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Raman and photoluminescence investigations of disorder in ZnSe films deposited on *n*-GaAs

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We report Raman and photoluminescence studies of ZnSe films deposited on a (100) *n*-GaAs substrate by pulsed laser deposition. We have investigated the disorder in the thin films of ZnSe by analyzing the asymmetry of the ZnSe LO modes. We find that the best fit of the line shape is obtained using the spatial correlation model and invoking the presence of a zone edge LO phonon. This zone edge LO phonon is attributed to the presence of disorder in the material. The intensity of this disorder activated zone edge phonon is found to correlate very well with the results of the crystal quality obtained from x-ray diffraction. In addition we have studied the variation of the depletion widths in the GaAs substrate as a function of the deposition parameters of ZnSe, using the intensity ratios of the LO and L_- modes of an *n*-GaAs substrate. We have also analyzed the origin of the deep center luminescence observed in these films. The information is found to be complementary and consistent with that obtained by Raman spectroscopy and the variations expected due to different deposition conditions. [S0163-1829(99)13439-8]

I. INTRODUCTION

ZnSe, with a band gap of 2.7 eV at room temperature, is an important material for blue light emitting diodes (LED) and laser diodes. The quality of ZnSe epilayers on GaAs is very crucial for good performance of ZnSe based optoelectronic devices. X-ray diffraction, TEM, photoluminescence, and Raman spectroscopy are usually used to characterize the ZnSe epilayers for their crystalline and optical quality. Raman analysis of various kinds of bulk semiconductors and heterostructures have been carried out previously for many systems, such as InAs,[1] *n*-GaAs,[2] and ZnSe/GaAs heterostructures.[3,4] In this paper, we report a systematic Raman and photoluminescence investigation of ZnSe films deposited on GaAs by pulsed laser deposition (PLD) and we correlate various aspects of the observed Raman spectra with the crystalline quality of the ZnSe films and the interface of ZnSe and GaAs.

Experimental details are described in Sec. II. The discussion of asymmetry of the LO phonon of ZnSe in terms of the spatial correlation model (SCM) and disorder activated zone edge LO phonon (DA-ZE-LO) is given in Sec. III. In the same section, we also discuss the details of the evaluation of the band bending on the substrate side of the interface for various samples using the intensity ratio of the lower branch of a coupled LO phonon-plasmon peak and the LO phonon of GaAs. In the analysis, band bending on the substrate side of the interface and the DA-ZE-LO phonon have been related to the crystalline quality of the films.

We have observed luminescence in the red region of the spectra, which is known to originate from deep centers, in all the films. The luminescence data has been found to be consistent with the conclusions drawn from Raman analysis and is also presented in Sec. III. Finally, we have correlated the Raman and photoluminescence data with the crystalline quality of the films and the deposition conditions. A brief description of the effects of the deposition parameters on the film quality as studied by Raman and photoluminescence is also given.

II. EXPERIMENT

The ZnSe films are grown by pulsed laser deposition (PLD) on (100) oriented *n*-GaAs substrates. These samples were deposited at 280 °C and 400 °C substrate temperatures. Two different ambients have been used for the depositions, 10^{-5} Torr and 1 mTorr of He. The details of the deposition have been discussed in another paper.[5] The deposition parameters and the high resolution (HR) x-ray diffraction (XRD) results of the films studied in this work are mentioned in the first three columns of Table I.

The unpolarized Raman spectra are recorded in backscattering geometry at room temperature (RT) using a 4880 Å line of Ar ion laser. The backscattered light is passed through a double monochromator U1000 (Jobin Yvon) and detected by photomultiplier tube R943-02 (Hamamatsu) in photon counting mode. The Raman spectra of all the films are shown in Fig. 1. The photoluminescence spectra were recorded also in the backscattering geometry using a 4579 Å excitation of the Ar ion laser.

III. RESULTS AND DISCUSSION

Figure 1 shows Raman spectra for all the samples in the range of 200 to 305 cm^{-1}. Raman spectra of all the samples shows three peaks at 205, 253, and 292 cm^{-1}, which correspond to the TO phonon of ZnSe, LO phonon of ZnSe, and LO phonon of GaAs, respectively. The Raman intensity in the region between the 253 and 292 cm^{-1} peaks suggests the presence of an additional mode. We attribute this mode to the lower branch of the coupled LO phonon-plasmon mode of GaAs. To elucidate the contribution of the lower branch of the plasmon-phonon coupled mode, each Raman spectrum was fitted with four Lorentzians corresponding to the two LO and one TO phonons mentioned above and the coupled mode. In addition, the background with a spectral dependence of the form $A+B\times\omega$ was used to account for the Rayleigh wing. The parameters A and B were calculated from the data away from the peaks. The least square fits

TABLE I. Table summarizes the growth parameters, crystalline quality, observed $I(\mathrm{LO})/I(L_-)$ ratio, and the calculated values of the barrier potential and the depletion widths.

Sample identity	Dep. temp. and pressure	HR XRD width (arc sec)	$I(\mathrm{LO})/I(L_-)$	V_b (V)	Depl. width (Å)
$S1$	280 °C 10^{-5} Torr	poly. cryst.	0.38		
$S2$	400 °C 10^{-5} Torr	$\sim$600	1.21	0.76	311
$S3$	280 °C 1 mTorr He	$>$700	0.97	0.67	293
$S4$	400 °C 1 mTorr He	320	0.75	0.57	272

obtained are shown by solid lines in Fig. 1 and experimental data by crosses. The actual line shape of the lower branch of the coupled phonon-plasmon mode is expected to be a modified Lorentzian.[6] However, in our case, where the full width half maximum (FWHM) of the mode is nearly 22 cm^{-1} in all the samples, including the bare n-GaAs substrate, it is reasonable to use the values of total intensity and position obtained by fitting a Lorentzian.

A. Asymmetry of the LO ZnSe mode

It has been observed that there is a distinct asymmetry on the lower frequency region of the ZnSe LO phonon, especially in samples $S1$ and $S3$. Much smaller asymmetry has been seen in the ZnSe LO phonon of film $S2$ and $S4$. This asymmetry can be related to the defects in crystalline structure of the films. The defects in the material breaks the translational symmetry of the crystal, leading to the contribution of $q \neq 0$ phonons to the Raman spectra. In ZnSe, the dispersion curve for the LO phonon has a negative slope near $q = 0$, giving rise to asymmetry on the lower frequency side of the phonon.[7] The line shape was calculated using the spatial correlation model (SCM). The model assumes that the phonons are freely propagating in a region of length L and are confined in that region. Beyond this length L, they get scattered from the crystal imperfections. We have used a Gaussian confinement function in the SCM fitting, as it has been empirically found that Gaussian confinement function gives a better fit to the Raman spectra in quantum dots.[8] We have taken isotropic and cosine square dispersion curves with a spherical Brillouin zone and maximum dispersion of 40 cm^{-1} (Ref. 7). Figure 2 shows the LO phonon of ZnSe in all the films with SCM fit to the line shape. The best fits obtained for each sample with the characteristic correlation lengths are 122 Å for film $S4$, 96 Å for the film $S2$, 94 Å for the film $S3$, and 77 Å for the film $S1$. It has also been shown by Wang *et al.*[9] that the correlation length is a good measure of the crystalline quality in many semiconductors, including ZnSe/GaAs systems. The correlation length can be physically interpreted as the average distance between two defects or dislocations or any other kind of imperfections in the crystal. Thus, higher dislocation density corresponds to a smaller value of the correlation length and vice versa. From SCM results, we find that film $S4$ has the best crystalline quality and film $S1$ is the worst among the films studied in this work. This is confirmed by the results obtained by XRD as mentioned in Table I.

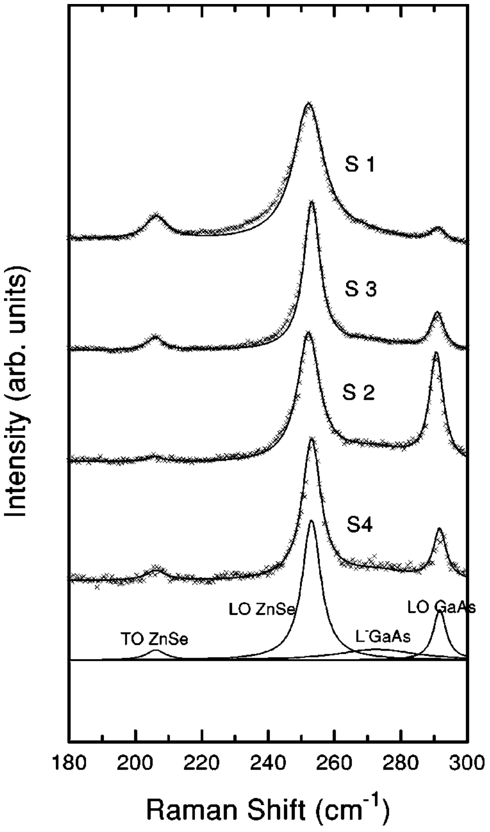

FIG. 1. Raman spectra for the films $S1$, $S2$, $S3$, and $S4$. Experimental points are shown by crosses. The result of the fitting of four Lorentzians are shown by the solid line. At the bottom, solid lines show individual Lorentzians for sample $S4$.

Figure 2 shows that though SCM gives proper trend for crystalline quality, it does not describe the asymmetry completely. The asymmetry can be fitted very well with an additional broad Lorentzian at $\sim 239\ \mathrm{cm}^{-1}$ (FWHM of $\sim 18\ \mathrm{cm}^{-1}$). The fitting using SCM and the additional Lorentzian is shown for sample $S1$ in the lowest curve in Fig. 2, where the misfit is the maximum. Similar fits have been obtained for other samples. This additional mode is attributed to the disorder activated zone edge LO phonon (DA-ZE-LO). Disorder of any kind can manifest itself in two ways. One is as described above by the spatial correlation model and the other by appearance of disorder activated modes, which are essentially a replica of the density of

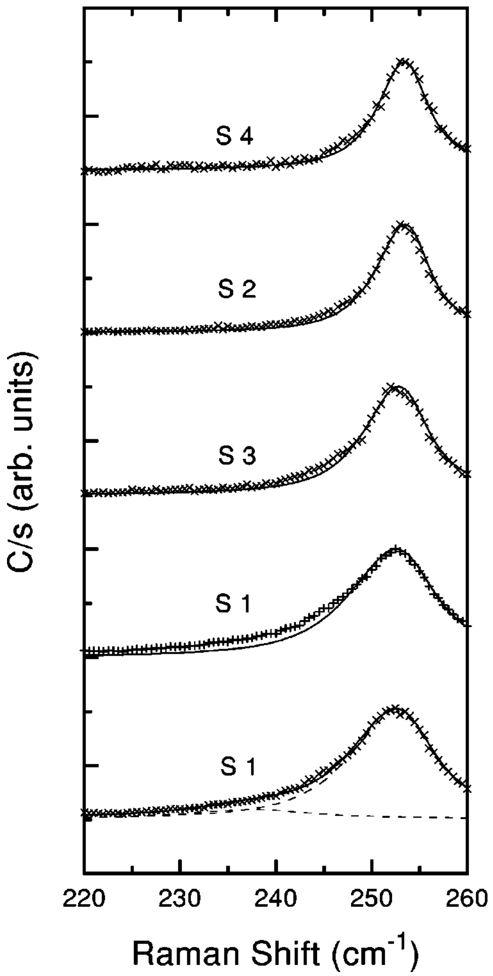

FIG. 2. The spatial correlation model fit for the samples $S1$, $S2$, $S3$, and $S4$. The one Lorentzian and SCM fit of the ZnSe DA-ZE-LO peak and LO phonon peak, respectively, is shown for sample $S1$. The Lorentzian and SCM fits are shown individually by dashed lines at the bottom.

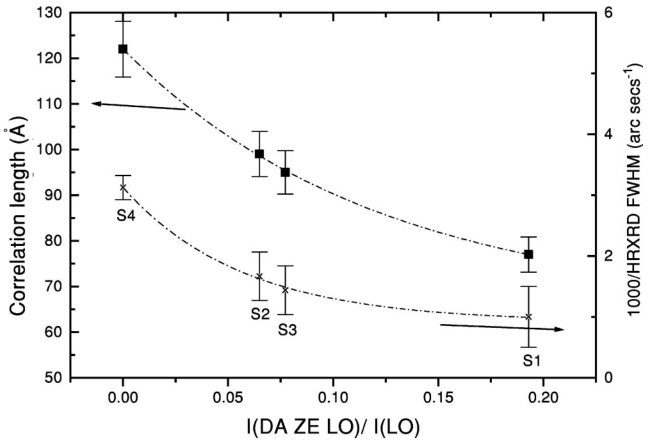

FIG. 3. The relation obtained between the correlation length L (right-hand y axis) and the normalized intensity of the DA-ZE-LO phonon for the four samples discussed. The relation between the inverse of the high resolution XRD-FWHM (left-hand y axis) and the normalized intensity of the DA-ZE-LO phonon. The dashed lines are a guide to the eye.

states.[9,10] Near resonance, q dependent intraband Frohlich interaction is the dominant contribution to Raman scattering and is also confirmed for our samples by polarized Raman measurements.

To see how well the intensity of DA-ZE-LO relates to disorder in the films, we have plotted the intensity of the DA-ZE-LO phonon normalized to the intensity of the zone center LO phonon of various films to the correlation length of the samples in Fig. 3. The plot of the intensity of the DA-ZE-LO phonon versus the inverse of the HRXRD-FWHM is also given in the figure. Figure 3 clearly shows that the normalized intensity of the DA-ZE-LO phonon is a good measure of the disorder in the ZnSe films.

B. L_{-} and LO GaAs mode

At the surface of the n-GaAs substrate band bending leads to the formation of a depletion layer, which is devoid of carriers. Generation of new interface states and change in surface states due to the deposition of ZnSe on the substrate results in the transfer of charges from the substrate to the interface. This modifies the depletion width on the substrate side. As the electron concentration is $\sim 10^{18}\,\mathrm{cm}^{-3}$ in the bulk of n-GaAs, there is a complete screening of the long-range electric field of the LO phonons. This region therefore contributes only to the L_{-} mode and the contribution to the observed LO phonon of GaAs comes only from the depletion layer. The broadband at $\sim 272\,\mathrm{cm}^{-1}$ observed in all the Raman spectra of the films is the coupled LO phonon-plasmon mode in n-GaAs substrate. Murase *et al.*[2] have calculated the dispersion relationship of the L_{-} modes for n-GaAs. In near backscattering geometry for an excitation wavelength of 4880 Å, the damped LO phonon-plasmon mode (L_{-} mode) is calculated to be $271.4\,\mathrm{cm}^{-1}$ (Ref. 2).

In our case the excitation energy is 2.54 eV. This is not far away from the E_1 critical point in the electronic band structure of GaAs ($E_1 = 3\,\mathrm{eV}$ for GaAs), small resonance effects can contribute to Raman scattering. The polarized Raman measurements show that forbidden LO is indeed the major contribution in the observed LO intensity. It is known that near resonance, electric field induced LO phonon contributes its largest, where, LO phonon intensity is obtained only from the depletion width. This electric field induced forbidden LO phonon intensity is proportional to the square of the electric field in the region of interest. Thus the ratio of the intensity of the LO phonon to the intensity of the L_{-} phonon can be written as

$$\frac{I(\mathrm{LO})}{I(L_{-})} = \frac{C\int_0^W E(x)^2 e^{-2x/D}dx}{\int_W^\infty e^{-2x/D}dx}, \tag{1}$$

where $E(x)$ is the electric field at a distance x inside the depletion width from the GaAs surface. D is the penetration depth of the laser line in GaAs and is taken from standard text.[11] The width W is related to the depletion width W_o by the relation

$$W = W_o - 50\,[\text{Å}]. \tag{2}$$

Both W and W_o are in Å. The 50 Å width is to take into account the finite transition region between the depletion region and the bulk in a degenerate semiconductor.[12] The constant C includes the Raman cross sections of the plasmon and the LO phonon of the substrate, which is a constant for all the films. We have evaluated the value of the constant C from the known value of the depletion width of bare n-GaAs measured from photoemission experiments[12,13] and our observed values of $I(\mathrm{LO})/I(L_{-})$ for bare n-GaAs. The electric field is evaluated using the depletion approximation and is given by

$$E(x)=\frac{qN_D}{\epsilon_s}(W_o-x), \tag{3}$$

where ϵ_s is the dielectric constant of GaAs and N_D is the doping density of the substrate. Table I summarizes the values of the depletion widths obtained for the four samples using the above formulation. Barrier heights for all the samples have also been evaluated by depletion approximation,[13] which are mentioned in Table I.

The depletion width shown by the film $S1$ is much smaller than the value expected from the trend shown by the other films. This may be understood in the light of the fact that the FWHM of the LO ZnSe peak is quite large ($\sim 11\,\mathrm{cm}^{-1}$) for this film, which leads to uncertainties in the values of the parameters obtained for the four Lorentzian fits. This introduces relative errors in the calculation of the ratio $I(\mathrm{LO})/I(L_{-})$, giving a lesser value. Furthermore, as this sample is a randomly oriented polycrystalline film, forbidden and allowed geometry does not have any definite meaning for the film. Ignoring the results of $S1$, the trend of depletion width shown by other samples will be discussed following the discussion of photoluminescence results.

C. Photoluminescence studies

We have observed luminescence in the red region of the spectra, in the wavelength range of 500 to 650 nm. However, the intensity and profile of this red luminescence varies between films deposited under different conditions. The samples deposited at 280 °C in vacuum and 1 mTorr of He both have negligible red luminescence. This can be explained from the crystalline quality of the films. Film $S1$ is a polycrystalline film, and $S3$, although oriented along the substrate, has a high resolution XRD FWHM is greater than 700. It is thus expected that film $S1$ and $S3$ have a large number of nonradiative recombination centers leading to a very small visible luminescence. Band edge luminescence is also negligible in these films.[5]

However, films $S2$ and $S4$ have large intensity of both band edge and deep center luminescence. Band edge luminescence in film $S4$ is four times more than film $S2$, whereas deep center luminescence from $S4$ is five times less than film $S2$. Deep center luminescence mainly originates from vacancies, intersites, and complexes and has been well studied for various II-VI materials including ZnSe.[14] Figure 4 shows the deep center luminescence observed in films $S2$ and $S4$. To resolve the contribution of different deep centers in the films, we fitted the observed profile, with two Gaussian profiles which is shown in Fig. 4. For film $S2$, the two peaks are at 647 and 617 nm with 68 and 73 nm widths, respectively. In film $S4$ the two peaks are at 652 and 605 nm with 65 and 50 nm widths, respectively. Further, in both the cases, we can see that the peak at ~ 650 nm has a higher intensity as compared to the other peak. The peak at ~ 650 nm is identified as due to Ga atoms in ZnSe film.[15] The peak at ~ 610 nm is due to the vacancies of Zn in ZnSe.[16]

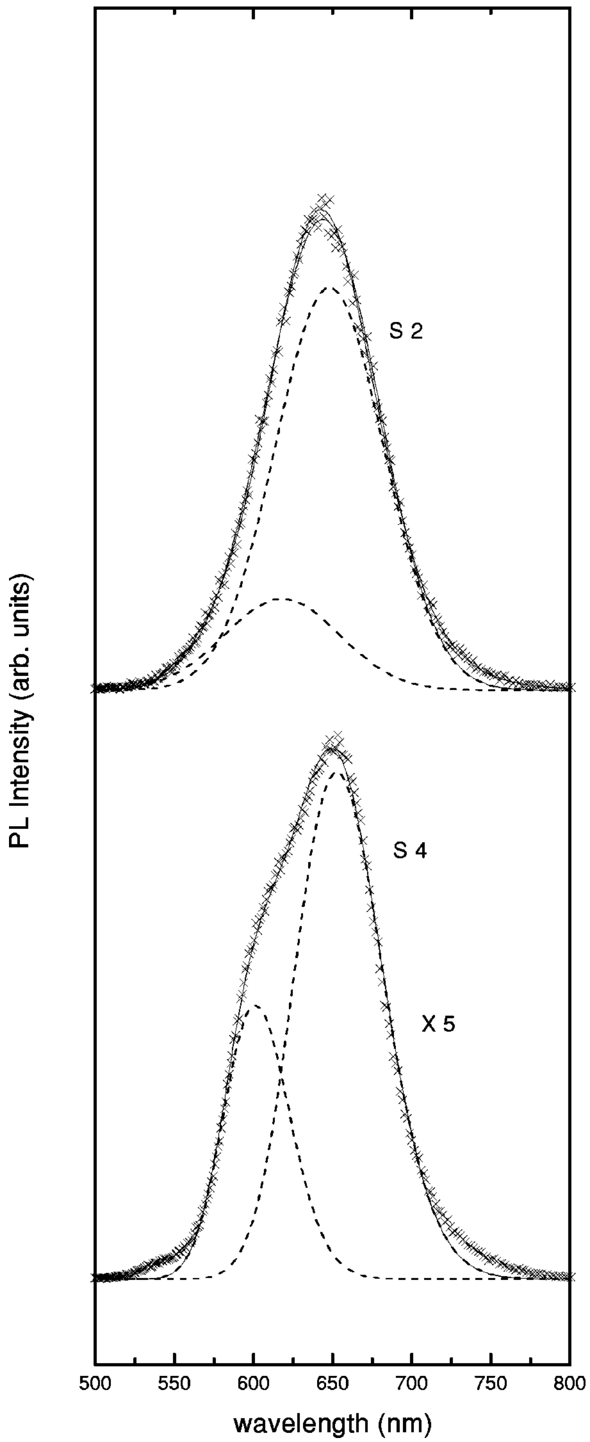

FIG. 4. Photoluminescence spectra of the two films $S2$ and $S4$. The dashed lines show the two fitted Gaussian profiles to the spectra.

D. Role of He in pulsed laser deposition (PLD)

The above analysis of the Raman and photoluminescence data can be used for the interpretation of the role of He in the deposition of the ZnSe films during the process of pulsed laser deposition. In the following section, we briefly review the role of 1 mTorr of He on the film quality as interpreted by the results of Raman and photoluminescence.

It has been observed by Olego for molecular beam epitaxy (MBE) grown ZnSe/GaAs systems that there is a systematic variation of the depletion width as the thickness of the ZnSe layer is increased beyond the critical thickness.[3] This increase in depletion width is attributed to an increase in interface density of states. The dislocation in the epilayer, formed to relieve the strain, contributes to this interface of density states, which in turn manifests in the form of an enhanced depletion width. The minimum barrier height obtained by Olego for ZnSe film deposited by MBE is $\sim 0.075\,\mathrm{eV}$. This corresponds to the condition of minimum interface states and dangling bonds which is achieved below the critical thickness of the ZnSe film on GaAs, i.e., $\sim 150\,\mathrm{nm}$. For a 1 μm thick film, which is the thickness of all our films, the barrier height obtained by Olego was $\sim 0.3\,\mathrm{eV}$. In our case, the minimum barrier height obtained was $0.41 \pm 0.05\,\mathrm{eV}$. The different barrier heights obtained for different films with similar thickness is thus due to the difference in the crystalline quality of the films. The excess barrier height obtained in our case can be due to: (i) Three dimensional growth in PLD, which leads to a higher dislocation density than the dislocation density created solely due to strain relaxation; (ii) High energy Zinc atoms and ions in the PLD plasma plume get implanted into the GaAs substrate; (iii) Ga outdiffusion from the substrate into the ZnSe film. Regarding crystalline quality and dislocation density, a comparison between the films deposited with and without He at the same temperature indicates that there is a reduction of dislocation density and hence an improvement in the crystalline quality when the deposition is carried out in 1 mTorr of He. This is indicated conclusively by the correspondence between the normalized intensity of the DA-ZE-LO phonon and the HRXRD width (as shown in Fig. 3), and a fall in the depletion width on the substrate side. The later two processes mentioned above, ie., Ga outdiffusion from the surface of GaAs substrate and Zn implantation in GaAs, both make the substrate p-type, thereby increasing the depletion width on the substrate side of the interface. The depletion width in GaAs side for film $S2$ is larger than the depletion widths obtained for the films $S3$ and $S4$, which has been deposited in 1 mTorr of He. This indicates that the presence of He reduces both the above mentioned phenomena. Local p-doping by Zn atoms is further expected to manifest itself in the form of Zn vacancies in the ZnSe film. Ga outdiffusion from the substrate would result in Ga incorporation in the film as either interstitials or substitutional defects. These effects are also indicated by the photoluminescence analysis where there is both a reduction of the Zn vacancy peak and the Ga interstitial peak when the deposition is carried out in 1 mTorr of He. These effects are expected due to the reduction of the energy of the plume particles when the deposition is carried out in 1 mTorr of He.

IV. CONCLUSION

We have used Raman scattering to study the disorder in the films of ZnSe deposited by pulsed laser deposition under different conditions. We have shown that the asymmetry in the ZnSe LO phonon peak can be directly related to the crystalline quality of the film using spatial correlation model. Minimum disorder, corresponding to maximum correlation length has been seen in the epitaxial ZnSe film (film $S4$) deposited in 1 mTorr of He at 400 °C. Further, we show that the mismatch of data to SCM fit at the wings is mainly due to the presence of a disorder activated zone edge LO phonon mode. The intensity of this disorder activated zone edge phonon is found to correlate very well with the results of the crystal quality obtained from XRD. Using the intensity ratios of the LO and L_- modes of GaAs, we have evaluated the interface band bending in GaAs substrate, when overlying layers of ZnSe have been deposited under different conditions. Raman results clearly show that there is an improvement in the crystalline quality of the films when the deposition is carried out in an ambient of 1 mTorr of He. Raman analysis of the LO and L_- modes of GaAs and the PL analysis show that the presence of He during deposition results in the reduction of outdiffusion of Ga from the substrate, and Zn implantation in the substrate. This reduces the defect luminescence and increases the band edge luminescence.

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