

Study of chemically synthesized SHI irradiated CdS nanostructured films

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ABSTRACT

Cadmium sulphide (CdS) nanostructured films were prepared by chemical bath deposition (CBD) method at room temperature. The prepared films were subjected to swift heavy ion (SHI) irradiation by using 100 MeV Si⁸⁺ ion beams at various fluences from 1×10^{11} to 1×10^{13} ions/cm². Structural, morphological, optical properties of the pristine and irradiated films were characterized by X-ray diffractometer (XRD), high resolution transmission electron microscope (HRTEM), UV-Vis spectroscopy and Raman spectroscopy. XRD study confirms the formation of nanocrystalline cubic phase in all the films. The crystallite size is found to increase from 7nm to 9 nm and shift of peak positions are observed due to irradiation. The lattice strain and dislocation density of the samples are of the order of 10^{-3} and 10^{16} m⁻² respectively and the values are found to decrease upon irradiation. HRTEM images show that the shapes of the particles are nearly spherical and the selected area electron diffraction (SAED) pattern of HRTEM have also supported the formation of cubic phase CdS. The optical absorption spectra exhibit shift in the fundamental absorption edge and the optical band gap decreases from 2.585eV to 2.513 upon SHI irradiation. Three intense Raman lines for pristine as well as irradiated CdS have been observed and all the samples show shift in Raman lines relative to bulk CdS due to phonon localization. The SHI irradiation on chemically deposited CdS films is an important tool used for modification of structural, morphological and optical properties of the films for possible applications in device fabrication. Copyright © 2015 VBRI press.

Keywords: Nanostructured CdS films; SHI; XRD; SSP; optical band gap energy.



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Introduction

Nanostructured materials have unique mechanical, optical, magnetic properties and find wide range of applications in various fields such as in solar cells, photo conductors, short wavelength laser diodes, UV sensors, various luminescence devices, etc. [1, 2]. CdS belonging to II-VI group has direct band gap of 2.42eV (bulk form) at room temperature and is most widely used in various areas such as in heterojunction solar cells, optoelectronic, piezo-electronic, gamma-ray detectors, luminescence devices, display

devices, biological labeling, photo-electrolysis, biotechnology, communication and many more in which the properties of CdS nanomaterials are influenced by their structures and morphologies. In recent years, different methods have been applied for the synthesis of nanostructured CdS films, few of them are thermal evaporation, solvothermal route, electrochemical synthesis, chemical synthesis, vapour-liquid-solid growth methods. The modification of various thin film material properties brought about by energetic ion beam is a largely studied area for scientific and technological importance [3]. SHI irradiation is a unique method applied to bring different phenomena in the material including phase change [4], formation of point defect, crystallization and amorphization [5-6], etc. and for generating surface nanostructures [7] in a precise and controlled manner. Irradiation can generate wide variety of defects as well as anneal out pre-existing defects that change physical, chemical and optical properties of the materials [8]. SHI irradiation displaces atoms from their sites in the lattice causing new electronic

configuration and as a result the optical properties of materials change [9].

Although lot of studies have been done by many workers on low energy implantation of CdS films but not much have been done on SHI irradiation on chemically synthesized CdS films. In our work, chemical bath deposition (CBD) method is adopted for the preparation of nanostructured CdS films because it is a simple, cost effective method and has capability to achieve large area coating. The films are irradiated by 100 MeV Si¹⁸⁺ ions at various fluences and modifications of various structural, optical parameters such as crystallite size, strain, dislocation density, energy band gap, refractive index and dielectric constant of CdS films due to ion irradiation are reported in this paper.

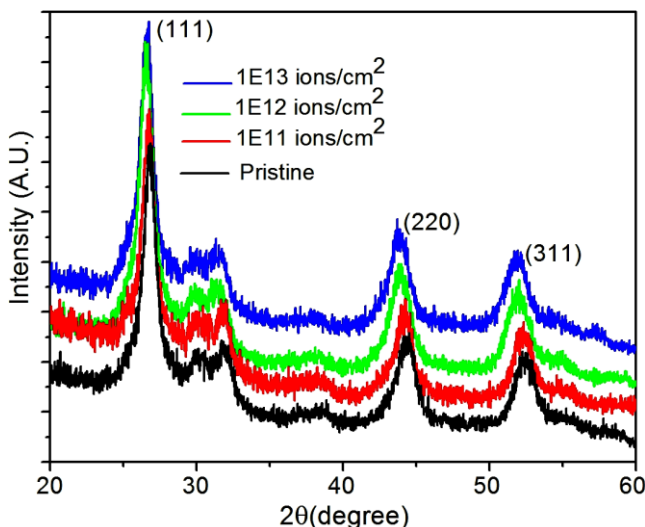


Fig. 1. XRD pattern of pristine and irradiated CdS films.

Experimental

Materials

Monohydrate cadmium chloride (CdCl₂·H₂O) (pure), purchased from Merck specialties private limited, Mumbai, India, nonahydrate sodium sulphide (Na₂S·9H₂O) (pure), purchased from Rankem, RFCL, New Delhi, India and polyvinyl alcohol (pure) purchased from sd fine CHEM limited, Mumbai, India were used for the preparation of nanostructured CdS films.

Method

Nanostructured CdS films were synthesized by ion exchange reaction in polyvinyl alcohol (PVA) matrix. 1.0 molar CdCl₂ solution was added to an aqueous solution (4wt %) of PVA in equal volume under a high stirring rate 200 rpm for 3 hours at constant temperature 70°C. The prepared solution was kept for 12 hours for complete dissolution. Na₂S (0.25M) solution was added to the above solution till the whole solution turns into yellow colour. The CdS nanoparticles were casted on cleaned glass substrates and are allowed to dry in a closed chamber at room temperature.

The prepared nanostructured CdS films were irradiated with 100 MeV Si¹⁸⁺ ions at three fluences viz. 1x10¹¹, 1x10¹² and 3x10¹³ ions/cm² using the 15 UD Pelletron

accelerator at Inter University Accelerator Centre, New Delhi, India. Samples were mounted on a copper ladder in an irradiation chamber evacuated at a pressure of 4x10⁻⁶ Torr at room temperature and the beam current was maintained at 0.7 pA. The beam was scanned over an area of 10 mmx10mm of the samples with an electromagnetic scanner.

In order to perform structural analysis of the samples the XRD patterns were recorded using Bruker (AXS D8 Advance) with CuK_α radiation (λ=1.5406Å). Surface morphology was analyzed by HRTEM (Jeol, JEM 2100) operated at 200KV. To study optical properties of the samples the optical absorption spectra were recorded in the region 350-800 nm using CARY 300 Scan U-V-Visible spectrophotometer. The Raman spectra were recorded in RENISHAW in Via Raman microscope.

Results and discussion

XRD analysis

The glancing angle X-ray diffraction (GAXRD) patterns of pristine and irradiated CdS films are shown in Fig. 1 and the peak positions are cited in Table 1. The pristine and all the irradiated CdS samples display three intense diffraction peaks which can be assigned to (111), (220) and (311) planes of the CdS cubic crystalline phase (JCPDS-800019). Pristine CdS film shows formation of compressive stress which is evident from the shift of peak position of (111) plane by 0.238° towards higher diffraction angles from its corresponding value for bulk CdS (2θ=26.547°; JCPDS -800019) which may be due to residual stress generated in the film during deposition or due to the lattice mismatch between the film and the substrate [10].

Table 1. Crystallite size, strain, dislocation density, band gap energy, refractive index and dielectric constant of CdS films.

CdS films	2θ (degree)	d (Å)	a(Å)	Crystallite size		Strain from SSP (e)x10 ⁻³	Dislocation density (δx10 ¹⁶ /m ²)	Band gap energy (eV)	Refractive index (n)	Dielectric constant (ε _r)
				(nm) from Scherrer formula	SSP method					
Pristine	26.785	3.326	5.760	7.277	7.132	2.294	1.274	2.585	2.483	6.164
	44.298	1.993	5.636							
	52.453	1.683	5.582							
1x10 ¹¹ ions/cm ²	26.706	3.305	5.725	8.195	7.703	2.276	1.169	2.538	2.499	6.247
	44.170	1.998	5.652							
	52.287	1.688	5.599							
1x10 ¹² ions/cm ²	26.596	3.319	5.748	8.929	8.253	2.17	1.037	2.525	2.504	6.269
	44.057	2.003	5.667							
	52.122	1.693	5.617							
1x10 ¹³ ions/cm ²	26.500	3.331	5.769	9.471	8.623	1.768	0.807	2.515	2.508	6.291
	44.004	2.006	5.674							
	52.093	1.694	5.620							

Irradiated samples exhibit shifting of peak positions towards lower diffraction angle and generation of tensile stress is observed for CdS irradiated at 1x10¹³ ions/cm² because its peak position of (111) plane shifts towards lower 2θ by 0.047° compared to corresponding value for bulk CdS (2θ=26.547°; JCPDS -800019). The transformation from compressive stress to tensile stress for the irradiated film may be due to the grain growth and annihilation of defects such as dislocations present in the pristine film [3]. The interplanar spacing (d) is calculated from Bragg's equation (λ=2d sinθ) and are cited in Table 1. The calculated value of lattice constant (a) for cubic phase structure is determined from the relation, $a=d(h^2+k^2+l^2)^{1/2}$ and are listed in Table 1. The broadening of the peaks

indicates that CdS particles are of nanoscale dimension. The broadening of the peak is mainly due to the combined effect of finite size of the crystallite and lattice strain due to dislocation. The instrumental broadening corrected full width at half maxima (FWHM), β of each reflection is calculated using the equation [11]

$$\beta = \left(\beta_{\text{measured}}^2 - \beta_{\text{instrumental}}^2 \right)^{1/2} \quad (1)$$

where β_{measured} and $\beta_{\text{instrumental}}$ are FWHM due to the material and standard material (such as silicon) respectively. The crystallite size (D) of the samples is obtained using Scherrer's formula [11]

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

where K is a constant equal to 0.94, λ is the wavelength of the radiation which is 1.54056 Å for CuK_α radiation and θ is the Bragg's diffraction angle. The estimated values of crystallite size of the samples are cited in **Table 1**.

In case of isotropic line broadening, another method called size-strain plot (SSP) is applied to find crystallite size and strain. In this method crystallite size and strain are described by Lorentzian and Gaussian profiles respectively [12-13]. Then one can write;

$$\left(\frac{d\beta \cos \theta}{\lambda} \right)^2 = \frac{1}{D} \left(\frac{d^2 \beta \cos \theta}{\lambda} \right) + \left(\frac{\varepsilon}{2} \right)^2 \quad (3)$$

By plotting $\left(\frac{d\beta \cos \theta}{\lambda} \right)^2$ vs $\left(\frac{d^2 \beta \cos \theta}{\lambda} \right)$ for different peak orientations as shown in **Fig. 2**, the crystallite size and the strain are estimated from the slope of the linearly fitted data and y-intercept respectively.

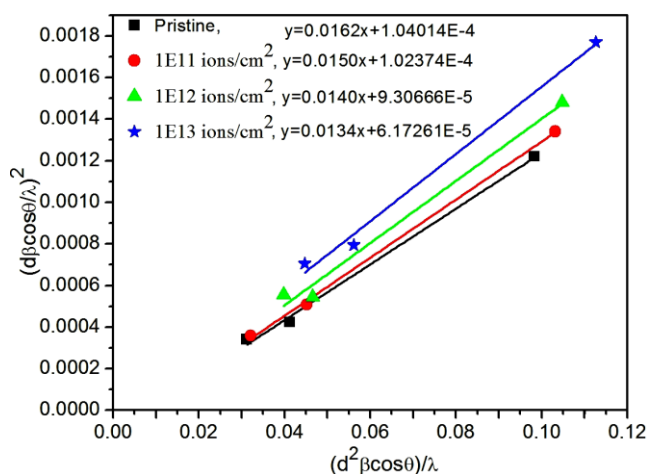


Fig. 2. SSP of pristine and irradiated CdS films.

The crystallite size (D) is obtained from $D = \frac{K\lambda}{\text{slope}}$, where $K=3/4$ for spherical particle and the root mean square strain

(ε) is $\varepsilon = \frac{\sqrt{y \text{ intercept}}}{\pi\sqrt{2}}$. The values of crystallite size and

strain obtained from SSP are cited in **Table 1**. Irradiation increases the crystallite size because of the fact that, during irradiation the kinetic energy of the electrons ejected from the target atom is transferred to the lattice which increases local lattice temperature forming non equilibrium state in grain volumes, thereby, the grain volumes are increased and agglomeration of grains on the surface take place, so crystallite size increases [14].

The dislocation density (δ) is estimated from the Williamson and Smallman method using the relation [15]

$$\delta = \frac{m\varepsilon}{aD} \quad (4)$$

where m is a constant having values 15, 24 and 28 for (111), (220) and (311) planes respectively. ε is microstrain, a is lattice constant and D the crystallite size. ε and D are obtained from SSP (**Table 1**). The calculated values of dislocation density of the samples are cited in **Table 1**. The values of micro strain and dislocation density of CdS films are found to decrease with the increase of ion fluence which is evident from **Table 1**.

HRTEM analysis

The morphological investigation of the samples is carried out with the help of high resolution transmission electron microscope (HRTEM). **Fig. 3(a)** shows HRTEM micrograph of pristine CdS which exhibits the presence of large number of nearly spherical CdS nanoparticles. HRTEM micrograph of CdS film irradiated at 1×10^{13} ions/cm² is shown in **Fig. 3(b)**. The shape of the particles after irradiation becomes irregular and the size is found to increase compared to that of pristine CdS in agreement with the result obtained based on XRD study. **Fig. 3(c)** shows selected area electron diffraction (SAED) pattern of irradiated CdS consisting of a central halo and concentric rings which indicates the crystalline structure of the sample. The pattern demonstrates three rings corresponding to (111), (220) and (311) planes respectively which is in agreement with the cubic phase of CdS.

Optical study

The optical absorption spectra of pristine and irradiated CdS films studied in the wavelength range 350-800 nm are shown in **Fig. 4(a)**. Irradiation causes shift in band edge towards higher wavelength and increase in absorbance. The enhancement in absorption occurs because of production of metallic cadmium cluster due to loss of sulphur atoms and the generation of defect levels in the band gap during irradiation [16]. CdS is a direct band gap material. The optical band gap energy of CdS films is estimated using Tauc's formula [17]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (5)$$

where α is the absorption co-efficient, $h\nu$ is incident photon energy, A is a constant and E_g is the optical band gap energy. E_g value has been estimated by extrapolating the linear region of the plots $(\alpha h\nu)^2$ versus $h\nu$ on the energy axis as shown in **Fig. 4(b)** and the values are cited in **Table 1**. The band gap energy of pristine CdS is found to be 2.585eV which shows that it is blue shifted with respect to band gap energy of bulk CdS (2.42 eV) due to quantum confinement effect. The value of band gap energy decreases with the increase of ion fluence which may be because of increase in grain size and generation of defect level or creation of intermediate energy levels [18] due to irradiation.

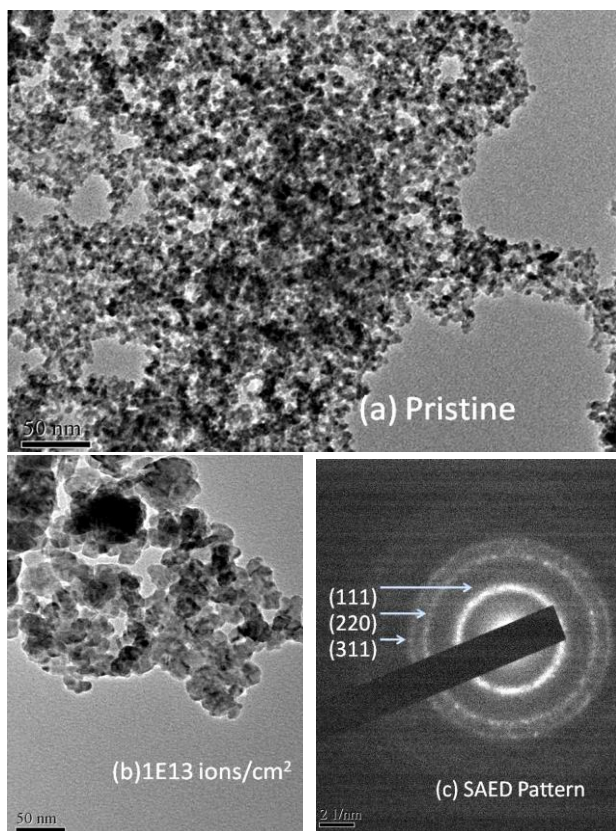


Fig. 3. HRTEM micrographs of (a) pristine CdS (b) irradiated ($1E13$ ions/ cm^2) CdS and (c) SAED pattern of irradiated ($1E13$) CdS.

In the design of optoelectronic devices such as heterostructure lasers and in solar cell applications the knowledge of refractive index, dielectric constant is essential. Refractive index (n) is estimated from the following equation given by Herve-Vandamme [19].

$$n = \sqrt{1 + \left(\frac{A}{E_g + B} \right)^2} \quad (6)$$

Here $A=13.6$ eV, $B=3.4$ eV are constants, E_g is optical band gap energy and the relation is suited well for most materials usually used in optoelectronic devices and high band gap materials. The high frequency optical dielectric constant (ϵ_∞) is obtained from the relation [20]

$$\epsilon_\infty = n^2 \quad (7)$$

The estimated values of n and ϵ_∞ of the samples are cited in **Table 1**. It is observed that the values of both the refractive index and dielectric constant increase with the increase of ion fluence.

Raman study

Fig. 5 shows the Raman spectra of pristine and irradiated CdS, where three Raman optical vibration modes are observed. The intense and broad peaks of pristine CdS centred at 299.496 cm^{-1} , 599.966 cm^{-1} and 903.78 cm^{-1} are assigned to the fundamental optical phonon mode (LO), the first overtone mode (2LO) and the second overtone mode (3LO) of CdS respectively. The LO peak shifts towards lower wave number from its corresponding value for bulk CdS (305 cm^{-1}). Irradiation causes slight decrease in intensity and shifting of peak positions slightly towards lower wave number compared to that of pristine CdS because of phonon localization by high density of lattice defects [21-22].

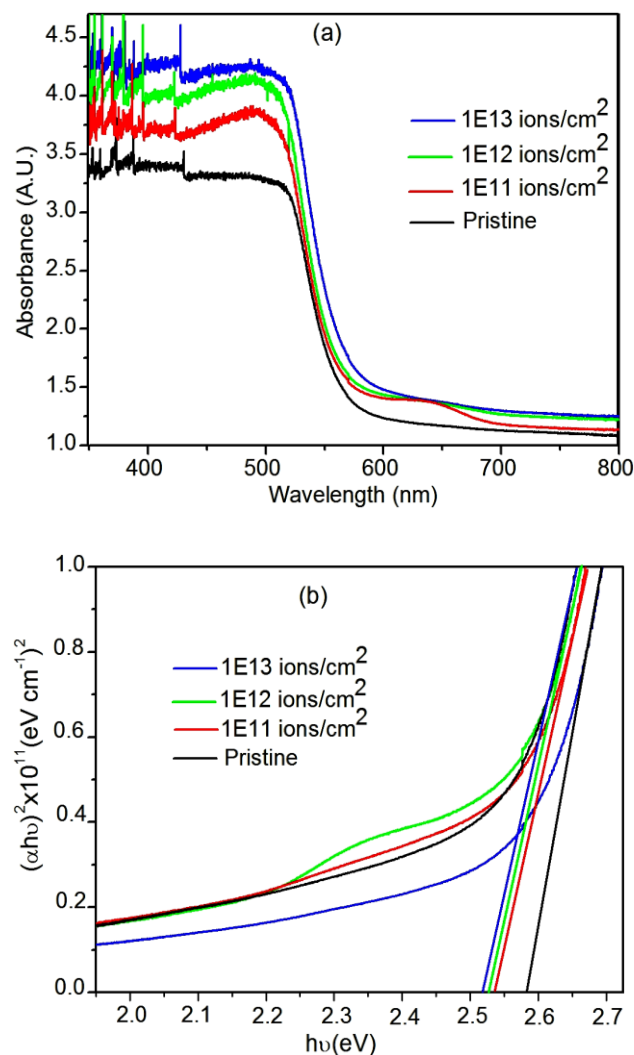


Fig. 4. (a) Absorption spectra of pristine and irradiated CdS films and (b) $(\alpha h\nu)^2$ vs $h\nu$ plots for the pristine and irradiated CdS films.

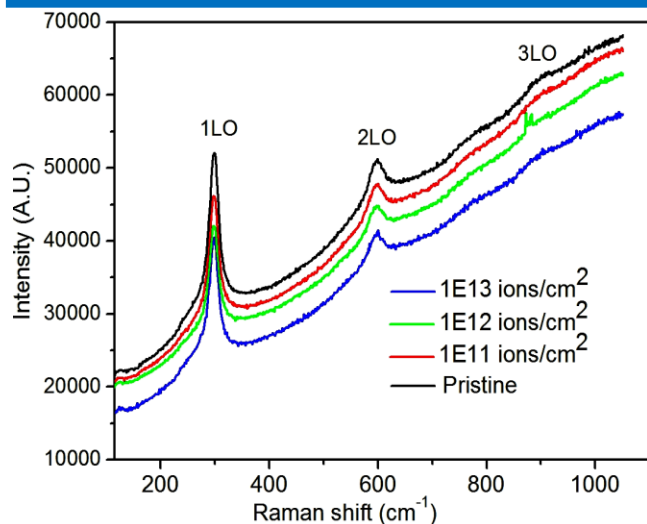


Fig. 5. Raman spectra of pristine and irradiated CdS films.

Conclusion

Chemically deposited nanostructured CdS films show structural stability as they retain crystallinity upon SHI irradiation. The structure of pristine as well as irradiated CdS is found to be cubic and the crystallite size increases but strain as well as dislocation density were found to decrease upon SHI irradiation. The increase of crystallite size upon irradiation is also observed in HRTEM image and SAED pattern of HRTEM also shows the formation of cubic phase CdS. The optical band gap energy of all the CdS samples are blue shifted with respect to their bulk CdS and decreases upon irradiation. This gives a significant result that SHI irradiation can be applied to material systems where optical band gap energy engineering is needed. Irradiation causes significant change in refractive index and high frequency optical dielectric constant of the samples. Three intense and broad Raman spectra are observed and irradiation affects their intensity and peak positions. The observed results show that SHI irradiation modifies the structural, morphological as well as optical properties of CdS films and the engineered properties are useful in photosensor applications, designing of solar cells and lasers, etc.

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