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Nitrogen-induced levels in GaAs$_{1-x}$N$_x$ studied with resonant Raman scattering

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Resonant Raman scattering is used to study the nature of the recently discovered nitrogen-induced level E_+ located in the conduction band of GaAs$_{1-x}$N$_x$ ($0.001 \leqslant x \leqslant 0.022$). Our data demonstrate that the E_+ state is derived from the nitrogen-induced Γ-L mixing of the bulk GaAs states and that it is not an isolated nitrogen impurity level. A broadening of the GaAs-like longitudinal-optical phonon line and an enhancement of the transverse-optical phonon line is observed near resonance, which is interpreted as being due to resonance with strongly localized states.

The Ga(In)As$_{1-x}$N$_x$ alloy system has attracted much interest recently due to its unique electronic properties.[1–4] When a small amount of nitrogen ($\leqslant 3\%$) is introduced into GaAs, the band-gap energy *decreases* rapidly relative to that of bulk GaAs despite the fact that GaN has a band-gap energy nearly 2 eV *larger* than that of GaAs. For example, 1% substitution of nitrogen into GaAs reduces the band-gap energy by ~0.18 eV. This ''giant bowing'' of the composition dependence of the band-gap energy has been explained in part as being due to the large differences between As and N atoms in their atomic orbital energies and sizes.[2] Recently, a nitrogen-induced level (E_+) in the conduction band has been observed in electroreflectance[4] (ER) and high-pressure measurements,[3] and it has been suggested that a band repulsion between the conduction-band minimum and the E_+ level is responsible for the reduction of the band-gap energy with nitrogen substitution. However, the nature of this nitrogen-induced E_+ level is yet unclear. Shan *et al.* interpreted the E_+ level as originating from a two-level interaction between the resonant isolated nitrogen level (N$_X$) and the conduction-band minimum in GaAs,[3] whereas recent calculations[5,6] suggest nitrogen-induced symmetry breaking and the resultant Γ-L mixing as the origin of the observed E_+ level. In this paper, we use resonant Raman scattering (RRS) to investigate the electronic band structure near the E_+ level by monitoring the changes in the Raman spectra near resonance.

RRS (Ref. 7) studies deal with one of the most fundamental properties of semiconductors: the interaction between lattice vibrations and electronic states. The Raman scattering probability for the Stokes scattering process can be written in a simplified form as[8]

$$I_{ph}(\omega_s)=\left(\frac{2\pi}{\hbar}\right)\left|\sum_{n,n'}\frac{\langle i|H_{eR}(\omega_s)|n'\rangle\langle n'|H_{e\text{-ph}}|n\rangle\langle n|H_{eR}(\omega_i)|i\rangle}{[\hbar\omega_i-(E_{-n}-E_i)][\hbar\omega_i-\hbar\Omega-(E_{n'}-E-i)]}\right|^2\delta(\hbar\omega_i-\hbar\Omega-\hbar\omega_s), \tag{1}$$

where H_{eR} and $H_{e\text{-ph}}$ are electron-radiation and electron-phonon interaction Hamiltonians, respectively; $|i\rangle$ the initial electronic state, $|n\rangle$ an intermediate electronic state with energy E_n, $\hbar\omega_i$ and $\hbar\omega_s$ the frequencies of incident and scattered photons, and $\hbar\Omega$ the frequency of the phonon being studied. For electron scattering, near resonance with an intermediate state $|a\rangle$,

$$I_{ph}(\omega_s)\approx\left(\frac{2\pi}{\hbar}\right)\left|\frac{\langle 0|H_{eR}(\omega_s)|a\rangle\langle a|H_{e\text{-ph}}|a\rangle\langle a|H_{eR}(\omega_i)|0\rangle}{[E_a-\hbar\omega_i-i\Gamma_a][E_a-\hbar\omega_i+\hbar\Omega-i\Gamma_a]}+C\right|^2, \tag{2}$$

where we take the ground state $|0\rangle$ with zero energy measured from the valence-band maximum as the initial state, and the constant C represents the contribution from the nonresonant terms in Eq. (1). Γ_a is the damping constant for the resonance. In general, there are two resonances, an incoming and an outgoing, at $\hbar\omega_i=E_a$ and $\hbar\omega_i=E_a+\hbar\Omega$, respectively. If the intermediate state $|a\rangle$ is a Bloch state then this state has a well-defined momentum $\mathbf{k}$. In the dipole approximation, only zone-center phonons with momentum $\mathbf{q}=0$ are involved in the light scattering process, and the phonon line shape is not expected to change near resonance. However, if $|a\rangle$ is not a Bloch state, $\mathbf{k}$ is no longer a good quantum number for the scattering process and so momentum conservation is relaxed.[9] In this case, the momenta of the phonons that participate in the Raman process near resonance are determined by the admixture of $\mathbf{k}$ for the intermediate state $|a\rangle$. For example, if $|a\rangle$ is a superposition of the bulk Γ and L states, the dipole matrix elements [the first and last matrix elements of the numerator in Eq. (2)] would be nonzero owing to the Γ component of $|a\rangle$. (The valence-band maximum is at Γ.) In the electron-phonon interaction matrix element, on the other hand, the initial state and the final state have both the Γ and L components. Therefore, the L (or Γ) component of the initial state interacts with the L (or Γ) com-

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ponenet of the final state via zone center (or Γ) phonons, whereas the L (or Γ) component of the initial state interacts with the Γ (or L) component of the final state via L-point phonons or vice versa. Therefore, the (forbidden) L-point zone-boundary phonons get activated near resonance with $|a\rangle$. On the other hand, if $|a\rangle$ is a strongly localized state so that the wave function is delocalized in **k** space, phonons with $\mathbf{q}\neq 0$ become allowed near resonance and as a result the phonon line should show broadening near resonance. The changes in the Raman spectrum near resonance thus provide strong clues to the nature of the intermediate state.

Four GaAs$_{1-x}$N$_x$ epilayers were grown on GaAs substrates by organometallic vapor phase epitaxy. The N compositions were estimated to be 0.1%, 0.8%, 1.0%, and 2.2%. The 0.1% N epilayer was 7 μm thick, and the others were 2 μm thick. The growth conditions and the characterization of these samples have been published elsewhere.[4] The data and analyses for the four samples lead to the same conclusion, and so in the following, we will concentrate mostly on the results for the sample with 1% N. RRS measurements were performed at room temperature in a quasibackscattering geometry on the (001) growth surface of the samples. The excitation source was either a Ti:sapphire laser (1.54–1.80 eV) or a dye laser with DCM (1.77–2.00 eV) or Rhodamine 6G (1.94–2.17 eV) dye, focused to a line of dimensions 5 mm $\times 100$ μm. The scattered photons were dispersed by a SPEX 0.6-m triple spectrometer and detected with a liquid-nitrogen-cooled charge-coupled-device detector. The spectrometer was calibrated at each excitation energy using the frequency of the longitudinal-optical (LO) phonon peak (292 cm^{-1}) of a GaAs epilayer. The accuracy of this frequency calibration is estimated to be approximately ± 0.5 cm^{-1}. The spectral resolution varies from 1.0 to 1.6 cm^{-1}, depending on the energy and the grating used.

In the zinc-blende structure of GaAs$_{1-x}$N$_x$, LO phonons are allowed in the $z(YY)\bar{z}$ configuration but forbidden in the $z(xx)\bar{z}$ configuration, whereas transverse-optical (TO) phonons are forbidden in both configurations. Here, z and $\bar{z}$ represent the incident and scattered light directions $[001]$ and $[00\bar{1}]$, respectively, and $Y=[110]$ and $x=[100]$ represent the polarization directions of the photons. Figure 1(b) is an ''off-resonance'' Raman spectrum of the 1% N sample, taken with the 5145 Å line of an Ar ion laser as the excitation source in the allowed $z(YY)\bar{z}$ configuration. A Raman spectrum of a GaAs epilayer [Fig. 1(a)], measured under the identical condition, is shown for comparison. A sharp GaAs-like zone-center (Γ) LO phonon line, red shifted by ~ 0.5 cm^{-1} relative to the LO phonon of GaAs, dominates the spectrum (b). The full width at half maximum (FWHM) of the GaAs-like LO phonon of the 1% N sample is 4.0 cm^{-1} as compared to 3.6 cm^{-1} for that of the LO phonon of a GaAs epilayer, measured using the same system. This indicates that inhomogeneous broadening is minimal for the GaAs-like LO phonon line and that the perturbation to the phonon spectrum due to N substitution into GaAs is relatively minor. In addition, there is a small signal from the forbidden TO(Γ) phonon mode at 267 cm^{-1} in both configurations due to alloy disorder. A closer inspection of the spectra reveals additional weak features: TO(X) due to X-point zone-boundary TO phonons at ~ 255 cm^{-1}, a weak shoulder on the higher-frequency side of the TO phonon peak, and a GaN-type impurity mode at ~ 475 cm^{-1}. We did not observe any significant change in the line shape of the TO peak for all the excitation energies used. These results are consistent with previous Raman measurements on GaAs$_{1-x}$N$_x$.[10,11] The redshift of the GaAs-like LO phonon (~ 0.5 cm^{-1}) is smaller than a ~ 1.4-cm^{-1} redshift observed in previous studies for thin ($\leqslant 0.2$ μm) GaAs$_{1-x}$N$_x$ epilayers with similar compositions,[10,11] which indicates that our GaAs$_{1-x}$N$_x$ epilayers are relaxed.

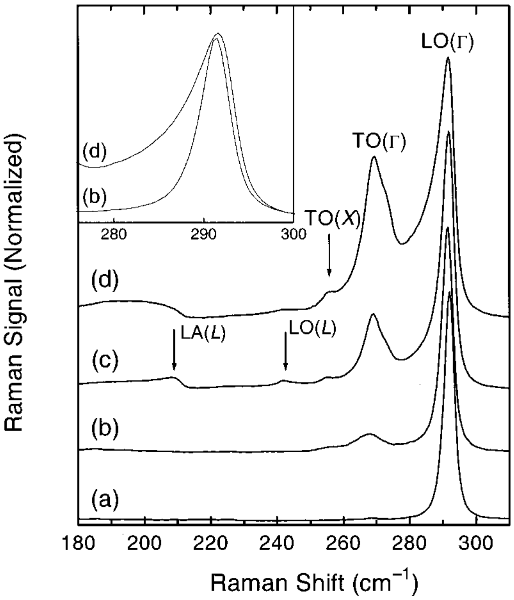

FIG. 1. (a) Raman spectrum of GaAs for 2.41-eV excitation; Raman spectra of the 1% N sample for various excitation energies: (b) off resonance, 2.41 eV, (c) near the E_+ resonance, 1.84 eV, and (d) near E_w, 1.76 eV. The arrows indicate two new phonon modes that become activated near resonance with E_+. The inset compares the line shapes of the LO(Γ) line in spectra (b) and (d).

Figure 2(a) is a plot of the peak intensity of the GaAs-like LO phonon, LO(Γ), as a function of the excitation energy for the 1% N sample. The inset is a room-temperature ER spectrum of the sample from Ref. 4. Three critical-point transitions are observed: the lowest-energy band gap E_0 at ~ 1.24 eV, the $E_0+\Delta_0$ transition from the spin-orbit split-off band to the conduction-band minimum at ~ 1.57 eV, and the E_+ transition at ~ 1.81 eV. The maximum intensity of the GaAs-like LO phonon is observed at ~ 1.85 eV, somewhat higher than the E_+ transition energy. This may be due to a strong outgoing resonance in this material. We found that the small different between the energy where the LO phonon intensity is maximum (E_I) and the E_+ transition varies with N composition, which is not yet fully understood. There is also a weaker resonance with the $E_0+\Delta_0$ transition, which is not as well-resolved due to larger uncertainties caused by a lower throughput of the spectroscopy system and the background luminescence at lower energies from the substrate. The resonance is seen in both the allowed and the forbidden polarizations.

When the excitation energy is close to the peak of the resonance curve, the Raman spectrum [Fig. 1(c)] shows two extra features at ~ 210 and ~ 240 cm^{-1}. These frequencies are close to the frequencies of L-point zone-boundary longi-

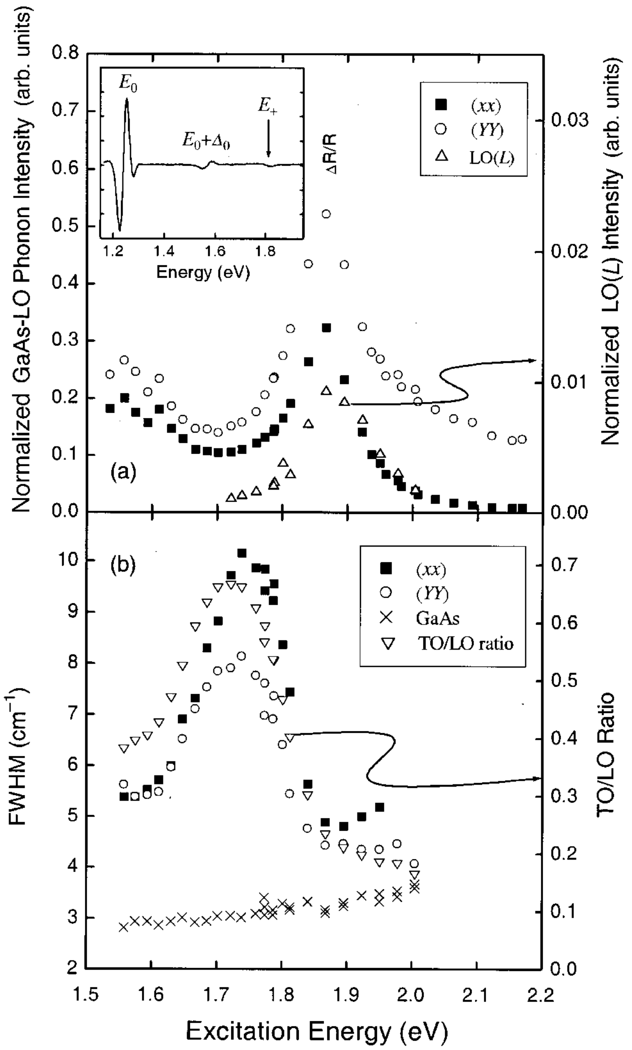

FIG. 2. (a) The intensity of the GaAs-like LO phonon lie of the 1% N sample as a function of the excitation energy for the allowed (○) and the forbidden (■) polarization. The inset is an ER spectrum of the same sample from Ref. 4. The open triangles are the intensities of the L-point LO phonon peak at ~240 cm^{-1}. (b) the FWHM of the GaAs-like LO phonon line as a function of the excitation energy for the 1% N sample. The ratio of the forbidden TO phonon intensity to the intensity of the allowed GaAs-like LO is also plotted. The FWHM of a LO phonon peak of a GaAs epilayer is presented for comparison.

tudinal acoustic (LA) and LO phonons, LA(L) and LO(L), respectively.[12] The TO(X) feature at ~255 cm^{-1} is also somewhat stronger, but its intensity relative to the main TO phonon peak TO(Γ) remains constant. The increase in the relative intensity of the TO phonons will be discussed later. In Fig. 2(a), the intensity of the LO(L) phonon peak at ~240 cm^{-1} in the $z(YY)\bar{z}$ configuration is also plotted. It is seen that the emergence of this peak coincides with the resonance, indicating that the L-point phonons are activated only near resonance with the E_+ state. On the contrary, there is no indication that the X-point zone-boundary LA phonons at 227 cm^{-1} are activated near resonance. These results indicate that the E_+ state contains a significant L component as explained earlier. This is consistent with recent calculations,[5,6] but does not agree with the model provided by Shan *et al.*[3] for the origin of the E_+ level.

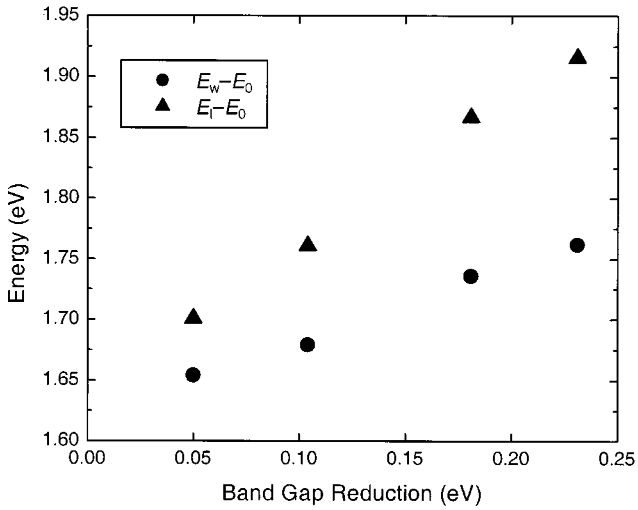

FIG. 3. E_I-E_0 and E_w-E_0 as functions of the band-gap reduction, $\delta E_0=E_0(\mathrm{GaAs})-E_0(\mathrm{GaAs}_{1-x}\mathrm{N}_x)$.

A closer examination of the resonant Raman spectra reveals a peculiar phenomenon. There is a significant asymmetric broadening of the LO(Γ) line and this broadening reaches a maximum value somewhat below the E_+ energy. Figure 1(d) is a Raman spectrum measured with an excitation energy of 1.760 eV. The line shape of the LO(Γ) phonon line is very asymmetric: the high-frequency side of the phonon line hardly changes from that of the off-resonance spectrum, while a broad tail is developed on the low-frequency side of the phonon line. The peak position of this phonon line does not vary in a systematic way beyond the experimental uncertainties. It also shows that the forbidden TO phonon becomes strong near resonance. Figure 2(b) plots the FWHM of the LO(Γ) line for the 1% N sample as a function of excitation energy. It shows that the FWHM reaches a maximum at ~1.74 eV in both polarizations. In order to further ascertain that this phenomenon of linewidth broadening near resonance is genuine and uniquely characteristic of the E_+ level of $\mathrm{GaAs}_{1-x}\mathrm{N}_x$, we measured the FWHM of the LO phonon line of a GaAs epilayer under the identical conditions. The data for GaAs in Fig. 2(b) shows no broadening as the excitation energy is tuned through the $E_0+\Delta_0$ resonance of GaAs at ~1.75 eV. The broadening of the LO(Γ) line was observed for all the four $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ samples studied, and the energy (E_w) at which the FWHM is the maximum varies with the band-gap energy (hence the N composition). E_w could be determined unambiguously even for the 0.1% N sample, for which the E_+ transition energy could not previously be determined from the ER spectrum.[4] Figure 3 plots E_w-E_0 as a function of the band-gap reduction δE_0, where δE_0 is the difference between the GaAs band gap and the band-gap energy. E_I-E_0 is also plotted for comparison. An additional peculiarity in the Raman spectrum near E_w is the observation of a relative strengthening of the forbidden TO mode. Figure 2(b) plots the ratio of the intensity of the TO phonon to that of the GaAs-like LO phonon as a function of the excitation energy, and shows that the strengthening of the TO phonon mode correlates with the broadening of the GaAs-like LO phonon line.

Since N incorporation is random, the eigenstate corresponding to E_+ is not a Bloch state. Also, there will exist a statistical distribution of these N-induced states due to the randomness of the N distribution. As a result, these states form a band of states, where the density of states in this band is determined by a statistical distribution function. This band is distinctly different from the usual electronic bands in crystals in that it results from the statistically disordered configuration of N atoms in the host GaAs lattice. Therefore, the band minimum need not be a critical point near which a maximum in Raman scattering intensity is expected at resonance. Instead, the position of the resonance peak (E_I) corresponds to the maximum in the statistical distribution for the density of the N-induced states (plus a LO phonon energy, possibly). Since these states are mostly L derived, L-point zone-boundary phonons are activated near resonance with these states, as discussed earlier. However, participation of phonons significantly away from the Γ or the L points would be minimal near this resonance, resulting in minimal broadening of the GaAs-like LO(Γ).

Using high-pressure studies of N isoelectronic impurities in GaAs,[13,14] it has been determined that the resonance isolated N impurity level (N_X) is located about 0.15–0.18 eV above the conduction-band edge of GaAs, and N_X is accompanied by a series of nitrogen pair states (NN_1, NN_2, etc.) below it. The more distant pair levels are located closer to N_X and are also more abundant. As the N concentration is increased, these pair states interact and form their own bands. However, since the states are farther away from the L point of GaAs, they remain strongly localized and are composed of significant contributions from host Bloch states away from the $\mathbf{k}=0$ Brillouin-zone center or the Brillouin-zone boundaries. This allows participation of phonons in Raman scattering whose wave vectors are significantly away from the zone center, resulting in a broadening of the LO(Γ) phonon line. Since $\mathbf{k}\neq 0$ LO phonons in GaAs always have lower energy than the zone center ($\mathbf{k}=0$) LO phonon, this broadening occurs only on the lower-energy side of the phonon line, thus making the phonon line appear asymmetric as seen in the inset of Fig. 1. There will exist a statistical distribution of N-pair states analogous to the case of isolated N impurity states. The density of such states in the dilute N limit decreases rapidly as one moves lower in energy from the E_+ state. Thus as the Raman excitation energy is lowered, the corresponding nitrogen pair states being brought into resonance are more localized, causing a larger linewidth broadening. However, the density of such states becomes smaller with decreasing excitation energy. Therefore, the observed phonon linewidth broadening reaches a maximum somewhat *below* the E_I energy, because the linewidth broadening increases with decreasing excitation energy below E_I, but the density of states diminishes as the excitation energy is decreased. This is why E_w is observed to lie below E_I (or E_+) and no significant broadening is observed for excitation energies higher than E_I. In the dilute N limit ($x\rightarrow 0$), E_w and E_I (or E_+) should merge according to this interpretation, which is exactly what is seen in Fig. 3. The increase in the relative intensity of the forbidden TO phonon near E_w can also be explained using this reasoning: since non-$\mathbf{k}$ conservation applies not just to the magnitude of the $\mathbf{k}$ vectors but also to their direction, forbidden TO phonons would become allowed due to strong $\mathbf{k}\neq 0$ scattering near E_w. A similar enhancement of the forbidden TO phonon was observed in RRS studies of nitrogen-doped GaP (Ref. 15 and $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ (Ref. 16) near resonance with the bound N_X state.

In summary, our RRS data demonstrate that the E_+ state observed in modulation reflectance spectra of $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ is derived from the N-induced Γ-L mixing of the bulk GaAs states and is not merely due to a two-level interaction between an isolated nitrogen impurity level and the conduction band in GaAs as Shan *et al.* suggested.[3] The observed broadening of the LO phonon line and the enhancement of the TO phonon line near resonance are interpreted as being due to resonance with strongly localized states derived from the nitrogen pair states of dilute GaAs:N.

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