Lineshape analysis of ZnSe longitudinal optical phonons near the E_0 gap excitation of epitaxial ZnSe/GaAs(001)

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Longitudinal optical (LO) phonon lineshape of pulsed laser deposited ZnSe epitaxial films on (001) oriented GaAs with near E_0 gap excitation is investigated. Temperature dependence Raman data with 4579 Å excitation show a shift of resonance from 2LO anti-Stokes to the LO Stokes in the temperature range of 150–300 K. The ZnSe LO lineshape does not fit a Lorentzian profile and is characterized by the presence of large wings on both the lower and higher frequency sides of the LO phonon. The wings on the lower frequency side of the LO phonon are attributed to the Fano interaction of the LO phonon and an electronic continuum due to photogenerated carriers. The electronic continuum is observed in Stokes and anti-Stokes Raman spectra when in resonance. We have proposed an electronic transition scheme based on the presence of donor states below the conduction band to explain the observed electronic continuum. The dependence of the intensity of the continuum with the incident laser intensity is also accounted for in the same scheme. Wings at the higher frequency side of the ZnSe LO phonon are attributed to a combination phonon $[\mathrm{TO}(\boldsymbol{q})+\mathrm{TA}(\boldsymbol{q})]$ at ~270 cm^{-1}, which is also confirmed by the temperature behavior of the mode.

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We have observed that the ZnSe longitudinal optical (LO) mode lineshape in the Raman spectra recorded with excitation near the E_0 gap is different from the ones that are recorded for excitations below the E_0 gap. Although similar results have been obtained earlier, we did not come across any systematic study or detailed explanation of the same.[1]

Modifications of the LO phonon lineshape can have many different origins. In an earlier work, we have shown that the presence of disorder activated zone-edge LO phonon contributes to producing an asymmetric LO phonon lineshape.[2] Changes in the LO phonon lineshape have also been observed in II-VI mixed crystal due to disorder activated zone-edge phonon.[3] Coupling between LO phonon and collective oscillations of free electrons (plasmons) leads to coupled LO phonon-plasmon modes, thereby modifying the LO phonon lineshape. These lineshapes have been discussed by several authors, and a detailed review of the same is given in Ref. 4. The presence of free carriers can also lead to single particle excitation electronic continuum (EC), whose interaction with discrete LO phonons leads to an asymmetric lineshape referred to as Fano lineshape.[5,6]

In the present work, we show that the LO phonon lineshape, when excited near the E_0 gap (4579 Å), is modified due to Fano interaction of the LO phonon with an electronic continuum. An electronic transition scheme between shallow donor levels and the conduction band is proposed to explain the presence of the observed EC.

The ZnSe epilayer was deposited by pulsed laser deposition on (001) oriented semi-insulating GaAs substrates.[7] The Raman spectra of the sample have been recorded in backscattering geometry on a JY U1000 double monochromator (Jobin Yvon, France) with various lines of an Ar ion laser (Coherent, USA). A Hamamatsu R649S Peltier cooled photomultiplier tube was used as the detector. The temperature dependent Raman measurements were carried out using a closed cycle He cryostat (Leybold, Germany).

Figure 1 shows Raman spectra of ZnSe/GaAs with excitations (i) below the band gap [4880 Å (2.54 eV)] and (ii) at the band gap [4579 Å (2.71 eV)]. Raman spectra in backscattering geometry with given sample orientation (001) allows only LO phonons for both GaAs and ZnSe. The dominant structures observed for 4880 Å excitation are identified as due to LO ZnSe at 251 cm^{-1} and LO phonon of GaAs at 292 cm^{-1}. The weak structure ~205 cm^{-1} is the forbidden TO phonon of ZnSe. Another weak structure observed ~270 cm^{-1} will be discussed later. Figure 1 also shows the fitting (solid line) of the LO phonons with a Lorentzian lineshape. From the fit, one can clearly see that the ZnSe LO phonon lineshape at 4880 Å excitation is a Lorentzian with a full width at half maximum (FWHM) of 5.5 cm^{-1}. The GaAs-LO phonon also fits a Lorentzian lineshape. However, we find that as the excitation approaches the E_0 gap of ZnSe (2.69 eV), i.e., at 4579 Å excitation, in addition to resonance enhancement of the Raman signal, the LO lineshape and FWHM (10 cm^{-1}) are also drastically altered than that observed with 4880 Å excitation. The LO phonon has large wings on high and low frequency sides, as seen from difference between the Lorentzian lineshape fitted for this spectrum (Fig. 1). Similar lineshape modification is also observed on the anti-Stokes side of Raman spectra. The modification of the lineshape and increase in the FWHM of the LO pho-

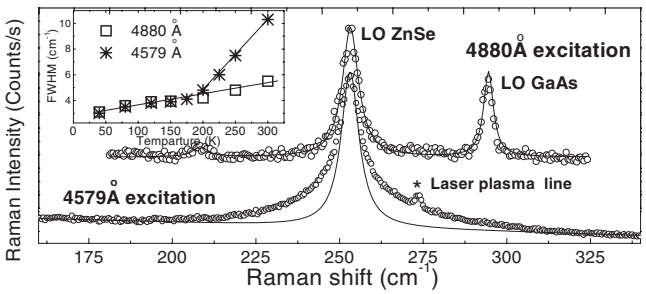

FIG. 1. Raman spectra for different excitations with inset showing FWHM of LO phonon of ZnSe vs temperature.

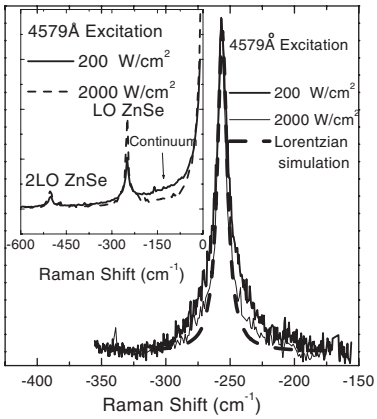

FIG. 2. LO lineshape and continuum (inset) for the LI and HI cases.

non are indicative of the presence of an interaction of the LO phonon with some other excitation of the system. The GaAs-LO phonon mode is not observed in the Raman spectrum with 4579 Å excitation. This can be due to (i) absorption of 4579 Å light in ZnSe film, thereby resulting in a reduced incident intensity reaching the GaAs substrate, and/or (ii) low incident power may not be enough to excite the Raman spectra in GaAs.

The inset in Fig. 1 shows the FWHM of the ZnSe-LO phonon vs temperature for 4880 Å and 4579 Å excitations. The FWHM of the LO phonons for two excitations follow the same path up to 200 K. Above 200 K, the FWHM for the two excitations deviate significantly from each other as shown in the inset. From the reported variation of the E_0 gap of ZnSe with temperature, one finds that at ~260 K, 4579 Å excitation (2.708 eV) matches the E_0 gap of ZnSe.[8] Thus, the absorption of the 4579 Å line would increase rapidly as the temperature increases beyond 260 K. This leads to the generation of excitons and free electron-hole pairs. Presence of free carriers can manifest in two possible ways: (i) by collective excitations and (ii) by single particle excitation.

(i) Collective excitation. Collective excitations leading to coupled plasmon-phonon modes would result in a carrier density dependent lineshape modification. Therefore, a greater modification of the LO phonon lineshape along with an increase in the frequency of the coupled mode is expected with an increase in carrier concentration. Figure 2 shows the Raman spectra measured using higher laser intensity (HI) by focusing the spot to ~10 μm (2×10^3 W/cm^2) and normal lower laser intensity (LI) with spot focus ~50 μm (~200 W/cm^2). We find a larger lineshape modification in the wings of the LO phonon mode for LI Raman measurements as compared to the HI Raman measurements. Furthermore, the two profiles have exactly the same peak positions. Both these observations confirm that ZnSe-LO phonon lineshape modification cannot be due to coupled plasmon-phonon modes.

(ii) Single particle excitations. To check the presence of an EC arising from single particle excitation, we have recorded Stokes and anti-Stokes Raman spectra at different temperatures with 4579 Å excitation (Fig. 3). Raman spectra for temperatures above 150 K show resonance enhancement.

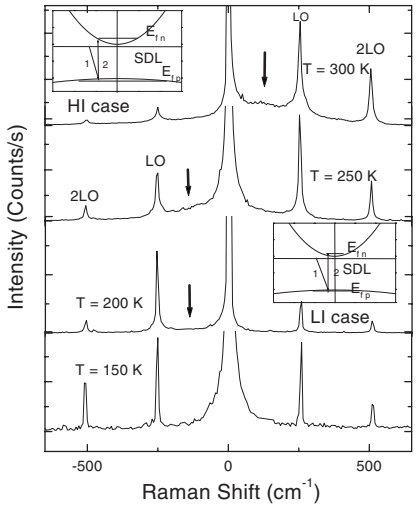

FIG. 3. The electronic continuum (shown by arrows) and the corresponding Raman transitions for the HI and LI cases are shown in the left and right insets, respectively. SDL refers to shallow donor levels.

The resonance shifts from 2LO (anti-Stokes) to LO (Stokes) as the temperature reaches 300 K. Most notable feature, as indicated by the arrow in Fig. 3, is a broad structure in the range of 50–300 cm^{-1}. This structure is attributed to the single particle excitation EC. We find that, like LO phonon, the continuum in the range 50–300 cm^{-1} also shows a shift of resonance with temperature in accordance with the shift of resonance from anti-Stokes to Stokes side. The resonance enhancement of this feature for the anti-Stokes and Stokes sides is observed at ~225 K and ~300 K, respectively, whereas at ~250 K, we observe similar intensity for this feature for both Stokes and anti-Stokes Raman spectra. This observation suggests that above 200 K, dominant contribution to the background in the ZnSe-LO phonon region arises from the continuum. It is important to note that this continuum is present only when the incident laser is sufficiently absorbed inside the ZnSe epilayer, i.e., for $T\geqslant200$ K, indicating that the presence of photogenerated carriers is responsible for the presence of the continuum. It is to be noted that the shift of the outgoing resonance from the 2LO anti-Stokes to the LO Stokes is a very rare observation and is only possible here due to fine tuning of band gap with temperature.

To find out the details and/or origin of the nature of the continuum, excitation intensity dependence of the continuum was studied. From HI and LI Raman spectra (inset in Fig. 2), it is clear that the continuum is much more prominent in the LI Raman spectrum as compared to the HI Raman spectrum. Furthermore, modification of the LO lineshape is larger in the case of the LI Raman spectrum and the LO phonon intensity is higher for the HI Raman spectrum compared to that of the LI Raman spectrum.

Consistent with the above stated observations, we propose that this continuum originates from shallow localized donor levels and/or shallow localized acceptor levels. A proposed electronic transition diagram for single particle excitation Raman scattering is schematically shown as insets in Fig. 3, wherein the valence band is the intermediate level for the Raman transition. This transition scheme has been reported

earlier in doped semiconductors (n type).[9] Absorption of 4579 Å increases as temperature increases above 200 K, thereby increasing the number of generated electron-hole pairs. Thus, the shallow donor levels get filled with electrons, i.e., the quasi-Fermi-level of the electrons is very close to or above the donor levels. Similarly, the shallow acceptor levels get filled with holes.

In the LI Raman case, the quasielectron Fermi level is close to the conduction band edge and some of the donor levels are filled with electrons. Thus, a transition, as shown in the right inset of Fig. 3, is possible. The donor level and the conduction band are the initial and final levels for the anti-Stokes Raman scattering, while the sequence is reversed for Stokes Raman scattering. Thus, for the anti-Stokes scattering, the energy of the transition from the intermediate valence band to the final state in the conduction band (near the conduction band edge) is close to the E_0 gap and, hence, shows outgoing resonance.

In the HI Raman spectrum, where the excitation intensity is much higher and a large number of carriers are generated in the conduction band, the quasielectron Fermi level is deep inside the conduction band, thereby filling all the donor levels. Thus, for the anti-Stokes scattering, the transition energy from the intermediate valence band to the final state deep in the conduction band is much larger than the E_0 gap and, hence, this is out of resonance. Similar argument can be given for Stokes scattering. This explains the reduction in the intensity of the continuum with an increase in the intensity of excitation. Similar transitions are also possible for the Stokes case, where the transitions are between the shallow acceptor levels and the valence bands through the conduction band as the intermediate level for the Raman process.

To confirm the existence of such levels in ZnSe, we have recorded the photoluminescence (PL) of the ZnSe epilayer on GaAs at 10 K. The PL spectrum at 10 K shows the presence of donor-acceptor pair (DAP) peak with its phonon replicas up to 2LO.[11] The DAP peak is observed at 2.744 eV. The presence of DAP in the low temperature PL spectra of undoped ZnSe has been reported earlier also by others.[12,13] The observation of the DAP implies that there are shallow donor levels just below the conduction band and shallow acceptor levels just above the valence band. The position of the donor and/or acceptor levels as determined from the low temperature PL data is consistent with the observation of the continuum in the Raman spectra reported here, and the lineshape calculation of the continuum following standard formulism shows a broad peak $\sim$100 cm^{-1} as given in Ref. 10.

Now that the presence of the single particle EC has been established, the lineshape modification due to the interaction of this EC with the LO phonon can be calculated. This discrete-continuum interaction leading to a Fano lineshape satisfactorily explains the observed wings on the low frequency side.

The presence of a broad mode at $\sim$270 cm^{-1} is observed for various excitations ranging from 5145 – 4579 Å. Figure 4 shows Raman spectra for the two extreme excitations at 5145 and 4579 Å, where the A mode is predominantly seen in the $z(x,x)z'$ geometry. The wings observed on the high frequency side of the LO phonon for 4579 Å excitation are attributed to the presence of the A mode.

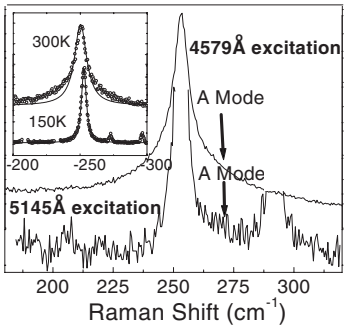

FIG. 4. Raman spectra showing the A mode, with the inset showing the Lorentzian fit to spectra at 150 and 300 K.

Some of the earlier reports of Raman spectra in ZnSe/semi-insulating GaAs have attributed a mode around 270 cm^{-1} to coupled plasmon-phonon mode originating from the interfacial region inside the GaAs substrate.[14] In the $z(x,x)z'$ geometry where this mode is predominantly observed, the most probable scattering mechanism is the charge density fluctuation.[4] A carrier concentration of about 4×10^{17} cm^{-2} is needed to have coupled plasmon-phonon mode at $\sim$270 cm^{-1}. Hall measurements did not show the presence of such a large carrier concentration in the samples by (1) making contacts on the sample surface or (2) directly accessing the interface after etching the ZnSe layer. Thus, we rule out the possibility of the A mode as a coupled plasmon-phonon mode from the ZnSe/GaAs interface.

The A mode has been observed in all the data recorded at various wavelengths below the E_0 gap of ZnSe. An enhancement of the A mode intensity as the excitation approaches the E_0 gap of ZnSe has also been observed, indicating a resonant enhancement at the E_0 gap of ZnSe. In addition, the A mode is proportional to the thickness of the ZnSe layers. The A mode is hardly visible for the ZnSe layers with thickness less than 100 nm. Therefore, the origin of the A mode is attributed to the ZnSe epilayer itself. From the phonon density of states and dispersion curves of ZnSe, the A mode could be attributed to a combination mode TO($\boldsymbol{q}$)+TA($\boldsymbol{q}$), where $\boldsymbol{q}$ is the phonon wave vector near the zone edge.[15] The phonon density of states peak at $\sim$70 cm^{-1} and $\sim$200 cm^{-1} correspond to the TA and TO phonons, respectively, close to the X point in the Brillouin zone.

The temperature dependence of the A mode shows that at temperatures below 200 K, the intensity of the A mode falls drastically and it vanishes at about 150 K (inset in Fig. 4). It is important to check whether this is a temperature or a resonance effect. At 150 K, the band gap of ZnSe is 2.78 eV, i.e., the excitation energy is less than the band gap by 0.09 eV, whereas for 5145 Å excitation at room temperature, the excitation energy is less than the band gap by 0.28 eV. In spite of being further away from resonance, we observe the A mode at room temperature for 5145 Å excitation. This clearly shows that the fall in the intensity of the A mode with temperature for 4579 Å excitation is not due to the detuning of resonance but is an intrinsic temperature dependent feature of the mode, confirming that the A mode is a combination phonon.

From the above discussion, it is imperative that for the

TABLE I. The fitted parameters at different temperatures.

Temperature (K)	Q (Stokes)	$\Gamma+\Delta\Gamma$ (Stokes) (cm^{-1})	Q (anti-Stokes)	$\Gamma+\Delta\Gamma$ (anti-Stokes) (cm^{-1})
200	−23.5	2.37	−18	2.72
225	−23	2.85	−11	3.36
250	−17.8	3.22	−13.8	3.59
300	−9.5	5.0	−7.4	5.8

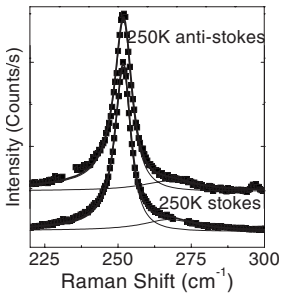

FIG. 5. Representative fit for LO phonon.

calculation of the lineshape of the LO phonon with 4579 Å excitation, we need to take into account two factors: (a) Fano interaction between the EC and the LO phonon, and (b) the presence of the A mode on the higher frequency side of the LO phonon.

The Lorentzian lineshape of the discrete LO phonon upon interaction with the EC gets modified to a Fano profile and is given by the expression[16]

$$I(\omega) \sim \frac{|Q+\varepsilon|^2}{(1+\varepsilon^2)}, \quad \varepsilon = \frac{\omega-\omega_0-\Delta\omega}{\Gamma+\Delta\Gamma}. \tag{1}$$

$\Delta\omega$ and $\Delta\Gamma$ are the change in the position and the broadening of the discrete mode due to the Fano interaction, and Q is the interaction parameter and is given by the expression $Q = VR_p/R_e$. R_p is the Raman scattering cross section of the discrete LO mode, R_e is the Raman scattering cross section for the EC, and V is the EC and phonon interaction matrix. Depending on the sign of R_p, R_e, and V, Q could be either negative or positive. Negative values of Q lead to an antiresonance in the higher frequency side, thereby leading to an enhanced intensity at the lower frequency side of the discrete mode.

The presence of the A mode modifies the observed lineshape on the high frequency side of the LO phonon. Thus, to obtain the lineshape of the observed LO phonon of ZnSe, we have fitted a Fano profile and a broad Lorentzian at $\sim$270 cm^{-1}, corresponding to the A mode. The best-fit parameters are summarized in Table I. It is interesting to observe that values of Q and Γ are different for Stokes and anti-Stokes Raman scattering. The theory of Fano interaction mentioned above indicates that the Fano interaction parameter Q depends on the R_p and R_e values. For outgoing resonance, the value of the Raman scattering cross section is different for Stokes and anti-Stokes Raman scattering. This leads to different values of Q and Γ, thereby leading to different lineshapes for Stokes and anti-Stokes LO phonons as observed. At all temperatures where the EC exists, the LO phonon lineshape is accompanied by an increase in its width. The separate contributions of the Fano and the A mode along with the final fit for Stokes and anti-Stokes Raman spectra at 250 K are shown in Fig. 5.

To conclude, we have observed an increase in width and the presence of wings on both sides of the ZnSe-LO phonon for the excitation wavelength of 4579 Å as compared to the Lorentzian lineshape of LO phonon for 4880 Å. We show that the low frequency side wings for near band-gap excitation are due to the presence of a Fano interaction between the phonon and an electronic continuum from photogenerated carriers. Further, the temperature dependent measurements confirm the presence of a combination mode at $\sim$270 cm^{-1} on the high frequency side of the LO phonon. We have proposed an electronic Raman transition scheme to explain consistently the high and low incident intensity Raman spectra along with the wings of the LO phonon in Stokes and anti-Stokes Raman spectra ZnSe for 4579 Å excitation above 150 K.

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