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Thin Film Technology

Elixir Thin Film Tech. 84 (2015) 33486-33489

ISSN: 2229-712X

Effect of Annealing on the Structural, Morphological and Optical Band Gap of Nanocrystalline Cadmium Selenide Thin Films Synthesized by Chemical Bath Deposition Technique

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ARTICLE INFO

Article history:

Received: 16 May 2015;

Received in revised form: 19 June 2015;

Accepted: 30 June 2015;

Keywords

Thin film,
Cadmium selenide,
Annealing,
Microstrain,
Chemical bath deposition.

ABSTRACT

The effects of annealing on the structural, morphological and optical band gap of chemically deposited cadmium selenide (CdSe) thin films have been investigated. The X-ray diffraction analysis revealed that both the as-deposited and annealed CdSe thin films had three major peaks corresponding to the cubic structure of CdSe with a preferred orientation along the (111) plane. After annealing, the intensity of the major peaks became more pronounced and a new low intensity peak was observed. There was also a slight shift in peak positions towards smaller 2θ angles. The average crystallite size increased after annealing whereas the microstrain and dislocation density decreased. The SEM micrographs of the annealed thin film showed a slight improvement in crystallinity and uniformly distributed all over the surface of the substrate without voids. The optical energy band gap of the thin films decreased from 1.86 eV to 1.74 eV after annealing.

Introduction

The synthesis and characterization of binary metal chalcogenides of group II–VI semiconductors in nanocrystalline form is a rapidly growing area of research [1, 2]. Cadmium selenide is one of the group II-VI compound semiconductors considered as a promising material for the development of many interesting applications such as light emitting diodes, solar cells, photodetectors, electro photography and laser [3-5]. CdSe is an n-type semiconductor material [6] with a direct band gap of 1.74 eV [7]. It has a high absorption coefficient, high photosensitivity and direct band gap corresponding to a wide spectrum of wavelengths from ultraviolet to infrared regions [8]. Bulk CdSe has two stable four-coordinated polymorphs, hexagonal and cubic structures that coexist at ambient conditions. Usually the cubic modification exists in thin layers, while the bulk CdSe has the hexagonal structure [9]. A variety of physical and chemical techniques are available for the deposition of cadmium selenide thin films such as hot wall [6] thermal evaporation [10], successive ionic layer adsorption and reaction [11], metal oxide chemical vapor deposition [12], chemical bath deposition (CBD) [13]. Among various deposition techniques, chemical bath deposition yields stable, uniform and adherent films with good reproducibility by a relatively simple process [14]. CBD has significantly contributed to the growth of high quality of thin films, well suitable for large area deposition at relatively low temperatures [1, 13]. The characteristics of chemical bath deposited CdSe thin films depend strongly on the growth condition by changing the deposition key parameters, one can control thickness, size of the nanoparticles, and the energy band gap of the thin films [15]. Post deposition annealing can also lead to significant changes in structural, electrical, morphological and optical properties of semiconductor thin films [16] hence, it is a phenomenon worth investigating. In the present work, we report the effect of annealing on the structural, morphological and optical band gap of nanocrystalline CdSe thin films prepared using the procedure described in our previous work [17].

Deposition and characterization of the thin film

The CdSe thin films were deposited on silica glass substrates and the detail deposition condition described in our previous report [17]. After deposition, the films were annealed in the air at a temperature of 350 ^{0}C for one hour, after which the furnace was switched off and allowed to cool to room temperature. The crystal structure of CdSe thin films were analyzed by PANalytical Empyrean X-ray diffractometer with a Cu-k_α radiation ($\lambda_{\alpha 1}$ = 1.5406 Å). The machine was operated at 40 mA and 45 KV. The surface morphology of the samples were studied by high resolution JEOL JSM-7600F scanning electron microscope and the machine was operating at an accelerating voltage of 15 kV and average working distance of 7.9 mm. The optical absorption spectra of the samples were measured at room temperature, using a Shimadzu UV/Vis mini-1240 Spectrophotometer within the wavelength range of 200 nm – 1100 nm.

Results and Discussion

Structural analysis

The X-ray diffraction patterns of the as-deposited and annealed CdSe thin films are shown in Figures 1.

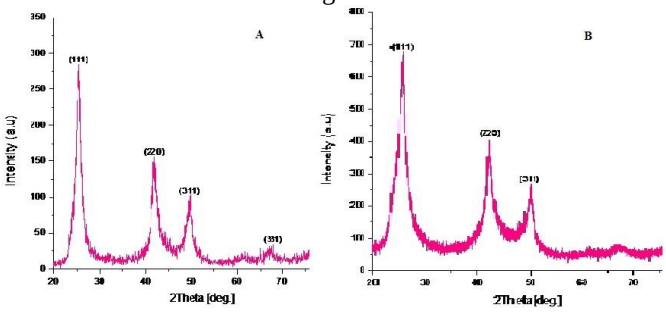

Figure 1. The XRD patterns of CdSe thin films: (A) annealed at 350 ^{0}C for 1 hour and (B) as-deposited

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From Figure 1, the X-ray diffraction patterns of the as-deposited and annealed CdSe thin films have three major peaks which correspond to reflections from the (111), (220), (311) planes of the cubic CdSe structure. The peaks in the annealed thin film are more intense, suggesting an improvement in crystallinity. This result is in agreement with an earlier report by [14]. In addition a new low intensity peak is observed at 67.1^0 and indexed to the (331) plane. A slight shift in peak positions towards lower 2θ angles is observed after annealing. It is also noticeable from Figure 1 that the width of the prominent peaks of the annealed film are smaller than that of the as-deposited film which implies a reduction in strain within the film and improvement in crystallinity [18]. The observed d-values and respective peaks positions for both as-deposited and annealed CdSe samples obtained from the XRD studies were in good agreement with JCPDS data file number 00-019-0191. No phase change was observed after annealing. Below the critical annealing temperature for CdSe thin film the cubic phase is retained [19].

Lattice constant a(Å) for cubic phase structure and the average crystallites size D_{hkl} were calculated using the Debye–Scherrer equation as described in reference [20]. Mathematically, the microstrain value ε was evaluated using the following formula [21].

$$\mathcal{E} = \frac{\beta \, Cos\, \theta}{4} \qquad 1$$

where θ is the Bragg angle in radian. The dislocation density δ which is a measure of the defects in the crystallite [22], was also calculated using Williamson and Smallman's formula [23]:

$$\delta = \frac{n}{D^2} \qquad 2$$

where n is a factor, which equals unity giving minimum dislocation density and D is the average crystallite size [10]. Strain and dislocation density were calculated from the highest intense peak of the X-ray diffraction pattern for both as-deposited and annealed CdSe.

These structural parameters obtained for both as-deposited and annealed CdSe samples are compared with standard data and presented in Table 1.

From Table 1, it can be observed that the average crystallite size increased with annealing whilst there was a decrease in dislocation density and strain. Dislocation density and strain are the manifestation of dislocation network in the films, the decrease in dislocation density indicates the formation of high quality films [21] a similar phenomena were reported by [18, 21]. The strain in CdSe thin film also decreased after annealing indicating the release of intrinsic film stress thereby reducing the imperfections within the crystalline lattice.

It was also observed that the value of the lattice constant a (Å) of the film deviates from its bulk value of 6.077 Å for both as-deposited and annealed CdSe samples. There are several possible sources of error like divergences of X-ray beams, refraction and absorption of X-rays by the specimen etc in the measurement of θ and d-values [24]. Accuracy in the determination of lattice constant is dependent upon the accuracy of their measurements. The most accurate value of the lattice parameter was estimated from the Nelson-Riley function.

$$f(\theta) = \frac{1}{2}\left(\frac{cos^2\theta}{sin\theta} + \frac{cos^2\theta}{\theta}\right) \qquad 3$$

where θ is the Bragg angle and $f(\theta)$ is an error function. The Nelson-Riley plot is obtained by plotting the calculated 'a_{hkl}' for each plane against the corresponding error function. The intersection at $f(\theta) = 0$ gives the corrected value of the lattice parameter which is more or less free from systematic errors as shown in Figure 2 and Figure 3.

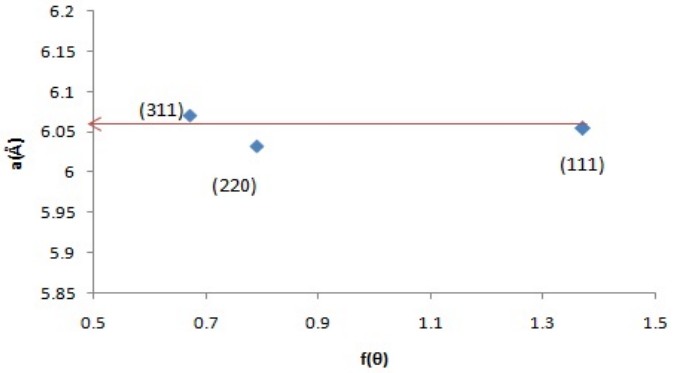

Figure 2. Nelson-Riley plot for as-deposited CdSe thin film

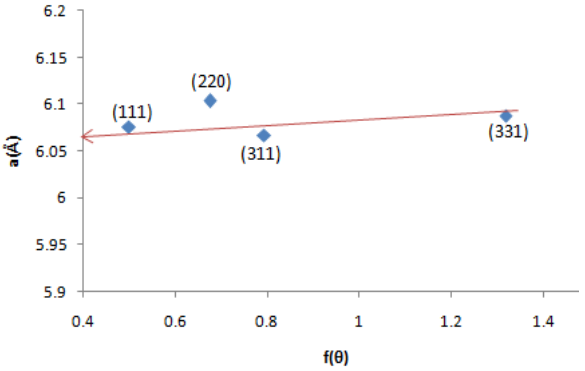

Figure 3. Nelson-Riley plot for annealed CdSe thin film

The corrected value of lattice parameter from Nelson–Riley plots for both as-deposited and annealed CdSe samples was estimated to be $a = 6.074\,\acute{A}$, which is very close to the JCPDS card number 00-019-0191 of cubic CdSe compound. The lattice parameter is independent of post-deposition annealing [25].

The texture coefficient (*TC*) represents the texture of the particular plane, deviation of which from unity implies the preferred growth. Quantitative information concerning the preferential crystallite orientation was obtained from the texture coefficient TC (hkl) defined as:

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1}\sum_N I(hkl)/I_0(hkl)} \qquad 5.13$$

where *I(hkl)* is the measured relative intensity of a plane *(hkl)*, $I_o(hkl)$ is the standard intensity of the plane *(hkl)* taken from the JCPDS data, N is the number of diffraction peaks. The value *TC*(*hkl*) = 1 represents films with randomly oriented crystallites, while higher values indicate the abundance of grains oriented in a given [*hkl*] direction *[26]*. The calculated texture coefficients are presented in Table 2. From the result it was observed that the crystallites are oriented in the (111) plane for both as-deposited and annealed CdSe thin films. However, the annealed films had a larger amount of crystallites oriented in the (111) plane as compared to the as-deposited film.

Surface morphology study

The SEM micrographs of the annealed and as-deposited CdSe thin films are shown in Figure 4 with two different magnifications (17KX and 50 KX). From the SEM micrographs, it can be observed that in the as-deposited films, the grains are nearly spherical in shape and uniformly distributed over the surface of the substrate without cracks and pinholes. In the annealed samples the grains appear to have coalesced to form larger grains which cover the entire substrate leaving no pores or voids.

Table 1. A comparison of calculated structural parameters with the standard XRD values

CdSe Samples	2θ in degree	hkl	d-space in Å		lattice constant a(Å)		Intensity (a.u)		Average Crystallite size (Å)	Strain (ε) lines^{-2}m^{-4}	Dislocation density (δ) lines/ m^2
			standard	observed	standard	observed	standard	observed			
As deposited	25.46	111	3.510	3.496	6.077	6.053	100	100	43.68	8.29 x 10^{-3}	5.24 x10^{16}
	42.34	220	2.149	2.133			55	51	38.24		
	49.77	311	1.833	1.830			25	15	38.62		
Annealed	25.32	111	3.510	3.515	6.077	6.083	100	100	65.24	5.55 x 10^{-3}	2.35 x10^{16}
	42.09	220	2.149	2.145			55	49	47.75		
	49.47	311	1.833	1.840			25	15	46.12		
	67.10	331	1.394	1.394			4	3.2	20.75		

Table 2. The texture coefficients of both as-deposited and annealed CdSe samples

CdSe samples	2θ in degree	hkl Planes	d-space (Å) observed	I/I_0	TC
As-deposited	25.46	111	3.496	1	1.20
	42.34	220	2.133	0.93	1.10
	49.77	311	1.830	0.60	0.71
Annealed	25.32	111	3.515	1	1.35
	42.09	220	2.145	0.89	1.20
	49.47	311	1.840	0.63	0.85
	67.10	331	1.394	0.80	1.08

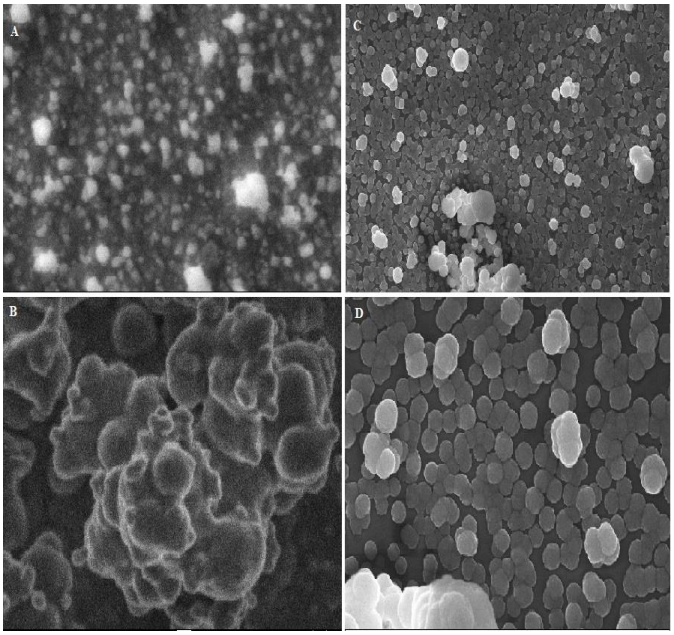

Figure 4. The SEM micrographs of annealed CdSe thin film (A) and (B) and the SEM micrographs of as-deposited CdSe thin film (C) and (D)

In addition, the SEM micrographs of the annealed film show a slight improvement in crystallinity. This is also consistent with the XRD result. The improvement of crystallinity after annealing may be due to the coalescing of smaller nanoclusters into larger clusters [27].

Optical study

The energy band gap and transition type was derived from mathematical treatment of data obtained from optical absorbance versus wavelength with the Stern relationship of near-edge absorption as described in reference [17]. The optical band gap is found to be 1.86 eV for the as-deposited film and 1.74 eV for annealed CdSe thin film (see Figure 5). The energy band gap decreased after the films were annealed. The observed decrease in energy band gap in the annealed film can be attributed to an increase in crystallite size of the material which agreed well with the XRD results. This phenomena is in good agreement with an earlier report by [28].

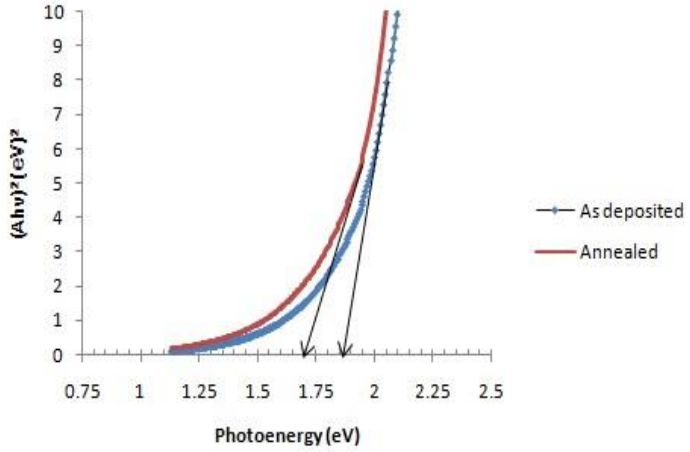

Figure 5. Plot of (A$h\nu$)^2 versus photon energy for as-deposited and annealed CdSe thin films

Conclusion

Annealing effect on the structural, morphological and optical band gap of the CdSe thin films were studied. From the XRD analysis it was observed that the annealed CdSe thin films mainly consisted of the cubic phase. No phase change was observed after annealing. However, a new low intensity peak was observed at 67.1^0 and the peak positions shifted slightly towards lower 2θ angles. The average crystallite size was found to increase from 40 Å to 45 Å whereas the dislocation density and microstrain decreased after annealing. The decrease in dislocation density and microstrain indicates the formation of high quality thin film by reducing the imperfections within the crystalline lattice. Texture coefficent results showed that the crystallites are oriented in the (111) plane for both as-deposited and annealed CdSe thin films. The SEM micrographs of the annealed film showed a slight improvement in crystallinity and the grains are interconnected to each other and cover the entire surface of the substrate without pores. The optical study revealed that the deposited samples have direct band transition and the optical band gap decreased from 1.86 eV to 1.74 eV after annealing. These results suggest an overall improvement in crystallinity of the CdSe thin films after introducing annealing treatment.

Acknowledgement

The authors wish to acknowledge the Department of Physics, University of Ghana, Legon for allowing us to use their XRD machine.

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