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Correlation between surface phonon mode and luminescence in nanocrystalline CdS thin films: An effect of ion beam irradiation

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The influence of swift heavy ion irradiation (SHII) on surface phonon mode (SPM) and green emission in nanocrystalline CdS thin films grown by chemical bath deposition is studied. The SHII of nanocrystalline CdS thin films is carried out using 70 MeV Ni ions. The micro Raman analysis shows that asymmetry and broadening in fundamental longitudinal optical (LO) phonon mode increases systematically with increasing ion fluence. To analyze the role of phonon confinement, spatial correlation model (SCM) is fitted to the experimental data. The observed deviation of SCM to the experimental data is further investigated by fitting the micro Raman spectra using two Lorentzian line shapes. It is found that two Lorentzian functions (LFs) provide better fitting than SCM fitting and facilitate to identify the contribution of SPM in the observed distortion of LO mode. The behavior of SPM as a function of ion fluence is studied to correlate the observed asymmetry (\(F_s/F_L\)) and full width at half maximum of LO phonon mode and to understand the SHII induced enhancement of SPM. The ion beam induced interstitial and surface state defects in thin films, as observed by photoluminescence (PL) spectroscopy studies, may be the underlying reason for enhancement in SPM. PL studies also show enhancement in green luminescence with increase in ion fluence. PL analysis reveals that the variation in population density of surface state defects after SHII is similar to that of SPM. The correlation between SPM and luminescence and their dependence on ion irradiation fluence is explained with the help of thermal spike model.

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I. INTRODUCTION

II–VI semiconductor nanostructures have emerged as a versatile building block for nanoelectronic and photonic devices ranging from sensors to light-emitting diodes. Simultaneously, they also offer numerous exciting physical phenomena arising from unique electronic states due to carrier confinement and/or the large surface-to-volume ratio. CdS thin films, in particular, have energy band gap in visible region and hence are exploited vitally in solar cells as win-

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et al.\textsuperscript{9,14} included one more characteristic regarding SPMs as, the full width at half maximum (FWHM) should increase with reduction in crystallite size due to increase in disorder.\textsuperscript{6} Till date, the effect of various factors on SPM like; dielectric media,\textsuperscript{15} thermal annealing,\textsuperscript{10} film thickness or particle size and laser excitation wavelength,\textsuperscript{9,13} and shell thickness\textsuperscript{14,16} has been studied for variety of nanostructures of different semiconductors including CdS.\textsuperscript{8–14,17–19} Particularly, for CdS nanoparticles and thin films deep understanding of SPMs is required, as the frequency of SPM varies from 249 cm\textsuperscript{-1} to 296 cm\textsuperscript{-1}.\textsuperscript{9,10,14,15,17} Moreover, the role of ion beam irradiation, i.e., fluence dependence of SPM is still unexplored.

Swift heavy ion irradiation (SHII) is an adaptable and flexible tool used for material engineering. The variety of effects in materials including high pressure phase generation\textsuperscript{20} defect creation,\textsuperscript{21} defect annealing,\textsuperscript{22} amorphization,\textsuperscript{23} and nanophase formation,\textsuperscript{24,25} etc., resulted due to rapid transfer of huge amount of energy during the electronic excitation within a narrow cylindrical region along the path of the heavy ion beam. SHII leads to many fold advantages over conventional annealing as; (1) one can increase/reduce (i.e., control) the particle size depending on the ion beam parameters, (2) the defect states can be controlled (creation/annihilation) in a precise way, and (3) the possibility of interdiffusion of elements at the interface with substrate can be avoided which usually occurs in the post deposition annealing at elevated temperature. Coulomb explosion\textsuperscript{26} and Thermal spike\textsuperscript{27} are mainly two approaches used to explain the energy transfer process in materials during ion beam interaction. The effect of SHII on various properties of CdS thin films grown by different deposition techniques\textsuperscript{28–31} has been reported.

In this article, we have investigated the cause of enormous distortion in Raman lineshape of LO mode due to the enhancement of SPM in irradiated nanocrystalline CdS thin films. The study is significant in context of its utility as an intermediate step in device fabrication consequently for the improvement of device performance. The analysis presented here confirms the structural phase transformation and presence of SPM in CdS thin films. The results are important in order to study SHII effect on CdS thin films and to understand the correlation of SPM to radiative defect states along with their dependence on ion fluence. Here, we demonstrated that the variation in SPM is related to the change in population density of surface state defects, which is a direct consequence of particle size variation caused by SHII. The elaborate dependence of SPM (viz., peak intensity, FWHM, position, and area) on surface states modified by SHII is discussed.

II. EXPERIMENTAL DETAILS

The CdS films were deposited on glass substrates from mixture of aqueous solutions of Cd(NO\textsubscript{3})\textsubscript{2} and Na\textsubscript{2}S with molarities 0.1 M and 0.5 M in deionized water. All chemicals, i.e., Cd(NO\textsubscript{3})\textsubscript{2}.4H\textsubscript{2}O and Na\textsubscript{2}S of analytical reagent grade were procured from Sigma Aldrich Ltd. (USA) and used without any further purification. Before deposition, the substrates were ultrasonically cleaned with acetone and rinsed in deionized water. The glass substrates were vertically immersed into a chemical bath containing mixture solution at a temperature of 80°C. The mixture was continuously stirred magnetically during film deposition. After dipping for 1 h, the films were washed thoroughly in deionized water to remove loosely adhered particles. The chemical reaction that undergone in this process is as given below

\[
\text{Cd(NO}_3\text{)}_2 + \text{Na}_2\text{S} \rightarrow \text{CdS} + 2\text{NaNO}_3. \tag{1}
\]

The thin films so prepared were irradiated with 70 MeV Ni\textsuperscript{6+} ions using 15 UD Pelletron at Inter University Accelerator Centre (IUAC), New Delhi, India. SHII was carried out in an experimental chamber having a vacuum of 5 x 10\textsuperscript{-6} Torr at room temperature. During irradiation, the ion beam current was maintained at \(\sim 1\) pA (particle nano-ampere) and to ensure uniformity of irradiation, the beam was scanned over an area of 1 cm\textsuperscript{2} of the sample with an electromagnetic scanner. SRIM simulations\textsuperscript{32} indicate the range, electronic energy loss and nuclear energy loss of the incident ion in the material as 10.94 \(\mu\)m, 1.060 \(\times\) 10\textsuperscript{-3} eV/A, and 3.086 eV/A, respectively. The irradiation dose was measured in terms of fluence and is varied from \(1 \times 10^{11}\) to \(1 \times 10^{14}\) ions/cm\textsuperscript{2} for this study.

Structural properties of the films were studied using glancing angle x-ray diffraction (GAXRD) at an angle 2\(^\circ\) using Bruker D8 diffractometer (Cu K\(_\alpha\) radiation, \(\lambda = 1.5406\) Å) and micro-Raman spectroscopy using Renishaw Invia Raman microscope equipped with Ar-ion laser (excitation wavelength = 514 nm). The optical band gaps of the films were determined by recording UV–Vis absorption spectra (Hitachi 3300 UV/visible spectrophotometer). Photoluminescence (PL) spectroscopy was carried out using HORIBA Jobin Yvon LabRAM 800 HR: excitation wavelength = 325 nm from He-Cd laser at room temperature to study the existence of different defect states in the film. Surface morphology and microstructure of the films were investigated by scanning electron microscopy (SEM) using MIRA\textlangle T\textrangle ESCAL FESEM.

III. RESULTS AND DISCUSSION

GAXRD patterns of as grown CdS thin film and films irradiated at different fluences of 70 MeV Ni ions are shown in Fig. 1. It is clear from diffraction patterns that as grown CdS film exhibits a preferred orientation corresponding to plane (111) of metastable cubic (zinc blende) phase at a diffraction angle 20 \(\sim 26.5°\) with other peaks at \(\sim 43.9°\) and 52.1° corresponding to the plane (220) and (311), respectively of cubic phase (PCPDF WIN-421411) with lattice constant 5.818 Å. Whereas, irradiated films show diffraction peaks at \(\sim 24.9°\), 26.7, 28.1°, 43.8°, 48.0°, and 52.1° corresponding to the planes (100), (002), (101), (110), (103), and (201), respectively, of stable hexagonal (wurtzite) phase of CdS (PCPDF WIN-800006) with lattice constants \(8 = 4.121\) Å and \(c = 6.82\) Å.

Here, we observe structural phase transition from cubic to hexagonal phase of CdS induced by SHII. It may be due to the atomic displacements followed by their collective rearrangements due to huge temperature generated during SHII. The crystallite size is estimated for all the samples...
corresponding to the common peak (at ~43.9°) using Debye
Scherrer’s formula given by

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

where $k = 0.9$, $\lambda$ is the wavelength of x-ray, $\beta$ is FWHM, and $\theta = \text{Bragg’s angle}$. The average crystallite sizes estimated for as-grown, $1 \times 10^{11}$, $1 \times 10^{12}$, $1 \times 10^{13}$, and $1 \times 10^{14}$ ions/cm$^2$ irradiated films are ~7.0, 9.1, 6.1, 5.3, and 4.3 nm, respectively. It suggests that at lowest fluence, ion beam does a constructive job (towards crystallization) and then destructive job (fragmentation or creation of defects) up to highest fluence. It has been reported by various groups that increase in average particle size may be due to defect annealing and reduction in particle size might be due to the formation of point defects, defect clusters, or creation of additional grain boundaries due to SHII.

Raman spectra of pristine and irradiated samples recorded in the range 150–750 cm$^{-1}$. The spectrum of pristine sample exhibits intense and broad peaks at $1570$, $962$, $930$, and $658$ cm$^{-1}$ corresponding to the common peak (at $43.9°$) using Debye–Scherrer’s formula given by

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

where $k = 0.9$, $\lambda$ is the wavelength of x-ray, $\beta$ is FWHM, and $\theta = \text{Bragg’s angle}$. The average crystallite sizes estimated for as-grown, $1 \times 10^{11}$, $1 \times 10^{12}$, $1 \times 10^{13}$, and $1 \times 10^{14}$ ions/cm$^2$ irradiated films are ~7.0, 9.1, 6.1, 5.3, and 4.3 nm, respectively. It suggests that at lowest fluence, ion beam does a constructive job (towards crystallization) and then destructive job (fragmentation or creation of defects) up to highest fluence. It has been reported by various groups that increase in average particle size may be due to defect annealing and reduction in particle size might be due to the formation of point defects, defect clusters, or creation of additional grain boundaries due to SHII.

The confinement function of first order Raman spectrum corresponding to Gaussian weighting function $e^{-8(\pi r^2/D^2)}$, is given by

$$I(\omega) = \Gamma_0 \frac{d^3 q e^{-\frac{(G q)^2}{8}}}{(\omega - \omega(q))^2 + \left(\frac{\Gamma_0}{2}\right)^2}, \quad (3)$$

where $\Gamma_0$ is natural linewidth (FWHM) of bulk crystal, $\omega(q)$ can be evaluated using phonon dispersion curve given as

$$\omega(q) = \sqrt{A^2 + B^2 \sqrt{1 + \cos(q a/2)}}, \quad (4)$$

where $a$ is lattice parameter of CdS, $A = 223$ cm$^{-1}$ and $B = 175$ cm$^{-1}$. It is found that SCM holds good only to estimate LO mode position in the experimental data and unable to fit FWHM and asymmetry of peak as seen in Fig. 2(b) for the sample irradiated at fluence $1 \times 10^{14}$ ions/cm$^2$. The average particle size $D$ used in SCM simulation is calculated by the formula used in

$$\Delta E = \frac{\hbar^2 \pi^2}{2 D^2} \left[ \frac{1}{m_e} + \frac{1}{m_b} \right] - \frac{1.786 e^2 c D}{2 \hbar} - 0.248 E_{gy}^T, \quad (5)$$

where $\Delta E$ is estimated by absorption studies, $m_e = 0.19 m_0$ and $m_b = 0.80 m_0$ are effective mass’s of electron and hole for CdS, respectively, $\varepsilon = 5.7$ is dielectric constant of CdS and $E_{gy}^T$ is effective Rydberg energy. Experimentally...
observed asymmetry is found to be smaller as compared to the calculated using SCM. In contrast, the function of the form of two LFs provides best fit to the asymmetry and FWHM of our experimental data. The fitting of LO with two LFs for the sample irradiated at fluence $1 \times 10^{14}$ ions/cm$^2$ is shown in Fig. 2(c).

Fig. 3 shows the variation of asymmetry and FWHM calculated using SCM, two LFs and experimental data as a function of ion fluence. It is obvious from Fig. 3 that the asymmetry calculated using two LFs is found to be very close to the experimental data though the FWHM of the samples irradiated at higher fluences is still smaller than that calculated from experimental data. It may be due to enhanced contribution of some other mode at higher fluences as can be clearly seen from Fig. 2(c). However, there is no obvious signature of peak or shoulder in low frequency wing of characteristic LO mode of experimental data, two LFs fitting enables us to recognize the existence of another mode lying between TO and LO modes of CdS centered at $\sim 252$ cm$^{-1}$. This peak may be ascribed to SPM since it exhibits two characteristics of SPMs as mentioned above and can be evidently seen from Fig. 2(c). Moreover, the frequency of observed mode is very close to the values as reported previously.

Further, to explore the cause of SHII induced enhancement in SPM, effect of ion fluence on various parameters of SPMs has been investigated. Fig. 4(a) shows the variation of area of SPM and LO phonon mode as a function of ion fluence. It is clear from Fig. 4(a) that area contributed by both modes is a linear function of ion fluence. On the other hand, the trend of variation in contributed area by two modes at fluence $1 \times 10^{11}$ ions/cm$^2$ is opposite. It may be ascribed to structural phase transition and reduction in density of surface defects due to SHII induced high temperature. It is found that the variation of FWHM of two modes with ion fluence is in opposite trend. Moreover, the variation of FWHM of LO mode is inversely proportional to the average particle size as in usual case, but FWHM of SPM is directly proportional to the particle size. The difference in asymmetry calculated using experimental data and two LFs fitting at fluence $1 \times 10^{14}$ ions/cm$^2$ is likely to a small enhancement in FWHM of LO mode relative to that at lower fluences. A discrepancy is observed between previous reports and present results, regarding variation in FWHM of SPM with average particle size. It may be because of the average particle size variation in present case is due to athermal annealing (SHII). Whereas, in Refs. 9 and 14 the particles of different sizes are synthesized.

Fig. 4(b) shows the variation of FWHM ratio of SP and LO mode ($SP_{FWHM}/LO_{FWHM}$) and asymmetry ($\Gamma_a/\Gamma_b$) of LO mode, calculated using two LFs, as a function of ion fluence. It can be seen that the variation of both $SP_{FWHM}/LO_{FWHM}$ and $\Gamma_a/\Gamma_b$ with ion fluence follows almost same trend. It is inferred here that the deviation of FWHM estimated using two LFs beyond fluence $1 \times 10^{13}$ ions/cm$^2$ is because of relatively higher rate of increment of $SP_{FWHM}/LO_{FWHM}$ only.

UV-visible absorption spectra are recorded for the films deposited on glass substrate to study effect of ion fluence on energy bandgap of CdS thin films. Fig. 5 show the Tauc plots of as-grown film and films irradiated at different fluences. The estimated values of direct bandgap are as $\sim 2.48$, $2.33$, $2.5$, $2.53$, and $2.61$ eV for as-grown, $1 \times 10^{11}$, $1 \times 10^{12}$, $1 \times 10^{13}$, and $1 \times 10^{14}$ ions/cm$^2$ irradiated films, respectively. Further, these values are used to estimate the average particle size using Eq. (5).

SEM micrographs are taken to visualize the surface morphology and average particle size on the surface and shown in Figs. 6(a)–6(e). It is obvious from micrographs that...
for the film irradiated at fluence $1 \times 10^{11}$ ions/cm$^2$ particles grow and then reduces up to highest irradiation fluence.

Fig. 7(a) shows the effect of ion fluence on the average particle size estimated using Debye Scherrer’s formula (Eq. (2)), effective mass approximation (Eq. (5)), and SEM micrographs. It can be seen that the average particle size estimated using Eqs. (2) and (5) are very close. However, the estimated size of particles by SEM images is relatively very large. It is probably due to the fact that SEM gives an image of the surface morphology, which depends on various growth parameters along with growth dynamics involves during post deposition treatments. Moreover, the particle size variation calculated either of the means shows similar behavior with variation in ion fluence. Fig. 7(b) shows the percentage change in average particle size with respect to particle size of as-deposited film estimated by means of above three techniques. It is obvious from Figs. 7(a) and 7(b) that though the particle size estimated using SEM micrographs are relatively very large to the particle size estimated using either UV-Visible absorption spectroscopy or GAXRD, the percentage change in particle size estimated either of three techniques is comparatively very close to each other and follows same trend.

The possible cause for enhancement in particle size in present study may be ion beam induced Ostwald ripening. The ion beam induced reduction in particle size is mainly explained by grain fragmentation $^{21,31,38}$ or by electronic sputtering from the surface of the film. $^6$ The previous one is due to the development of strain and the latter is because of transport of mass during imparting of huge energy by ion beam through the material. The two phenomena can be explained by Coulomb explosion $^{26}$ and thermal spike models. $^{27}$ The Coulomb explosion model predicts that a highly ionized zone of charged particles is formed along the ion path. If target electrons cannot retain the charge neutrality on the time-scale of lattice vibration, a rapid expansion of the material in the charged domain is produced due to the electrostatic repulsion of ionized target atoms. This rapid expansion generates shock waves in the path of ion trajectory. The
shock waves so developed in the material cause strain in the grains. Conversely, the thermal spike model suggests that the projectile ion deposits its energy through the electronic subsystem of the target. This energy spread among the electrons by electron–electron coupling and transferred subsequently to the lattice atoms via electron–lattice interactions, leading to vast increase in the temperature above the melting point of the material, along and in the vicinity of the ion path. The temperature spike builds up pressure waves that causes strain in the grains and strain leads to fragmentation of grains, which results reduction in particle size. The above discussed models; Coulomb explosion and spikes refer to the early and late aspects of the ionization track produced in a solid by a fast incident ion as proposed by Bringa et al.\textsuperscript{39} Electronic sputtering from surface is explained using extended version of thermal spike postulate. At large deposited energies, the flow of mass within the spike becomes relevant, where the thermal pressure in the hot core of the spike develops an elastic wave that governs the sputtering yield.\textsuperscript{40} Though both the phenomena take place simultaneously, the increment in defect density with increase in ion fluence suggests that inside the films, grain fragmentation is taking place whereas on the surface sputtering may be responsible for particle size reduction.

Fig. 8(a) shows PL spectra of as-deposited film and thin films irradiated at different fluences. It is obvious from spectra that pristine film shows a peak centered at $\sim 2.34$ eV corresponding to characteristic green emission (GE) with two humps at $\sim 2.1$ eV and 1.93 eV corresponding to yellow emission (YE) and red emission (RE) respectively. The origin of characteristic GE in nanocrystalline CdS thin films is ascribed to the transition of S-vacancy donors ($V_S^-$) to the valence band and conduction band to S-interstitial ($I_S$).\textsuperscript{28,31,41} The YE is described either as a result of recombination via surface localized states, radiative transition from donor levels, i.e., Cd atoms located in interstitial sites ($I_{Cd}$) to the valence band,\textsuperscript{28,31,42–44} or the transition from interstitial cadmium–cadmium vacancy complexes ($I_{Cd} - V_{Cd}$) which is a donor to acceptor level transition.\textsuperscript{31,43,45} The origin of RE is attributed to the transition of bound electrons from surface states to the valence band ($VB$).\textsuperscript{44,46} Sulfur vacancies ($V_S^{2-}$)\textsuperscript{47} or cadmium vacancies ($V_{Cd}^{2-}$)\textsuperscript{48} are the defects accountable for such transitions. In present study, all emission may be due to non-stoichiometry of as-deposited film. It is evident from Fig. 8(a) that the intensity of all emissions first decreases for the film irradiated at fluence $1 \times 10^{11}$ ions/cm$^2$ and then increases up to highest fluence. It may be due to annealing of defect causes by the heating effect produced during SHI at irradiation fluence $1 \times 10^{11}$ ions/cm$^2$ as the particle size is increased, which is suggested by other techniques.

The enhancement in emissions intensity suggests increase in defect level after irradiation at higher fluences due to fragmentation of grains, which is in agreement with reports of Kumar et al.\textsuperscript{21} They examined the effect of SHII on polycrystalline thin films of LiF, effect of grain size on the color centers, effect of fluence on grain size and hence on defects and reported that SHII of nano-granular LiF thin films leads to the formation of color centers as well as grain fragmentation simultaneously. We carried out a multi-peak fitting of PL spectra using a Gaussian function for insightful analysis of the presence of different emission peaks corresponding to various defect levels and their contribution in SPM as a function of irradiation fluence. Figs. 8(b)–8(f) shows the de-convoluted peaks in the experimental data of all the samples achieved by fitting of three peaks.

The variation of area contributed by GE, YE and RE is plotted in Fig. 9 as a function of ion fluence, to study the behavior of intensity variation of defects in CdS thin films. It is apparent that area contributed by different emissions first decreases for the sample irradiated at fluence $1 \times 10^{11}$ ions/cm$^2$ and indicates an annealing of defects at this fluence due to grain growth. Further, increase in ion fluence increases the...
contributed areas, suggested that at higher fluences population density of defects corresponding to different emissions increase due to grain fragmentation. Since, the origin of the SPM modes can be attributed to the defects on the surface of microspheres, because the surface potential is affected by the surface defects, which leads to the breakdown of symmetry on the surface of microspheres. In present study, the variation in contributed area of RE with ion fluence suggests that density of surface state defect (responsible for RE) first decreases for the film irradiated at fluence $1 \times 10^{11}$ ions/cm$^2$ and then increase up to highest fluence. This behavior of area contributed by RE as a function of ion fluence is analogous to the behavior of area contributed by SPM (Fig. 4(a)). Moreover, the SPMFWHM/LOFWHM and asymmetry variation of spectral Raman line shape with ion fluence is in same manner with the variation in contributed area of RE. Keeping these observations in mind, we may conclude that the behavior of SPM mode is purely dependent on the variation in surface state defects of nanocrystalline CdS thin films caused by the SHII. In present study, a clear signature of peak or shoulder related to SPM is not observed in Raman spectra, may be due to the fact that the enhancement in population density of surface state defects are relatively small than other defects (interstitial or vacancies) related to GE and YE. Moreover, it gives an insight to realize the surface conditions (defects and particle size) by studying the Raman spectra.

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**IV. CONCLUSION**

In summary, the effect of SHII on CBD grown nanocrystalline CdS thin films is investigated and observed that SCM is unable to fit asymmetry and FWHM of our experimental data. Whereas, two LFs enables best fitting in present study and allocate SPM. The distortion in Raman spectral line shape of LO mode as a consequence of SHII is due to the contribution of SPM. The characteristics of RE and SPM as a function of ion fluence are analogy. Therefore, the SPM may attribute to the surface state defects caused by SHII. The absence of clear peak or shoulder related to SPM may be due to the fact that the enhancement in population density of surface state defects are relatively very small than other defects (interstitial or vacancies) related to GE and YE. The enhancement in different emissions is ascribed to creation of defect levels and grain fragmentation. SHII induced grain fragmentation is the possible mechanism for observed reduction in particle size and enhanced band gap beyond irradiation fluence of $1 \times 10^{11}$ ions/cm$^2$. The reduction in bandgap at fluence of $1 \times 10^{11}$ ions/cm$^2$ is attributed to ion beam induced grain growth due to Ostwald ripening.