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Synthesis and characterization of chemically deposited nickel substituted CdSe thin film

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ABSTRACT

The technologically important $Cd_{0.5}Ni_{0.5}Se$ thin film has been developed by solution growth technique on non-conducting glass substrate in tartarate bath containing Cd^{+2}, Ni^{+2} ions and sodium selenosulphate in an aqueous alkaline medium at room temperature. Various preparative conditions of the thin films are outlined. The films were characterized by X-ray diffraction, scanning electron microscope, optical absorption and electrical measurements. The X-ray diffraction study indicates that the film is polycrystalline in nature with hexagonal phase. Scanning electron micrograph shows that the film is homogeneous with well-defined grains. The films have high optical absorption coefficient. Thermoelectric power measurement shows p-type conduction mechanism.

1. Introduction

Solid solutions with semiconducting properties are of intrinsic interest because of their potential applications in semiconductor technology. The electronic and optical properties of binary and ternary semiconducting materials of groups II–VI have been extensively studied due to their important non-linear, luminescent properties and quantum size effect [1,2]. CdSe is a direct band gap material with optimum band gap. CdSe has high absorption coefficient and suitable to cope up with the solar spectrum [3]. A ternary system $Cd_{0.5}Ni_{0.5}Se$ composed of NiSe and CdSe can be engineered for better application purpose. Semiconductor with band gap of 1.2 eV [4] has appropriate electrical and optical characteristics suitable for solar applications. Therefore, our interest is to study electrical and optical properties of nickel substituted CdSe semiconducting material which is useful for solar applications. CdSe and NiSe thin films have been prepared by molecular beam epitaxy, electron beam evaporation, electrodeposition, chemical vapour deposition, spray pyrolysis, sputtering and chemical bath deposition [3–5]. The chemical bath deposition is emerged as an important method due to several advantages such as low cost, low processing temperature and large area deposition capability [6–10]. An intimate contact between the reacting solution and the substrate material permits for pinhole free and uniform deposits on the substrates. The process of film growth is slow which facilitates better orientation of the crystallites with improved grain structure [11,12]. Chemical bath deposition method requires a source of chalcogen ions and complexed metal ions of interest. The stability equilibrium of the complex provides a concentration of ions small enough for controlled homogenous precipitation of the material in the form of thin film on the substrate [13,14].

In this paper, we report the synthesis of typical $Cd_{0.5}Ni_{0.5}Se$ thin film by chemical bath deposition method. The various aspects of thin films like growth mechanism, characterization and its properties are discussed.

2. Experimental details

2.1. Substrate cleaning

The deposition was carried out on glass slides of 76 mm × 26 mm × 2 mm dimensions. The substrates were cleaned by boiling them in chromic acid for 1 h, then degreased with acetone and finally washed repeatedly with double distilled water.

2.2. Reagents and preparation of solution

All reagents used for the deposition were of analytical grade. Regents used were cadmium sulphate octahydrate (99%, E-Merck), nickel sulphate octahydrate (98%, E-Merck), tartaric acid (99.5%, s.d. fine), anhydrous sodium sulphite (98%, Qualigens), selenium powder (99.99%, s.d. fine), and ammonia solution (25%, s.d. fine). The solutions were prepared in double distilled water. Sodium selenosulphate (∼0.25 M) solution was prepared by refluxing 5 g of selenium powder with 15 g

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anhydrous sodium sulphite in 200 ml double distilled water for 9 h at 363 K. The solution was cooled, filtered to remove undissolved selenium and stored in an airtight container.

2.3. Deposition of $Cd_{0.5}Ni_{0.5}Se$ thin film

For the deposition of a typical $Cd_{0.5}Ni_{0.5}Se$ thin film, the chemical bath constituted 5 ml (0.25 M) cadmium sulphate octahydrate, 5 ml (0.25 M) nickel sulphate octahydrate, 2.5 ml (1 M) tartaric acid, 7 ml ammonia solution and 10 ml (0.25 M) sodium selenosulphate solution. 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. The glass substrates were kept vertically in the reaction mixture and rotated with a speed of 50 ± 2 rpm. The temperature of the solution was allowed to rise slowly to room temperature. After four hours, the deposited substrates were taken out of the bath and washed several times with double distilled water. The film was dried at room temperature and preserved in desiccator.

2.4. Sample characterization

The $Cd_{0.5}Ni_{0.5}Se$ thin film was characterized by using a Philips PW-1710 X-ray diffractometer in 2θ range from 10° to 80° using Cu $K_{\alpha1}$(λ = 1.54056 Å). The film composition was determined by using Perkin-Elmer 3030 atomic absorption spectrophotometer. The electrical conductivity measurement was carried out in temperature range 300–525 K on Zintek-502 BC Miliohmmeter using d.c. two-probe method. Silver paste was used for good ohmic contact purpose. Thermoelectric power measurement was done by applying temperature gradient on a length of a film. A chromel–alumel thermocouple (24 gauge) was used to sense the working temperature. The optical absorption spectra were recorded in wavelength range 400–1200 nm by using a Hitachi-330 (Japan) double beam spectrophotometer at room temperature. A study of surface morphology of thin film was done under scanning electron microscope (SEM) Stereoscan 250 MK-III (Cambridge, UK). The thickness of $Cd_{0.5}Ni_{0.5}Se$ film was measured by weight difference method by using sensitive microbalance.

3. Results and discussion

3.1. Kinetic studies and reaction mechanism

The rate of deposition of $Cd_{0.5}Ni_{0.5}Se$ thin film mainly depends upon supersaturation, pH, temperature of the bath and composition of the reactive species. The reaction mixture prepared by mixing cadmium sulphate, nickel sulphate, ammonia, tartaric acid and sodium selenosulphate at 278 K. It forms clear solution and no film or precipitate is observed. After induction period of 30 min, colour of the mixture changes and results in dissociation of metal complexes and sodium selenosulphate in the formation of thin film. Alkaline medium favours the deposition of film. The growth kinetics of the film can be understood from the following reaction.

$$M^{+2} + nA^{-2} \leftrightarrow [M(A)_n]^{-2(n-1)} \quad (M^{+2} = Cd^{+2}/Ni^{+2})$$

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^-$$

$$HSe^- + OH^- \rightarrow H_2O + Se^-$$

$$(1/2)[Cd(A)_n]^{-2(n-1)} + (1/2)[Ni(A)_n]^{-2(n-1)} + Se^{-2} \rightarrow Cd_{0.5}Ni_{0.5}Se + nA^{-2}$$

where 'A' is a tartarate ions used as a complexing agent.

In chemical bath deposition method, the ionic product exceeds or becomes equal to the solubility product and the film formation takes place by the recombination of ions on the substrate surface via nucleation followed by growth process. For pseudo binary cadmium chalcogenide film obtained from the alkaline medium, $Cd(OH)_2$ is known to act as a seeding nucleus [15]. The temperature increase creates free Cd^{+2} ions, which combine with Se^{-2} ions preferentially on the substrate than Ni^{+2} ions producing orange layer of CdSe. This CdSe layer acts as a catalyst for further growth of the film. The formed layer grows further by adsorbing more and more Cd^{+2}, Ni^{+2} and Se^{-2} ions to form ternary $Cd_{0.5}Ni_{0.5}Se$ thin film.

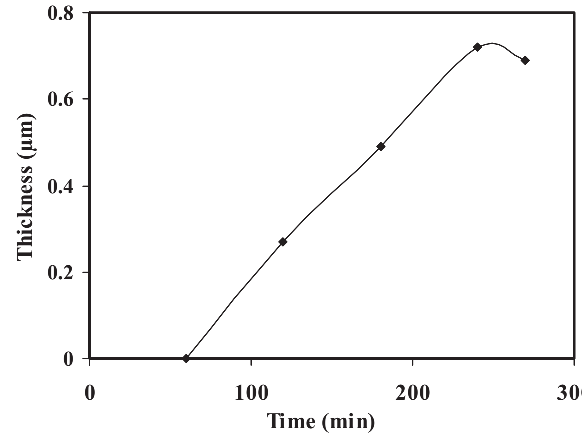

Fig. 1. A plot of thickness versus time (for $Cd_{0.5}Ni_{0.5}Se$ thin film).

During the growth of the film, nucleation was not observed within the first 30 min and hence the process requires an induction period for the nucleation on the substrate. This suggests ion-by-ion growth mechanism instead of cluster-by-cluster formation. The present study indicates that homogeneous $Cd_{0.5}Ni_{0.5}Se$ thin film has been deposited at 240 min. The thickness was measured every 30 min and plotted against time as shown in Fig. 1. All the films were homogenous, reflecting and well adherent to the substrate.

3.2. X-ray diffraction studies

Fig. 2 shows X-ray diffraction pattern of $Cd_{0.5}Ni_{0.5}Se$ thin film deposited on glass substrate annealed at 373 K. The spectra for pure CdSe [JCPDF Card No.08-0459] and pure NiSe [JCPDF Card No. 75-0610] were used for identification purpose. The presence of large number of peaks indicates that the films are polycrystalline in nature with hexagonal structure.

The analysis of XRD pattern in terms of $h\,k\,l$ planes, interplanar distances and cell size have been done by considering hexagonal structure and data is summarized in Table 1. The lattice parameters of hexagonal phase were calculated by using the standard relation

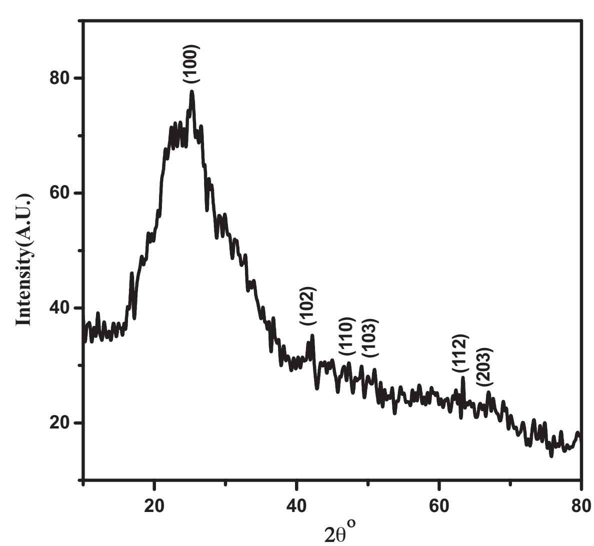

Fig. 2. XRD pattern of $Cd_{0.5}Ni_{0.5}Se$ thin film.

Table 1
Crystallographic parameters of $Cd_{0.5}Ni_{0.5}Se$ thin film.

Composition	d_{obs} (Å)	d_{std} (Å)		hkl planes	Grain size (Å)		Lattice constant (Å)
		NiSe (H)	CdSe (H)		XRD	SEM	
$Cd_{0.5}Ni_{0.5}Se$	3.444	3.169	3.720	100	342	348	a = 3.430, c = 5.277
	2.294	2.039	2.554	102			
	1.991	1.830	2.151	110			
	1.765	1.549	1.980	103			
	1.672	1.509	1.834	112			
	1.319	1.183	1.456	203			

[16],

$$\frac{1}{d^2}hkl = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (1)$$

The lattice parameters 'a' and 'c' of $Cd_{0.5}Ni_{0.5}Se$ thin film were found to be 3.4300 Å, 5.2770 Å, respectively. These lattice parameter values were compared with pure CdSe [17] and NiSe [18] parameters and its observed that, the values are shifted towards lower 'd' values in $Cd_{0.5}Ni_{0.5}Se$ thin film. The average crystallite size was determined by using Scherrer's formula,

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where 'D' is crystallite size, 'λ' is the wavelength of X-ray used, 'β' is the angular line width of half maximum intensity, 'θ' is Bragg's diffraction angle and 'K' is constant (0.9). The average crystallite size of $Cd_{0.5}Ni_{0.5}Se$ thin film was 342 Å.

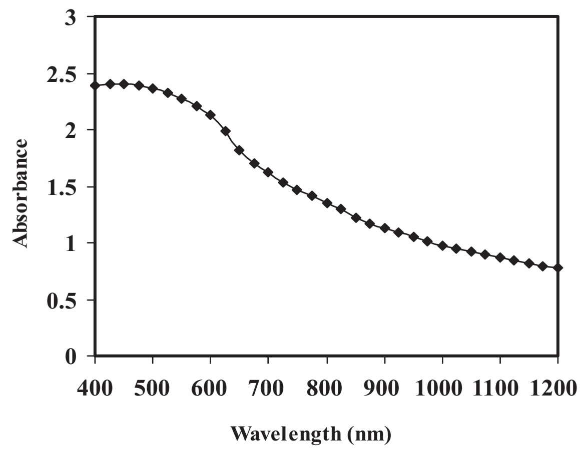

Fig. 4. Absorption spectra for $Cd_{0.5}Ni_{0.5}Se$ thin film.

3.3. Morphological studies

The scanning electron micrograph of annealed $Cd_{0.5}Ni_{0.5}Se$ thin film is shown in Fig. 3. Examination of the figure indicates that the film is homogeneous with well-defined spherical grains. The average grain size calculated from SEM was found to be 348 Å and well matched with XRD.

3.4. Optical studies

The optical absorption spectra of $Cd_{0.5}Ni_{0.5}Se$ thin film deposited onto glass substrate was studied at room temperature in the wavelength range of 400–1200 nm without considering losses due to reflection and transmission. The optical absorption spectra of $Cd_{0.5}Ni_{0.5}Se$ thin film is shown in Fig. 4. The data were examined in the vicinity of the absorption edge on the basis of three-dimensional model. The simplest form of equation obeyed near and above absorption edge is [19],

$$\alpha h\nu = A(h\nu - Eg)^n \quad (3)$$

where, 'α' is absorption coefficient (cm^{-1}), $h\nu$ is the proton energy (eV). 'A' and 'n' are constants. 'A' is a complex parameter which depends on temperature, photon energy, etc. The 'n' values are 0.5, 1.5, 2 and 3 for allowed direct, forbidden direct, allowed indirect and forbidden indirect transition, respectively [20]. A plot of $(\alpha h\nu)^2$ versus photon energy should be a straight line whose intercept to the energy axis yields the optical band gap. The graph of $(\alpha h\nu)^2$ versus photon energy for 'as deposited' sample is shown in Fig. 5. The band gaps of CdSe and NiSe have been reported earlier [2,18].

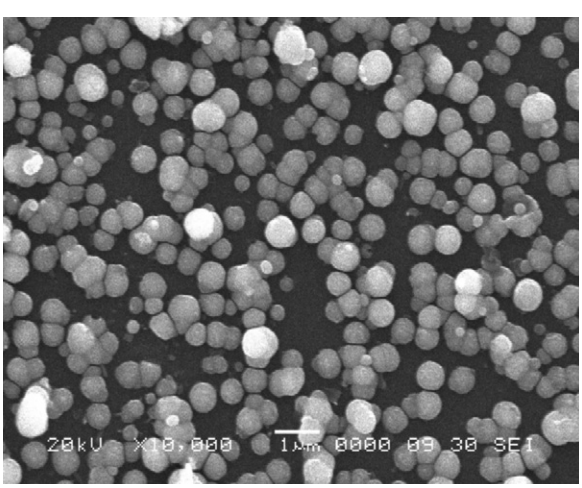

Fig. 3. SEM micrograph of $Cd_{0.5}Ni_{0.5}Se$ thin film.

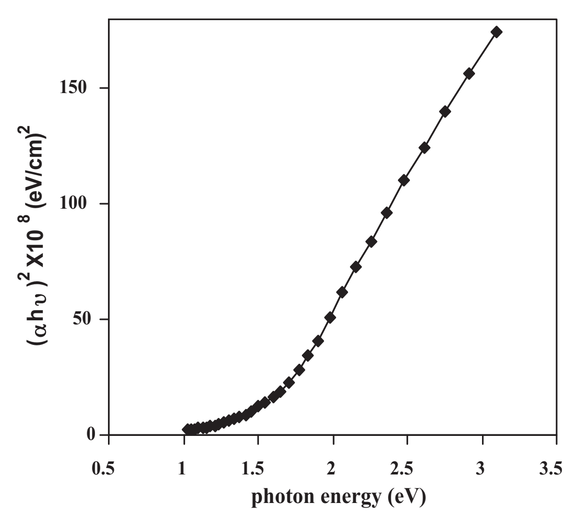

Fig. 5. Determination of band gap for $Cd_{0.5}Ni_{0.5}Se$.

Table 2
Optical and electrical parameters of $Cd_{0.5}Ni_{0.5}Se$ thin film.

Composition	Band gap (eV)	Specific conductance $(\Omega\,cm)^{-1}$		Thickness (μm)	Activation energy (eV)	
		(At 525 K)	(At 300 K)		HT	LT
$Cd_{0.5}Ni_{0.5}Se$	1.50	2.95×10^{-8}	1.82×10^{-11}	0.72	0.755	0.129

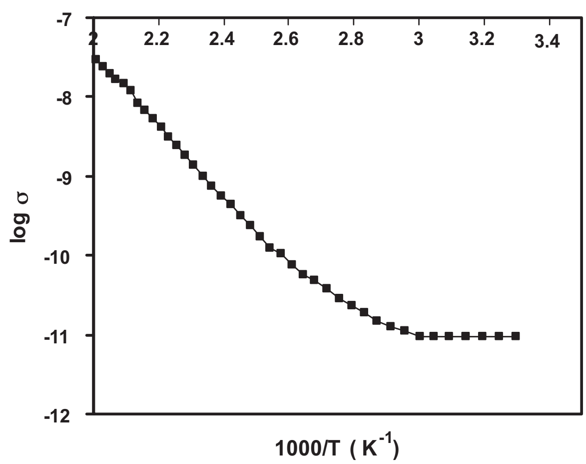

Fig. 6. A plot of log (conductivity) versus inverse absolute temperature for $Cd_{0.5}Ni_{0.5}Se$ thin film.

The band gap was found to be 1.50 eV for $Cd_{0.5}Ni_{0.5}Se$ thin film and is listed in Table 2.

3.5. Electrical and thermoelectrical properties

The electrical conductivity of 'as deposited' $Cd_{0.5}Ni_{0.5}Se$ thin film on the glass substrate was measured by using a d.c. two probe technique in the temperature range of 300–525 K. The specific conductance of NiSe and CdSe at room temperature were found to be in the order of 10^{-4}–10^{-12} $(\Omega\,cm)^{-1}$, respectively [2,18]. The values of specific conductance at 300 K and 525 K are listed in Table 2. The conductivity of the film increases with increase in temperature indicating the semiconducting nature of the film. A plot of log (conductivity) versus inverse absolute temperature is shown in Fig. 6. A plot shows that electrical conductivity has two linear regions; an intrinsic region setting at low temperature, characterized by lower slope. High temperature region is associated with extrinsic conduction due to the presence of donor states. The activation energy is calculated using the Arrhenius equation.

$$\sigma = \sigma_0 \exp\left(\frac{-Ea}{KT}\right) \tag{4}$$

where the terms have usual meaning. The activation energies for low and high temperature regions are 0.129 eV and 0.755 eV, respectively.

In thermoelectric power measurements, the open circuits thermovoltage generated by sample, when a temperature gradient is applied across 2 cm length of samples was measured using a digital microvoltmeter. From the sign of potentiometer terminal connected at cold end of the sample, one can decide the sign of the predominant charge carriers [21–25]. In our study, the positive terminal was connected to cold end; therefore the film exhibits p-type semiconductor.

4. Conclusions

Using chemical bath technique, $Cd_{0.5}Ni_{0.5}Se$ film was successively deposited on glass substrates. The film formation takes place by ion-by-ion growth mechanism. The X-ray diffractogram shows that the film is polycrystalline in nature with hexagonal phase. Optical studies show that $Cd_{0.5}Ni_{0.5}Se$ film has high optical absorption coefficient. The conductivity of the film increases with increase in temperature indicating the semiconducting nature. Thermoelectric power measurement shows p-type conduction mechanism for $Cd_{0.5}Ni_{0.5}Se$ thin film.

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