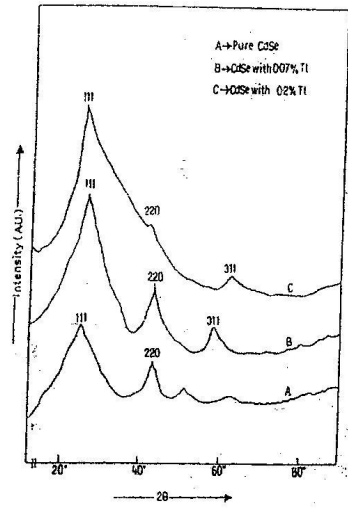
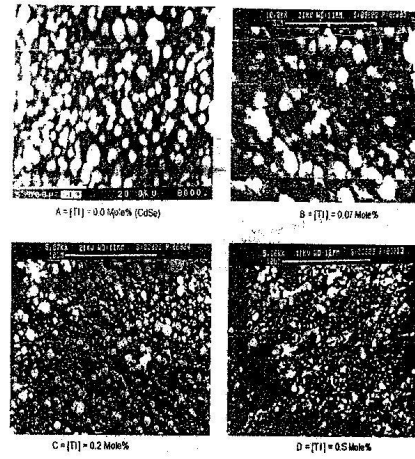Fig.-1 : XRD patterns of pure and TI(III) CdSe thin fim.

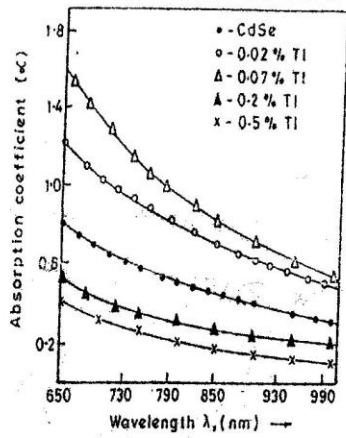Fig.-2 : SEM photographs of pure CdSe and doped CdSe thin films.

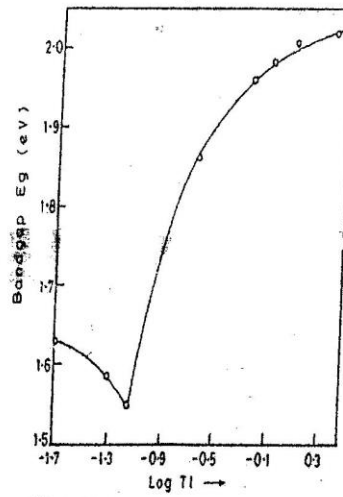Fig.- 3 : The variation of absorption coefficient vs. wavelength of CdSe thin film and Tl(III) doped thin films.

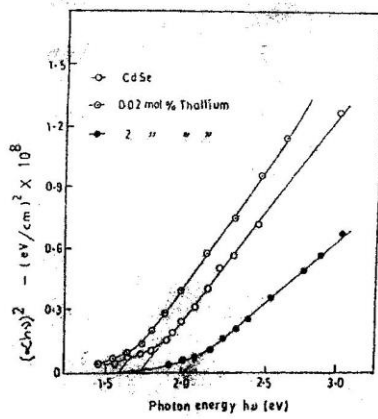Fig.-5 : Variation of bandgap (Eg) with Tl(III) concentration.

Fig.-4 : The variation of $(\alpha h\nu)2$ vs hν for various Tl(III) doped thin fims.
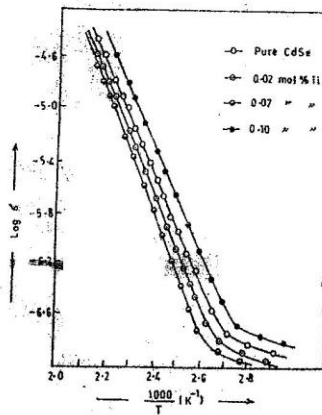

Fig.-6 : The logα vs 10^3 lT for various films.