2014

Aarhat Multidisciplinary International Education Research Journal (AMIERJ)

(Bi-Monthly)
Peer-Reviewed Journal
Impact factor: 0.948

VOL – III Issues: V

Chief-Editor:

Ubale Amol Baban

30/11/2014

Aarhat Multidisciplinary International Education Research Journal (AMIERJ)

(Bi-Monthly) Peer-Reviewed Journal Vol No III Issues V
Oct-Nov 2014 ISSN 2278-5655

ANTIMONY- DOPED $Cd_{0.7}Ni_{0.3}Se$ THIN FILMS: SYNTHESIS AND CHARACTERIZATION

B.V. Jadhav*

*Department of Chemistry, Changu Kana Thakur A.C.S. College, New Panvel-410206, Maharashtra, India.

Abstract

Antimony doped $Cd_{0.7}Ni_{0.3}Se$ thin films have been synthesized by chemical bath deposition method. The various deposition parameters such as composition of reactive bath, pH of the solution, deposition temperature, deposition time, speed of rotation, etc. have been optimized for obtaining good quality films. X-ray diffraction studies revealed the polycrystalline nature of samples with the solid solution of $Cd_{0.7}Ni_{0.3}Se:Sb$, having a hexagonal phase structure. Scanning electron micrograph suggested that the films are homogenous, without cracks and well cover the glass substrate. Film composition was determined by atomic absorption spectroscopy. Optical absorption data showed the presence of direct band gap transition. The specific conductance of $Cd_{0.7}Ni_{0.3}Se:Sb$ thin films for all the films was found to be of the order of 10^{-6} $(\Omega\ cm)^{-1}$.

Keywords: Chemical bath, Crystal growth, Thin film, Electrical conductivity
*** Corresponding author:** 9869653944
E-mail address- bvjadhav02@yahoo.com (B.V. Jadhav).

1. Introduction

The binary and ternary semiconductor thin films are being actively investigated for their potential to photovoltaic applications. The study of these materials is important due to the fact that the band gap and lattice parameters can be varied by changing the cation composition. In previous research paper, we report the synthesis of $Cd_{1-x}Ni_xSe$ thin films by chemical bath deposition method with an emphasis on their structural, compositional, morphological, optical and electrical properties.[1]

An efficient way to decrease the resistivity and to improve the properties of semiconducting material is to dope with a suitable impurity like copper, silver, antimony, bismuth, indium etc. The dopant has shown to enhance properties in number of host lattices. [2-6] Antimony (Sb) is one of the most extensively studied dopant in the various host lattices. [7-11]Liu Huiyong[12] pointed out that AgInSbTe thin film with high antimony content was easy to separate-

out antimony crystalline state firstly when heat-treatment was carried out at low temperature. The reason for the formation of antimony crystalline state may be the introduction of other nucleation sites into the network of alloy.

The electronic and optical properties of semiconductors are strongly influenced by the doping process, which provides the basis for tailoring the desired carrier concentration and consequently, the absorption, emission and transport properties as well. When the density of n-type or p-type doping becomes sufficiently high, the impurity merges with conduction and valence band and causes the formation of band tail and band gap shrinkage.[13-15]

The attempts are made to study the effect of antimony dopant on the physical, compositional, structural, morphological, optical, electrical properties of optimum $Cd_{0.7}Ni_{0.3}Se$ composition and the results are presented and discussed in this paper.

2. Experimental Details

2.1 Deposition of $Cd_{0.7}Ni_{0.3}Se$:Sb thin films

The deposition of typical $Cd_{0.7}Ni_{0.3}Se$:Sb thin films was made in a reactive solution containing 7 mL cadmium sulphate octahydrate (0.25M), 3 mL nickel sulphate (0.25M), 8.5 mL tartaric acid (1M), 14 mL ammonia, 2 mL hydrazine hydrate (50%), 6 mL (5M) NaOH and 10 mL sodium selenosulphate (0.25M). The varying concentration of antimony from 0.01 to 1.0 mol % was used. To obtain Sb-doped $Cd_{0.7}Ni_{0.3}Se$ thin films, the calculated volume of $SbCl_3$ solution was directly added to the reaction bath. Sodium selenosulphate was prepared by following the method reported earlier.[16]All the chemicals used were of AR grade. The total volume of the reaction mixture was made to 150 mL by adding double distilled water. The beaker containing reactive solution was transferred to ice bath of 278 K. The pH was found to be 12.00 ± 0.05. Four-glass substrates were kept vertically in a reaction mixture and rotated with a speed of 50±2 rpm. The temperature of the solution was allowed to rise slowly to room temperatures. After the deposition for 240 min, the substrates were taken out of the bath, rinsed with distilled water, dried in air and kept in desiccator.

2.2 Characterization of Sb-Doped $Cd_{0.7}Ni_{0.3}Se$ Thin Films

The thickness of all thin films was measured with usual weight difference method. The structural properties of the 'annealed' Sb-doped $Cd_{0.7}Ni_{0.3}Se$ thin film samples were recorded by a Philips PW-1710 X-ray diffractometer (XRD) with Cr $K\alpha_1$ radiation in the 2θ range from 10^0-100^0.

The electrical conductivity of all the film was measured using a 'dc' two-probe method. A quick drying silver paste was applied at the ends of the film for ohmic contact purpose. For the

measurements of conductivity, aconstant voltage of 30V was applied across the sample. The current was noted at different temperatures. Maintaining a temperature gradient along the length of a film and the potential difference between the points separated by a 1cm was recorded with a digital microvoltmeter. A calibrated thermocouple probe (chromel-alumel, 24 gauge) with a digital indicator was used to sense the working temperature.

The optical absorption measurements were made in the wavelength range 400-1500 nm by using a Hitachi-330 (Japan) UV-VIS-NIR double beam spectrophotometer at room temperature. Placing an identical, uncoated glass substrate in the reference beam made a substrate absorption correction. The analysis of the spectrum was carried out by computing the values of absorption at every step of 2 nm. A 250MK-III Stereoscan (USA) scanning electron microscope (SEM) was used for the microscopic observations.

3. Results and discussion

3.1 Physical Properties and Compositional Analysis

The 'as deposited' antimony doped, $Cd_{0.7}Ni_{0.3}Se$ thin films were found to be uniform and well adherent to the substrate. The color of the films was found to darken with increase in concentration of Sb. The film thickness increases from 0.65 to 0.74 μm as doping concentration increases upto 0.075 mol%, thereafter it decreases. The increase in film thickness can be explained on the basis of substitutional inclusion of antimony ions in the interstitial position of lattice or in cationic vacancies already present in the host. The thickness of the film is also dependent on the factors such as deposition temperature, deposition time, pH, molar concentration, speed of the rotation, etc. However, in our investigation, all parameters except doping concentration were kept at their optimum values and the films were doped with antimony concentration from 0.0 to1.0 mole %. At higher doping concentration, the impurity atom might be occupying interstitial sites causing an impurity scattering and thereby preventing the further growth of the film. [17] The thickness was measured every 30 minutes and plotted against time of deposition as shown in **Fig.1** for 0.075 mol % antimony concentration. The nucleation was not observed within first 30 minutes which indicates that the process requires an induction time for the nucleation on substrate. This also suggests that the process of deposition follows ion-by–ion growth mechanism instead of cluster-by-cluster. Growth kinetics for the development of typical $Cd_{0.7}Ni_{0.3}Se$:Sb (0.075 mol% Sb) is shown in **Fig.2** The figure shows that, in early stages of growth the deposition varies linearly with deposition temperature and then decreases after typical temperature.

The film composition was determined by dissolving the known weight of film material in concentrated HNO_3 and analyzing the film by atomic absorption spectroscopy. From these studies, the actual amount of antimony entered into the lattice of $Cd_{0.7}Ni_{0.3}Se$ was calculated. The amount of metal ion is taken in the bath and those obtained from AAS analysis are given in **Table 1**

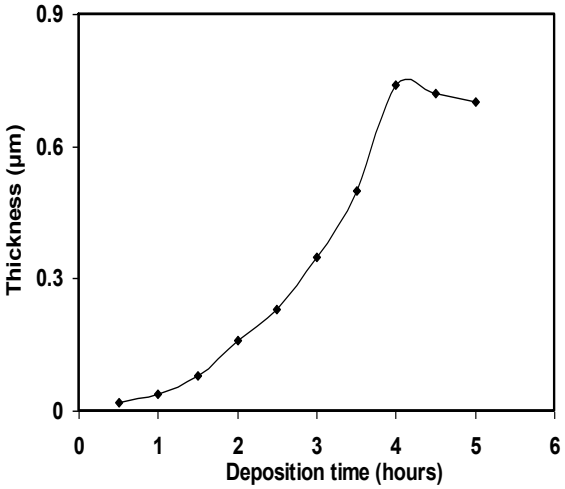


Fig.1. A plot of film thickness versus time for $Cd_{0.7}Ni_{0.3}Se$: Sb thin film (0.075 mol% antimony concentration)

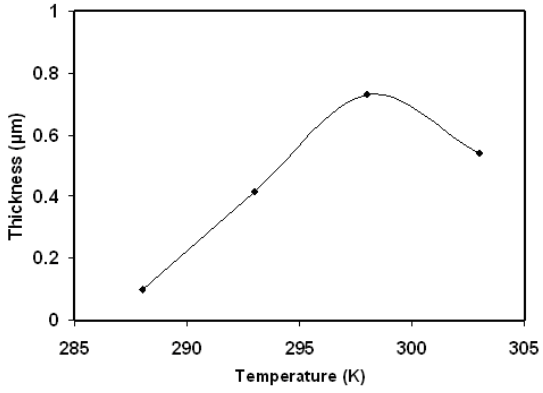


Fig.2. A plot of film thickness versus temperature for $Cd_{0.7}Ni_{0.3}Se$: Sb thin film (0.075 mol% antimony concentration)

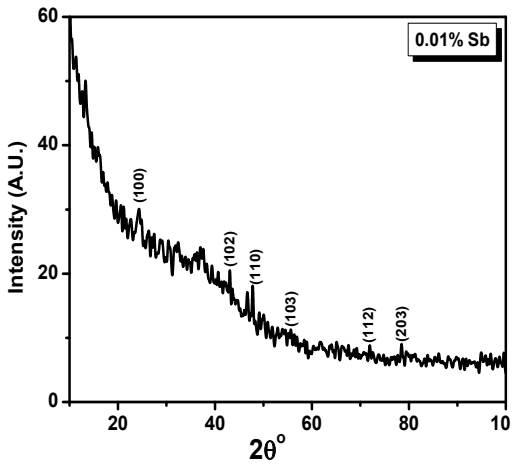
3.2 X-Ray Diffraction Studies

X-ray diffractograms of 'annealed' antimony-doped $Cd_{0.7}Ni_{0.3}Se$ thin films deposited on glass substrate are shown in **Fig.3.** The crystallographic study reveals that doped samples are polycrystalline in nature. In the present investigation, Sb-doped $Cd_{0.7}Ni_{0.3}Se$ thin films were found to be hexagonal in nature. The spectra for pure CdSe [JCPDF Card No.08-0459] and pure NiSe [JCPDF Card No.75-0610] were used for identification purpose.

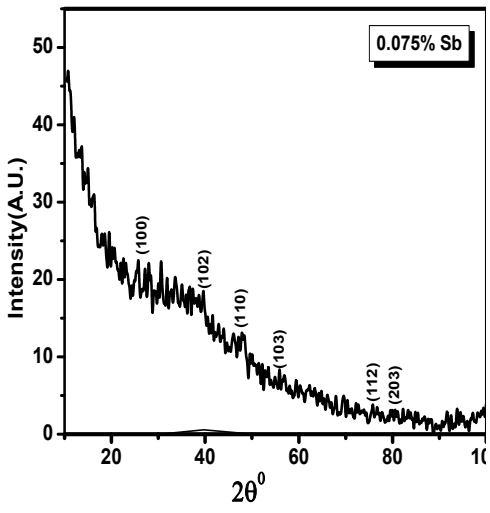
The analysis of spectrum indicated that the films are having hexagonal structure in the whole range of compositions studied. The analysis of XRD patterns in terms of hkl planes, interplanar distances, cell size and lattice parameters has been done by considering hexagonal structure and is cited in **Table-2**. The most intense reflection observed for all the thin films were originating from (100) plane. Along with (100) plane, (102) (110) (103) (112) (203) planes are also observed. The peak intensity and crystallinity of the films were found to increase with dopent concentration upto 0.075 mol %. Lattice constants were determined by using following equation;

$$1/d^2_{hkl} = 4/3\ (h^2+hk+k^2/a^2) + l^2/c^2 \quad \text{----------1}$$

It is found that upto 0.075 mol% Sb, the lattice parameter increases smoothly from 5.3063 to 5.3071 Å for 'c' and 3.4794 to 3.4805 for 'a' and thereafter decreases upto 5.3062 Å for 'c' and 3.4790 Å for 'a' for 1.0 mol% antimony concentration. The average crystallite size was calculated by resolving the highest intensity peak (100). The average crystallite size was determined by using Scherrer's formula. Upto 0.075 mol% Sb, the particle size increases from 318 to 377 Å, thereafter decreases upto 246 Å for 1.0 mol% Sb concentration.



(a)



(b)

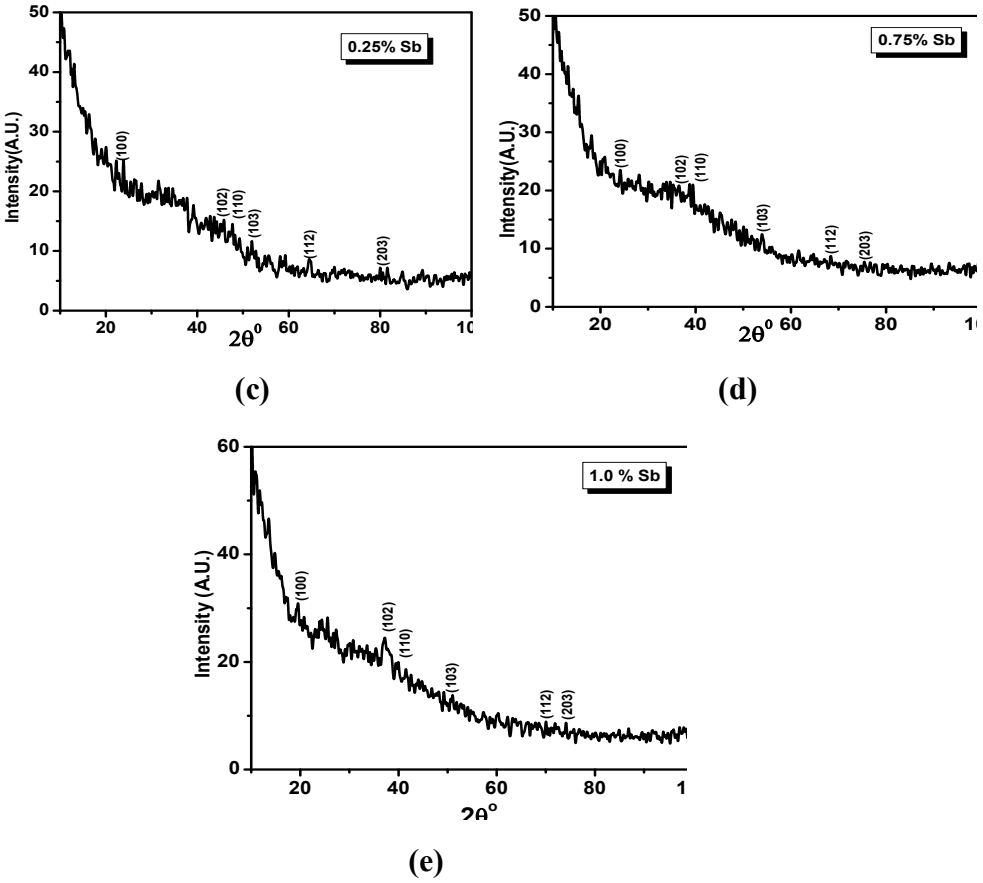


Fig.3.XRD patterns of representative Sb-doped $Cd_{0.7}Ni_{0.3}Se$ thin films
(a) 0.01 mol% Sb (b) 0.075 mol % Sb (c) 0.25mol % Sb (d) 0.75 mol% Sb(e) 1.0 mol % Sb

3.3 Microscopic Analysis

The SEM micrographs of$Cd_{0.7}Ni_{0.3}Se$:Sb samples are shown in **Fig.4** at 10000X magnification. $Cd_{0.7}Ni_{0.3}Se$:Sb thin films are seen to be homogenous, without cracks or pinhole and well cover the glass substrate. Smooth background that may correspond to some amorphous phase of NiSe as well as CdSe. The presence of fine background is an indication of one-step growth by multiple nucleations. The grain size calculated from SEM was found to tally with those obtained using the XRD. The observed grain size is listed in **Table-2.**

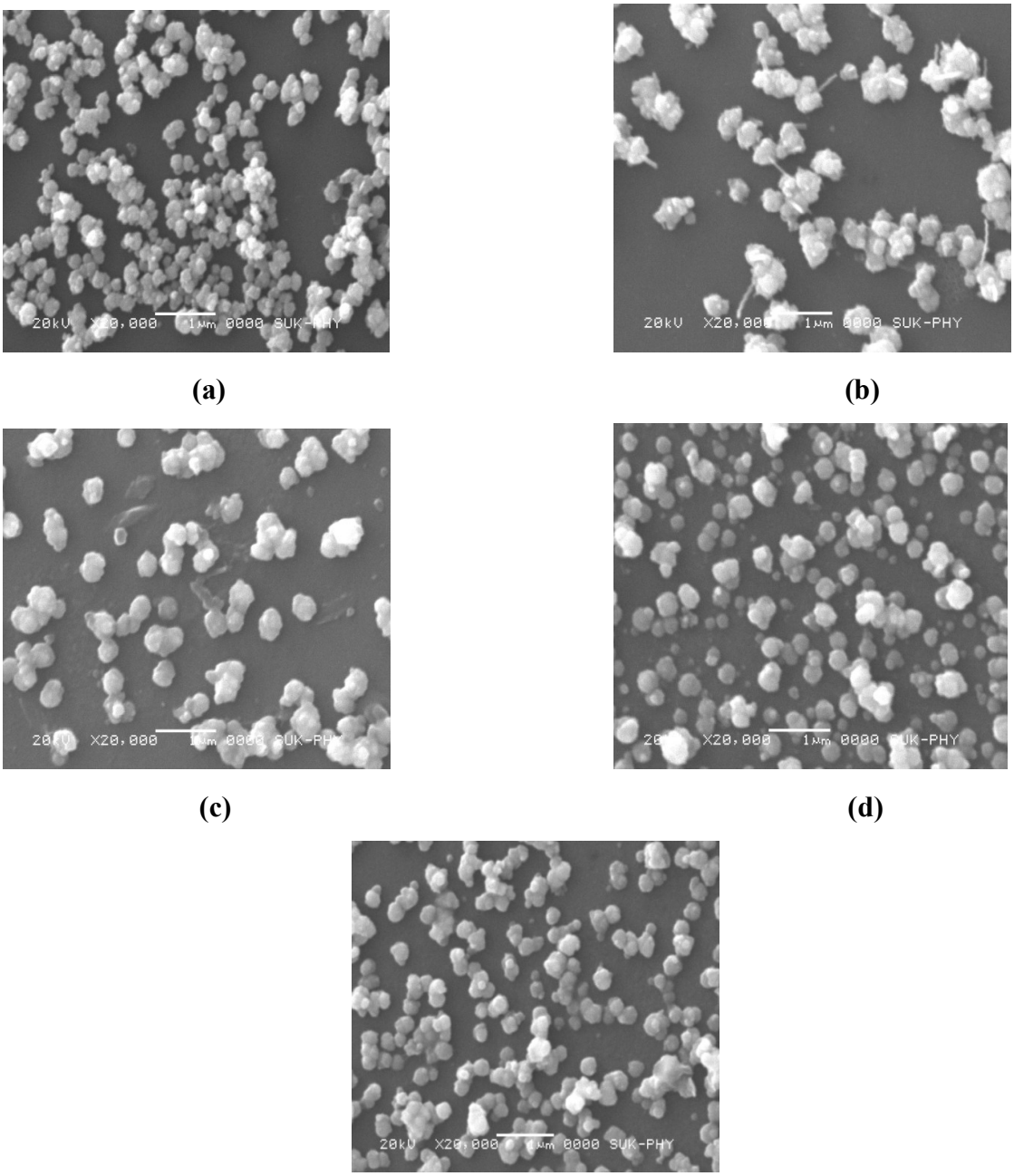


Fig.4.SEM micrographs of representative Sb-doped $Cd_{0.7}Ni_{0.3}Se$:Sb thin films
(a) 0.01 mol% Sb (b) 0.075 mol % Sb (c) 0.25mo l% Sb(d) 0.75 mol% Sb (e) 1.0 mol% Sb

3.4 Optical Studies

The optical properties of as deposited samples have been studied in the wavelength range from 400-1500 nm without considering losses due to reflection and scattering at room temperature. The absorption spectra are used to calculate absorption coefficient, optical band gap and type of transition. The absorption spectra of representative antimony doped films are shown in **Fig.5.** For all compositions, the value of absorption coefficient is high ($\alpha \times 10^4$ cm^{-1}). The value of absorption coefficient depends upon radiation energy as well as composition of the film. The data were systematically studied in the vicinity of the absorption edge on the basis of three-dimensional model. The interpretation of the results can be easily done with the help of formula derived for three-dimensional crystal. The simplest form of equation obeyed near and above absorption edge is; [18]

$$\alpha h\upsilon = A(h\upsilon - Eg)^n \text{----------2}$$

where the symbols have their usual meaning. Upto 0.075 mole % Sb, the absorption is edge shifted towards higher wavelength. This is due to filling of low lying energy level by conduction electron and segregation of the impurity along the grain boundary.[19] A plot of $(\alpha h\upsilon)^2$vs. $h\upsilon$ should be a straight line whose intercept to the x-axis gives the optical band gap. The plots of $(\alpha h\upsilon)^2$vs. $h\upsilon$ for 'as deposited' samples are shown in **Fig.6.** The linear nature of plot shows the existence of direct transition. It is observed that the band gap decreases from 1.61 eV to 1.54 eV as the antimony concentration increases upto 0.075 mol %. Above 0.075 mol % Sb the band gap increases from 1.54 to 1.64 eV. This is probably due to increased amount of disorder caused by addition of antimony in the host lattice.[20] The variation of band gap with different concentrations of antimony is shown in **Fig.7.**

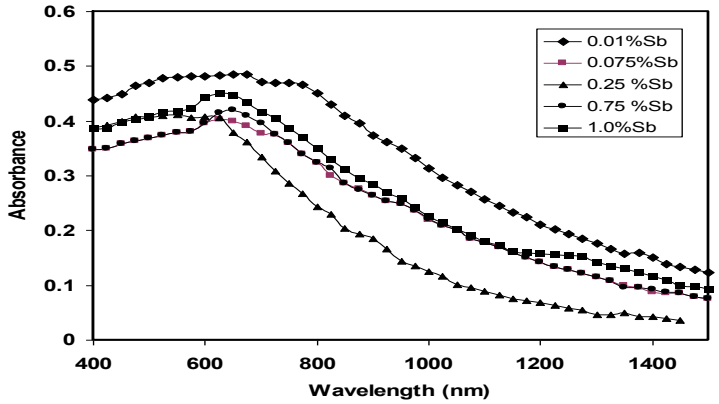
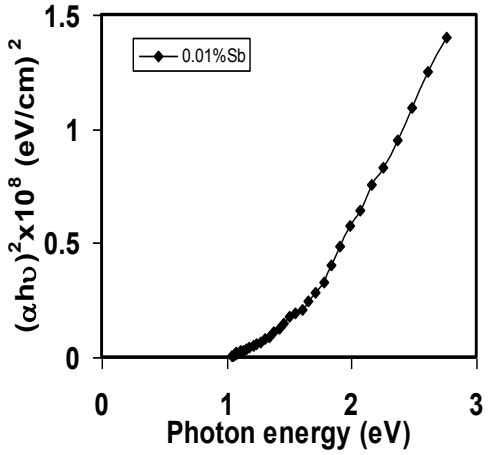
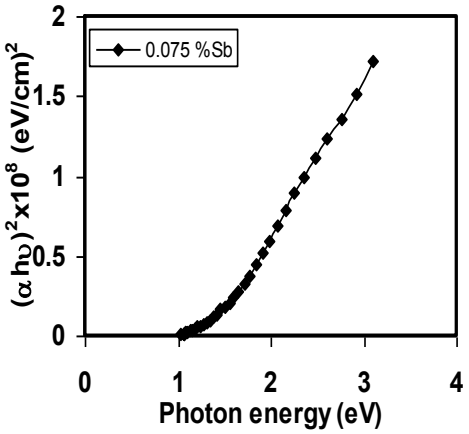


Fig.5. Absorption spectra of Sb-doped $Cd_{0.7}Ni_{0.3}Se$ thin films

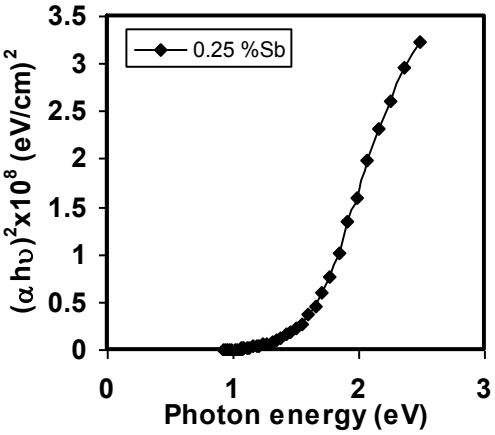
(doping concentration 0.01, 0.075, 0.25, 0.75, 1.0 mol %, antimony)


0.01%Sb
$(\alpha h\upsilon)^2 x10^8$ (eV/cm)^2
Photon energy (eV)

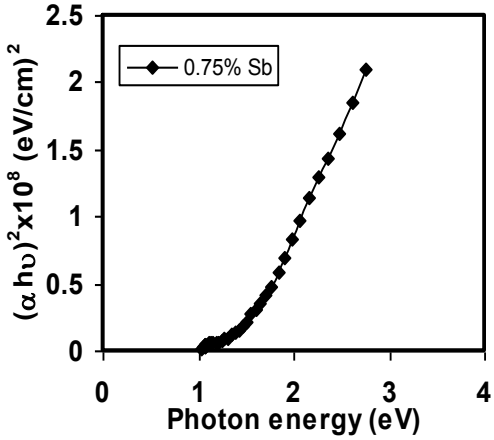
(a)


0.075 %Sb
$(\alpha h\upsilon)^2 x10^8$ (eV/cm)^2
Photon energy (eV)

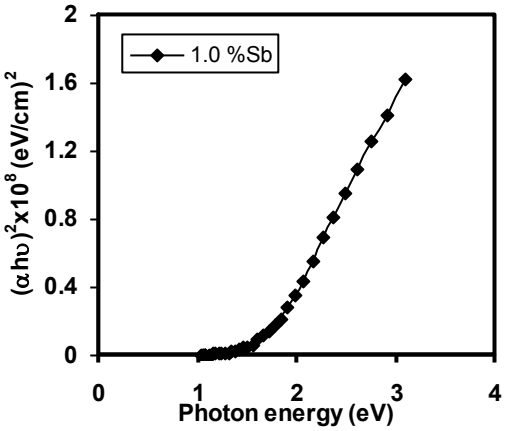
(b)


0.25 %Sb
$(\alpha h\upsilon)^2 x10^8$ (eV/cm)^2
Photon energy (eV)

(c)


0.75% Sb
$(\alpha h\upsilon)^2 x10^8$ (eV/cm)^2
Photon energy (eV)

(d)



(e)

Fig.6. Determination of band gap of $Cd_{0.7}Ni_{0.3}Se$:Sb thin films (doping concentration 0.01, 0.075, 0.25, 0.75 and 1.0 mol % antimony)

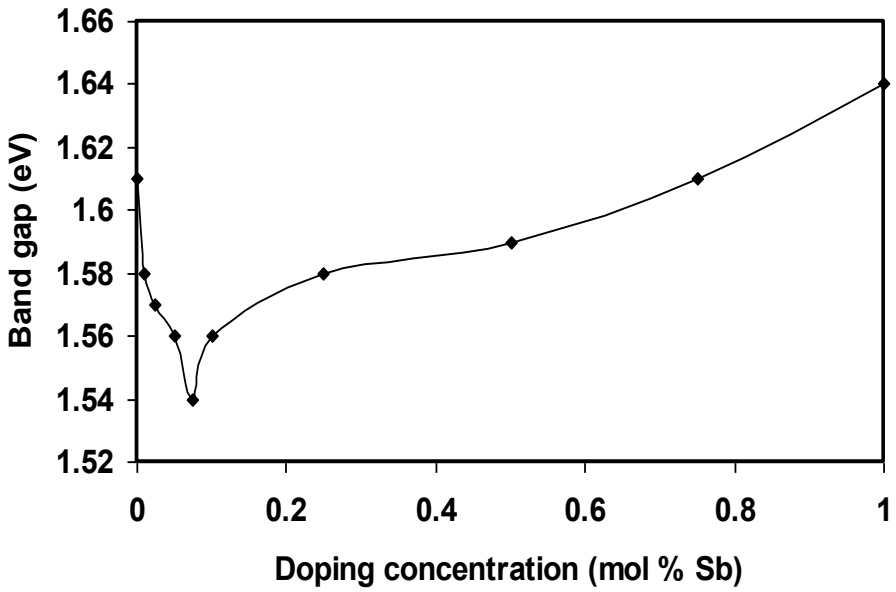


Fig.7. Variation of band gap with doping concentration for Sb-doped $Cd_{0.7}Ni_{0.3}Se$ thin films

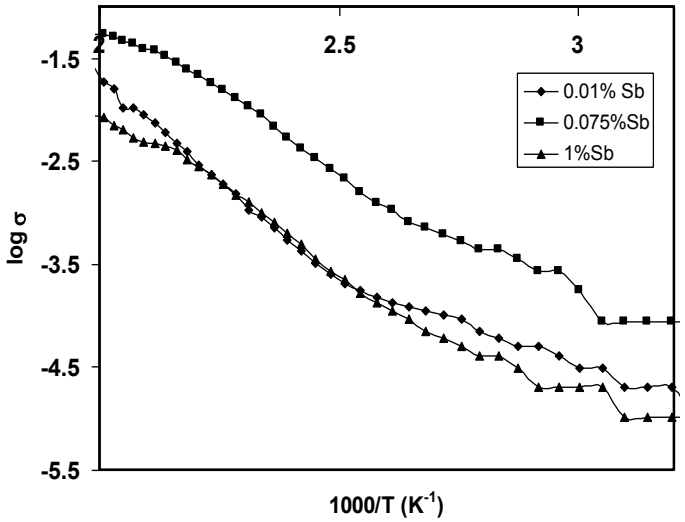
3.5 Electrical and Thermoelectrical Properties

The electrical conductivity of 'as deposited' Sb-doped $Cd_{0.7}Ni_{0.3}$Sethin film on non-conducting glass slide was determined by using a 'dc' two-probe method in the temperature range 300-525 K. The variation of log (conductivity) versus inverse absolute temperature for the

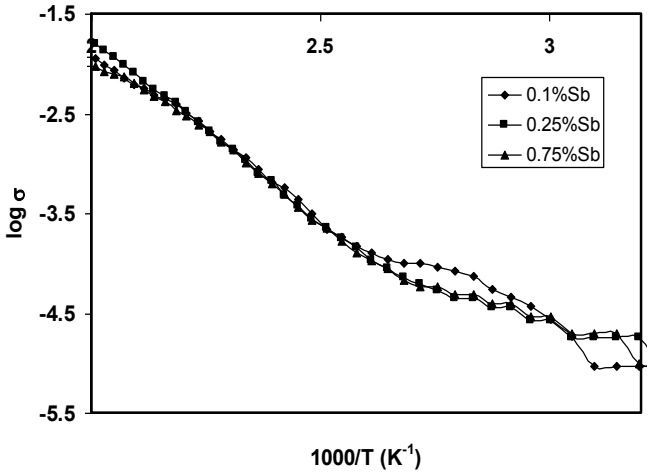
cooling curve is shown in **Fig.8**. The electrical conductivity at room temperature increases as the antimony concentration increases upto 0.075 mol % and there after value decreases for higher concentration. Up to 0.075 mole % incorporation of Sb in the lattice results in decrease in boundary potential and improvement in crystallite size, which results in increase of carrier concentration as well as mobility.[21] As the size of Sb^{3+} ion is less than that of Cd^{2+} ion, the incorporation could cause a scattering process thereby reducing the mobility.[22-23] Above 0.075 mole % Sb the conductivity decreases, as more and more distortion is observed in the lattice structure, which results in increase in grain boundary scattering, thereby reducing the carrier mobility. [24-28] The electrical conductivity variation with temperature during heating and cooling cycles was found to be different and this shows that the 'as deposited' films undergo irreversible changes due to annealing out of non-equilibrium irreversible changes defects during first heating. The activation energy is calculated using exponential form of Arrhenius equation;

$$\sigma = \sigma_o \exp(-Ea/kT) \text{---------- 3}$$

Where the terms have usual meaning. The activation energy is found to decrease upto 0.075 mole % and increase for higher concentration. The value of activation energy as well as specific conductivity at 300 and 525 K is listed in **Table -3**.



(a)



(b)

Fig.8. Plot of log (conductivity) versus 1000/T for $Cd_{0.7}Ni_{0.3}Se$:Sb thin films

Table-1: Compositional analysis of $Cd_{0.7}Ni_{0.3}Se$:Sb thin films

Sr. No.	Mole % of Sb in $Cd_{0.7}Ni_{0.3}Se$	Bath content in ppm				Film content in ppm			
		Cd	Ni	Se	Sb	Cd	Ni	Se	Sb
01	0.0	786.87	172.77	760	----	210.13	47.20	218.00	------
02	0.01	786.87	172.77	760	0.283	207.12	45.46	201.20	0.0745
03	0.025	786.87	172.77	760	0.708	212.66	46.70	205.41	0.1913
04	0.05	786.87	172.77	760	1.418	201.76	44.51	195.68	0.3639
05	0.075	786.87	172.77	760	2.124	223.12	49.36	216.48	0.6068
06	0.1	786.87	172.77	760	2.837	218.57	47.99	211.15	0.7881
07	0.25	786.87	172.77	760	7.094	204.23	44.84	213.59	2.0864
08	0.5	786.87	172.77	760	14.18	219.57	48.80	186.14	3.4586

09	0.75	786.87	172.77	760	21.28	209.16	47.12	180.95	5.0667
10	1.0	786.87	172.77	760	28.36	214.31	45.10	188.56	9.1483

Table-2: Crystallographic parameters of $Cd_{0.7}Ni_{0.3}Se$:Sb thin films

Mole % of Sb in $Cd_{0.7}Ni_{0.3}Se$	Observed 'd' values (Å)	Std. 'd' values(Å)		hkl	Grain Size(Å)		Cell Parameters (Å)
		NiSe (H)	CdSe (H)		XRD	SEM	
0.0	3.555	3.169	3.720	100	318	322	a=3.4794 c=5.3063
	2.398	2.039	2.554	102			
	2.055	1.830	2.151	110			
	1.851	1.549	1.980	103			
	1.737	1.509	1.834	112			
	1.374	1.183	1.456	203			
0.01	3.557	3.169	3.720	100	300	325	a=3.4796 c=5.3064
	2.399	2.039	2.554	102			
	2.056	1.830	2.151	110			
	1.853	1.549	1.980	103			
	1.739	1.509	1.834	112			
	1.376	1.183	1.456	203			
0.025	3.559	3.169	3.720	100	326	333	a=3.4798 c=5.3065
	2.401	2.039	2.554	102			
	2.058	1.830	2.151	110			
	1.855	1.549	1.980	103			
	1.741	1.509	1.834	112			
	1.378	1.183	1.456	203			

0.05	3.562	3.169	3.720	100	358	364	a=3.4801
	2.403	2.039	2.554	102			c=5.3067
	2.061	1.830	2.151	110			
	1.858	1.549	1.980	103			
	1.745	1.509	1.834	112			
	1.380	1.183	1.456	203			
0.075	3.565	3.169	3.720	100	377	384	a=3.4805
	2.407	2.039	2.554	102			c=5.3071
	2.062	1.830	2.151	110			
	1.858	1.549	1.980	103			
	1.748	1.509	1.834	112			
	1.385	1.183	1.456	203			
0.1	3.562	3.169	3.720	100	349	355	a=3.4800
	2.405	2.039	2.554	102			c=5.3069
	2.063	1.830	2.151	110			
	1.860	1.549	1.980	103			
	1.746	1.509	1.834	112			
	1.383	1.183	1.456	203			
0.25	3.560	3.169	3.720	100	301	307	a=3.4797
	2.403	2.039	2.554	102			c=5.3067
	2.060	1.830	2.151	110			
	1.858	1.549	1.980	103			
	1.744	1.509	1.834	112			
	1.382	1.183	1.456	203			
0.50	3.558	3.169	3.720	100	281	286	a=3.4794
	2.400	2.039	2.554	102			c=5.3066
	2.058	1.830	2.151	110			
	1.856	1.549	1.980	103			

	1.744 1.380	1.509 1.183	1.834 1.456	112 203			
0.75	3.556 2.394 2.056 1.852 1.739 1.378	3.169 2.039 1.830 1.549 1.509 1.183	3.720 2.554 2.151 1.980 1.834 1.456	100 102 110 103 112 203	277	270	a=3.4792 c=5.3063
1.0	3.553 2.393 2.054 1.849 1.736 1.375	3.169 2.039 1.830 1.549 1.509 1.183	3.720 2.554 2.151 1.980 1.834 1.456	100 102 110 103 112 203	246	250	a=3.4790 c=5.3062

Table -3: Optical and electrical parameters of $Cd_{0.7}Ni_{0.3}Se$:Sb thin films

Sr. No.	Mole % of Sb in $Cd_{0.7}Ni_{0.3}Se$	Band Gap (eV)	Specific conductivity $(\Omega\ cm)^{-1}$		Thickness (µm)	Activation energy (eV)
			At 300K	At 525K		
1	0.0	1.61	1.04×10^{-5}	7.1×10^{-3}	0.64	0.530
2	0.01	1.58	1.0×10^{-5}	3.2×10^{-2}	0.66	0.502
3	0.025	1.57	9.95×10^{-6}	2.4×10^{-2}	0.70	0.503
4	0.05	1.56	9.66×10^{-6}	8.5×10^{-3}	0.72	0.495
5	0.075	1.54	8.88×10^{-5}	5.5×10^{-2}	0.74	0.493

6	0.1	1.56	9.25×10^{-6}	1.2×10^{-2}	0.73	0.512
7	0.25	1.58	9.1×10^{-6}	1.6×10^{-2}	0.70	0.524
8	0.5	1.59	9.52×10^{-6}	1.1×10^{-2}	0.68	0.521
9	0.75	1.61	9.8×10^{-6}	9.4×10^{-3}	0.66	0.501
10	1.0	1.64	0.10×10^{-6}	8.7×10^{-3}	0.65	0.509

4. Conclusions

Antimonydoped $Cd_{0.7}Ni_{0.3}Se$ thin films have been deposited by chemical bath deposition method using tartarate bath at 298 K. The antimony donor atoms were found to dissolve substitutionally in the lattice of $Cd_{0.7}Ni_{0.3}Se$ upto a certain range of doping concentration. The films grow highly oriented in the hexagonal phase. The crystallinity and particle size were found to increase with antimony concentration upto 0.075 mol % whereas for higher values of antimony, the material shows decreased crystallinity. The grain size calculated by SEM tallies with the particle size calculated by XRD. The absorption study shows presence of direct band gap transition. The band gap decreases from 1.61 to 1.54 eV as the doping concentration increases from 0.0 to 0.075 mol % whereas for higher values of antimony, the band gap increases. The specific conductance at room temperature for all the films was found to be of the order of 10^{-6} $(\Omega\ cm)^{-1}$. The electrical conductivity study indicated presence of only one conduction mechanism. The conductivity increases while activation energy decreases upto 0.075 mol% Sb

References

1) B. V. Jadhav,P. P. Hankare, S. D. Delekar, J. Mater Sci: Mater Electron.,22 (2011) 1433–1442
2) L.P.Deshmukh, S.G.Holikatti, B.M.More, *Mater. Chem. Phys.,* 39 (1995) 743.
3) S.H.Pawar, L.P.Deshmukh, *Ind. J. Pure Appl. Phys.,* 22 (1884) 315.
4) N.R.Pavaskar, C.A.Menezes, A.B.P.Sinha, *J. Electrochem. Soc.,*124 (1977) 743.
5) H.Gerischer, *Electroanal.Chem.,*58 (1975) 263.
6) L.P.Deshmukh, A.B.Palwe, V.S.Sawant, *Sol. Ener. Mater.,* 20(1990) 341.
7) C. E. C. Wood, T. M. Kerr, T. D. McLean, D. I. Westwood, J.D. Medland, Bright S, Davies R, *J. Appl. Phys.,* 60 (1986) 1300.

8) X .Jang, M. J. Jurkovic, J. B. Heroux, W I Wang, *Appl. Phys. Lett.,* 75 (1999) 178.
9) E. U. Masumdar, S.H. Mane, V.B. Pujari, L. P. Deshmukh, *Ind. J. Pure and Appl. Phys.,* 40 (2002) 624.
10) W. Ha, V. Gambin, M.Wistey, S. Bank, H. Yuen, S. Kim, J .S. Harris, *Electron. Lett.,* 38 (6) (2002) 277.
11) K .Volz, V .Gambin, W Ha, Wistey M, H .Yuen, S. Bank, J. Harris, *J. Crystal Growth*, 251 (2003) 360.
12) H .Y. Liu, Ph.D. Thesis, Shanghai Institute of Optics and Fine Mechanics, *Chinese Academy of Sciences,* 1998.
13) G.Perna, V.Capozzi, A.Minafra, M.Pallara, M.Ambrico, *Eur. Phys. J.* B,32 (2003) 339.
14) E.O. Kane, *Phys. Rev.* 131 (1969) 79.
15) A.Haufe, R.Schwabe, H.Fieseler, M.Ilegems, *J. Phys. C,* 21 (1988) 2951.
16) P.P.Hankare, P.A.Chate, S.D.Delekar, V.M.Bhuse, M.R.Asabe, B.V.Jadhav, K.M.Garardkar, *Crystal Growth,* 291 (2006) 40.
17) S.Jatar, A.C.Rastogi, V.G.Bhide, *Pramana,* 16 (1978) 477.
18) J. Bardeen, F.J. Blutt, L.H. Hall, *in: R. Brechepride Russel, E Hahn (Eds.)Proceedings of the Photoconductivity Conference, Wiley, NY* (1975).
19) L.P.Deshmukh, B.M.More, S.G.Holikatti, *Bull. Mater. Sci.,*17 (1994) 455.
20) S.Bhushan, S.Srivastav, *Ind. J. Pure Appl. Phys.,* 33 (1995) 371.
21) J. Rodriguez, G .Gordillo, *Sol. Ener. Mater., 19* (1989) 421.
22) B.D.Culity, *Elements of X-ray Diffraction, 2nd edition, Wesley Pub. Co; Inc. Phillipine,* (1978).
23) S.Chandra in *"Photoelectrochemical Cells" Vol. 5 (Ed) D.S.Campbell, Gardon and Breach Science Publishers, New York,* 1985.
24) L.P.Deshmukh, C.B.Rotti, G.S.Shahane, *Ind. J. Pure Appl. Phys.,* 36 (1998) 322.
25) K.Subramanian,V.Sunder Raja, *Sol. Ener. Mat. Sol. Cells,* 32 (1994) 1.
26) C.N.R.Rao,*"Modern Aspects of Solid State Chemistry", Plenum Press, New York,* (1970) 531.
27) L.P.Deshmukh, G.S.Shahane, *Int. J. Electron.,* 83 (1997) 341.
28) B.N.Oshchenin, *Phys. Status Solidi (a),* 31 (1976) 35.