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Annealing temperature dependence of the optical and structural properties of selenium-rich CdSe thin films

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ABSTRACT

Structural and optical properties of selenium-rich CdSe (SR-CdSe) thin films prepared by thermal evaporation are studied as a function of annealing temperature. X-ray diffraction (XRD) patterns show that the as-prepared films were amorphous, whereas the annealed films are polycrystalline. Analyzing XRD patterns of the annealed films reveal the coexistence of both (hexagonal) Se and (hexagonal) CdSe crystalline phases. Surface roughness of SR-CdSe films is measured using atomic force microscope (AFM). Analyses of the absorption spectra in the wavelength range (200–2500 nm) of SR-CdSe thin films indicates the existence of direct and indirect optical transition mechanisms. The optical band gap (E_g) of as-prepared film is 1.92 and 2.14 eV for the indirect allowed and direct allowed transitions respectively. After annealing, the absorption coefficient and optical band gap were found to decrease, while the values of refractive index (n) and the extinction coefficient (k_{ex}) increase. The dispersion of the refractive index is described using the Wimple–Di Domenico (WDD) single oscillator model and the dispersion parameters are calculated as a function of annealing temperature. Besides, the high frequency dielectric constant (ε_∞) and the ratios of the free carrier concentration to its effective mass (N/m^*) are studied as a function of annealing temperature. The results are discussed and correlated in terms of amorphous-crystalline transformations.

1. Introduction

Chalcogenide glasses have many interesting properties and applications [1,2]. Cadmium selenide system is an example of the wide-bandgap II–VI systems that is considered as a promising semiconductor material for optoelectronics and photovoltaic devices [3–5]. Thin films of CdSe have been deposited using different techniques such as electron beam deposition [6], spray pyrolysis [7], vacuum deposition [8] and chemical bath deposition [9]. Electrical and optical properties of these semiconducting films are found to be sensitive to ambient conditions and deposition technique. The thin film growth conditions and thermal annealing process were found effective to achieve the performance devices [10–12]. The stoichiometry of the films is expected also to have a significant influence on the electrical and optical properties of these films. However; no enough studies are reported on the growth, characterization and properties of non-stoichiometric films [13]. Previously we have studied the electrical properties of selenium-rich cadmium selenide, SR-CdSe, thin films deposited by thermal evaporation [14]. The aim of the present work is to study the influence of thermal annealing on the structural, spectral behavior and optical constants of thermally evaporated SR-CdSe, $Cd_{10}Se_{90}$, thin films.

2. Experimental techniques

The bulk $Cd_{10}Se_{90}$ were prepared from a mixture of Cd and Se elements with purity 99.999% (Aldrich Chem Co., USA). The constituent elements were weighed according to their atomic percentage and were sealed in a quartz ampoule (inner diameter ∼ 8 mm) under vacuum of 10^{-3} T. The sealed ampoules were kept inside a furnace and heated gradually up to 1173 K and kept at that temperature for 16 h. Continuous stirring of the melt was carried out to ensure good homogeneity. The melt was then rapidly quenched in ice–water mixture. After quenching, the solid ingots were removed from the ampoules and kept in dry atmosphere.

Thin films of SR-CdSe were then deposited onto well-cleaned glass substrates kept at room temperature by thermal evaporation technique using a high vacuum coating unit (E306A, Edwards Co., UK). During the deposition process (at normal incidence), the substrates were suitably rotated in order to obtain films of uniform thickness. The thickness of the films (∼150 nm and 600 nm for optical and structural respectively) was measured by a mechanical profilometer (KLA Tenchor P.15). Annealing of the films was carried out in Pyrex tube furnace at 348 K, 373 K, 398 K and 423 K for 30 min under flow of pure nitrogen in order to avoid the oxidation of the samples during annealing.

The structure and phases of the films were confirmed by using X-ray diffractometer (Philips type PW 1710 with Cu as a target and Ni as a filter, $\lambda = 1.5418$ Å). The surface roughness of the films was measured using the Digital Instrument 3100 Atomic Force Microscope (AFM). The chemical composition of the films was studied using the standard energy dispersive analysis of X-ray (EDX) technique. An EDX unit

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attached to the scanning electron microscope (SEM), Jeol (JSM)-T200 type, was used for these measurements.

The optical transmittance, T, and reflectance, R, of the films were measured at room temperature with unpolarized light at normal incidence in the wavelength range (200–2500 nm) using a double beam (ultraviolet–visible) scanning spectrophotometer (SHIMADZU 2101) attached to a personal computer.

3. Results and discussions

3.1. Structural analysis: EDX, XRD, SEM and AFM

The EDX analysis of as-prepared thin film yielded an average atomic percentage of Cd:Se of 9.92:90.08 which is very near to our targeted Cd:Se ratio (10:90). X-ray diffraction patterns of as-prepared and annealed films are shown in Fig. 1. As-prepared films were of amorphous nature, Fig. 1(a). However, thin films annealed for 30 min in N_2 atmosphere at 348 K, 373 K and 423 K, Fig. 1(b)–(d) shows a polycrystalline structure indicating an amorphous-to-crystalline phase transition. Peaks were indexed according to JCPDS files no. 02-0330 and no. 86-2246 for hexagonal CdSe and hexagonal Se respectively.

The annealed films at 348 K and 373 K, Fig. 1(b) and (c), are characterized by the predominant appearance of Se hexagonal phase peaks. Only one tiny peak situated at $2\theta = 25.18°$ ($d = 3.537$ Å) is corresponding to (0 0 2) plane of CdSe hexagonal phase. With further increase of the annealing temperature up to 423 K, the CdSe peak showed a much greater intensity which indicates a considerable increase in the volume fraction of CdSe crystalline phase.

The interplanar spacing (d) was calculated using Bragg's formula ($d = \lambda/2\sin\theta$) where θ is the Bragg's angle, λ is the wavelength of the used X-ray. The lattice constant (c) for different SR-CdSe films was calculated for hexagonal structure by the equation [15]:

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

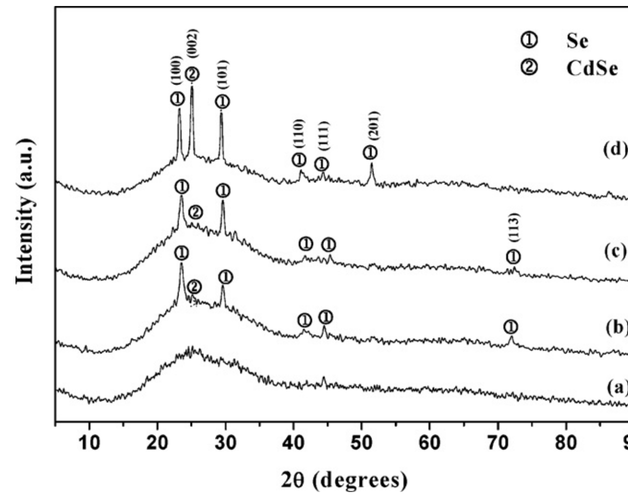

Fig. 1. XRD patterns of $Cd_{10}Se_{90}$ thin films: (a) as-prepared, (b) annealed at 348 K, (c) annealed at 373 K, (d) annealed at 423 K.

From Table 1, we note that the calculated values for the parameters d and c for SR-CdSe thin films are in a good agreement with the standard JCPDS data files for Se and CdSe hexagonal phases. In fact the tensile strain of the annealed films of SR-CdSe [14] is thought to be the reason of the relatively larger values of these parameters for SR-CdSe as compared to the standard lattice parameters.

Fig. 2 shows the AFM images of the as-prepared SR-CdSe film and after annealing at 423 K. Before annealing the root mean square (RMS) roughness was 3.31 nm. After annealing, the RMS roughness of the surface decreased to 1.45 nm. This may be understood as some small amounts of material diffuse from the surface to the inside of the film during the annealing process resulting in a roughness reduction and grain growth.

Table 1
Structure parameters of annealed SR-CdSe thin films.

Phase	Annealing temperature (K)	h k l	Lattice spacing, d (Å)		Lattice parameters, c (Å)	
			Observed	Standard	Observed	Standard
CdSe	348	0 0 2	3.537	3.52	7.074	7.02
	373	0 0 2	3.553		7.106	
	423	0 0 2	3.553		7.106	
Se	348	1 0 1	3.017	3.007	5.006	4.958
	373	1 0 1	3.073		4.989	
	423	1 0 1	3.072		4.998	

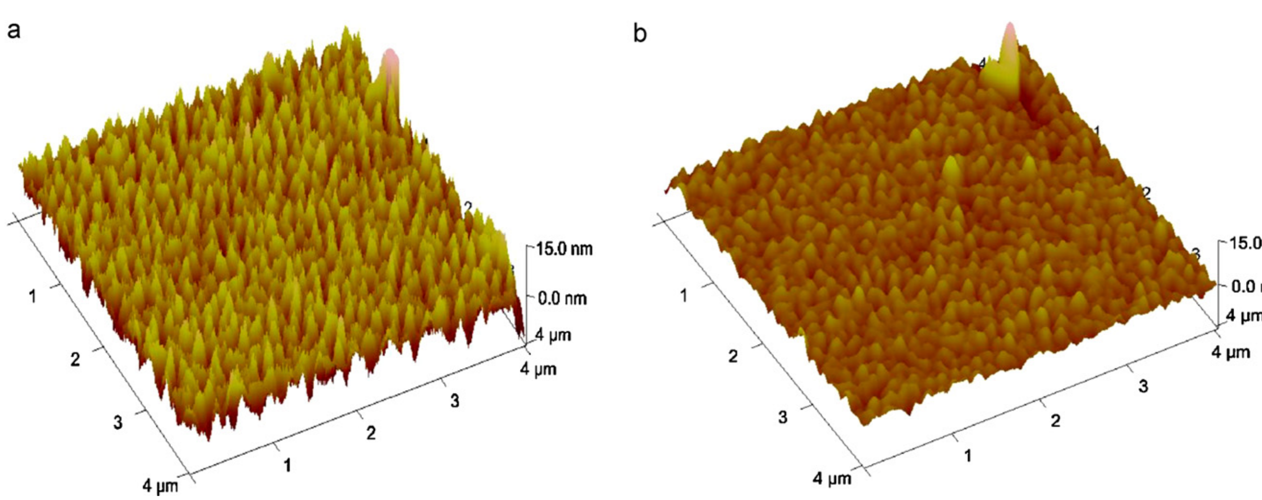

Fig. 2. AFM image for SR-CdSe thin film: (a) before and (b) after annealing at 423 K for 30 min.