Evolution of electronic states in $GaAs_{1-x}N_x$ probed by resonant Raman spectroscopy

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Two distinct maxima E_W and E'_W are observed in the resonant Raman-scattering profile for the LO phonon asymmetric linewidth broadening in $GaAs_{1-x}N_x$ and are attributed to states arising from a splitting of the quadruply degenerate conduction band near the L point. The data provide further insight into the physics underlying the giant band-gap bowing observed in $GaAs_{1-x}N_x$, as well as reveal asymmetric linewidth broadening to be a powerful signature for studying strongly localized impurity states in semiconductors.

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There have been several attempts made during the past few years to provide an explanation for the giant band gap bowing observed in dilute $GaAs_{1-x}N_x$ alloys.[1] The recent discovery[2] of a resonant level E_+ in the conduction band of the alloy and an anticrossing behavior between this level and the conduction-band minimum (CBM) E_- exhibited in pressure dependent photoreflectivity studies[3] led to speculation about the origin[2,3] of the resonant level and the role it plays in the giant band-gap bowing. Shan *et al.* used the anticrossing behavior as compelling evidence for level repulsion between E_+ and the CBM (a two-level interaction model) as the reason for the giant band-gap lowering. But pseudopotential calculations indicated that the band-gap lowering was a result of electronic coupling between the CBM at Γ, and the conduction-band extrema at the L and X points of the Brillouin zone induced by the isolated nitrogen impurity level and the ensuing repulsion between all these levels.[4–7] The isolated nitrogen impurity level resonant 170 meV above the CBM of GaAs had been predicted using tight-binding calculations over two decades ago.[8] Over a decade ago, in studies of the low-temperature photoluminescence of GaAs:N ($<6\times10^{17}$ cm^{-3}N) this level denoted as N_X was directly observed as it emerged into the band gap at high pressures.[9,10] The two-level repulsion model had assumed that it was from the interaction of this level with the CBM at Γ that the resonant impurity level E_+ had evolved. However, pseudopotential calculations indicated that E_+ originated from a nitrogen-induced splitting of the conduction band at the L point.[7] The different opinions on the origin of E_+ have led to a great deal of controversy regarding the mechanisms underlying the giant band-gap bowing. In this Brief Report we present results for the perturbation of the conduction-band states near the L point that are induced by nitrogen impurities, which help clarify the above issue.

$GaAs_{1-x}N_x$ epilayers, 0.4−1.5 μm thick, were grown by organometallic vapor phase epitaxy or low-pressure metal-organic chemical vapor deposition using arsine, triethylgallium, and dimethylhydrazine (DMHy) precursors on (100) GaAs substrates. The details on growth conditions of these samples have been published elsewhere.[12,13] Resonant Raman-scattering measurements were performed at 80 K in a quasibackscattering geometry on the (001) growth surface of the samples. A Ti:sapphire laser or a dye laser with DCM or Rhodamine 6G was used as an excitation light source depending on the spectral range. The scattered photons were dispersed by SPEX 0.6-*m* triple spectrometer and detected with a liquid-nitrogen-cooled charge-coupled detector. The spectrometer was calibrated at each excitation energy using the frequency of the longitudinal-optical-phonon peak (295 cm^{-1}) of a GaAs epilayer.

A typical resonant Raman profile of the LO(Γ) phonon intensity in $GaAs_{1-x}N_x$ is shown in Fig. 1, where a strong resonance enhancement occurs at the excitation energy E_I that is approximately near the E_+ transition energy measured by electroreflectance. A very weak LO phonon intensity maximum is also observed near the $E_0+\Delta_0$ transition energy of $GaAs_{1-x}N_x$. The LO phonon Raman signatures in ternary semiconductor alloys exhibit linewidth broadening due to alloy-induced disorder but the phonon linewidth shows no excitation energy dependence in resonant Raman scattering. Recently, Cheong *et al.*[14] reported that the LO Raman signature in $GaAs_{1-x}N_x$ showed a very unusual linewidth broadening for resonant excitation energies below the E_+ transition. As illustrated in the inset of Fig. 1, the width broadening is highly asymmetric towards the lower-frequency side of the LO Raman line. Since the LO phonon frequency is highest at the zone center and continuously decreases as the phonon wave vector **q** moves away from the Γ point, the observed asymmetric broadening strongly suggests that it is due to activation of LO phonons with wave vectors that span a significant portion of the Brillouin zone. The selective activation of non-Γ phonons only for certain excitation energies indicates that the asymmetric linewidth broadening is not due to nitrogen-induced disorder but is closely related to the nature of the intermediate electronic state participating in the resonant Raman process. Since an electronic state that is delocalized in the Brillouin zone must be strongly localized in real space, the observed asymmetric LO Raman linewidth broadening indicates that the intermediate electronic state involved in this resonant Raman process is strongly spatially localized. Similar arguments can be applied to account for the concomitant resonance enhancement of the TO/LO Raman intensity ratio: the non-Γ components of the localized electronic state involved in the Raman process relax the momentum conservation rule, resulting in a further strengthening of the forbidden TO phonon intensity aside from the excitation-energy-independent alloy disorder effect.

Resonance enhancement of the LO(Γ) phonon linewidth and the concomitant enhancement of TO/LO intensity ratio

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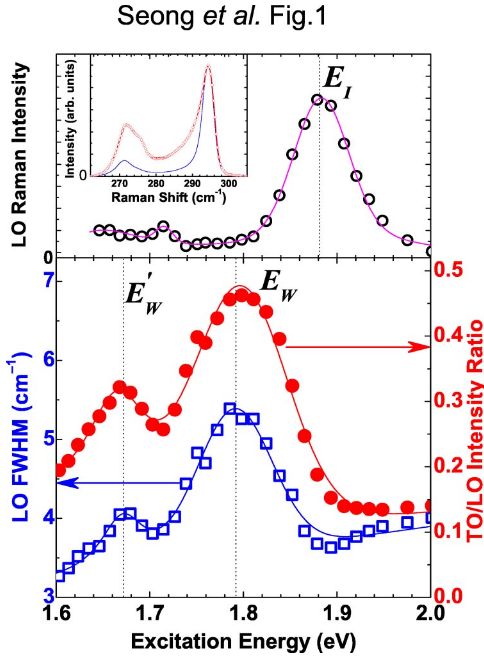

FIG. 1. (Color online) The lower panel shows resonant Raman profile for the full width at half maximum (empty square) of the LO(Γ) phonon, left axis, and TO(Γ)/LO(Γ) intensity ratio (full circle), right axis, for $x=0.78\%$. Raman scattering was performed at T=80 K in the $\bar{z}(Y,Y)z$ quasi-backscattering geometry. Solid lines are guide for the eye. The upper panel shows the LO(Γ) phonon intensity resonance profile. In the inset, two Raman spectra excited with photon energies of 1.789 eV and 1.907 eV for the dotted and solid curve, respectively, are displayed, where the Raman intensity is normalized with respect to the GaAs-LO Raman intensity.

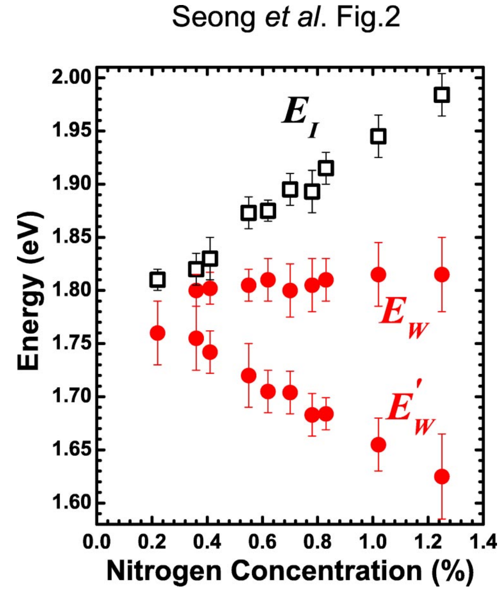

FIG. 2. (Color online) Energy positions determined from RRS measurements at $T=80$ K as a function of nitrogen composition in $GaAs_{1-x}N_x$. E_I is the excitation energy for which the LO phonon intensity is maximum and the excitation energies for which the LO phonon linewidth is maximum are labeled as E_W and E'_W, respectively.

for 0.78% $GaAs_{1-x}N_x$ are displayed in Fig. 1, where two distinct maxima (labeled as E_W and E'_W, respectively) for both the LO full width at half maximum and TO/LO intensity ratio are observed. Similar double maxima E_W and E'_W are distinctly observed in $GaAs_{1-x}N_x$ samples with several different nitrogen compositions exceeding ~0.35% and their peak positions are plotted as a function of nitrogen concentration in Fig. 2. E_W and E'_W are not clearly resolved for $x<0.3\%$ presumably due to their proximity. It should be pointed out here that Cheong *et al.*[14] used data obtained, as a first approximation, in an unpolarized configuration in their paper. However, since the alloy disorder induced linewidth broadening effect is stronger in a forbidden geometry than in an allowed one, we have used only allowed scattering geometry in the present work in order to minimize the alloy disorder induced linewidth broadening effect. This could explain that E_W observed in the unpolarized configuration in Ref. 14 and E_W measured in the allowed scattering geometry in the present work exhibit a larger difference for high concentration samples ($>1\%$) where the alloy disorder effect is increasingly important. It is also worth mentioning that the recently grown samples studied in the current work have improved sample quality, as compared to those studied in Ref. 14 that were grown in the past. The excitation energy positions for the LO Raman intensity maximum (E_I) are shown in Fig. 2. There exists a strong correlation between E_I and E_+ transition observed in modulated electroreflectance[2,15]. In contrast, none of the E_W and E'_W exhibit any correlation with E_+ implying that they have a completely different origin from that for E_+. It is important to note that the linewidth of the LO(Γ) phonon in pure GaAs remains almost constant despite changing the excitation energy from 1.55 eV to 2.0 eV, a range which encompasses the $E_0+\Delta_0$ transition of pure GaAs and the E_+ transition of $GaAs_{1-x}N_x$ for $x<3\%$ at $T=300$ K.[14] Thus, the observed resonance maxima E_W and E'_W for the LO phonon linewidth are solely due to nitrogen-induced changes to the electronic states.

We will first discuss the origin of the E_+ state. Numerous theoretical[4,7,5,11] and experimental[14,16] studies have indicated that the E_+ state originates from the nitrogen-induced coupling of the conduction-band minima at the Γ, L, and X points that breaks the L valley degeneracy, resulting in a triplet state L_{3c} and a singlet state L_{1c}[4,5,7,11] that has been attributed to the origin of E_+.[7] As evidenced by the activation and strong resonance enhancement of the sharp L and X zone-boundary phonons near the E_+ transition,[14,16] E_+ comprises wave functions with definite Γ, L, and X components induced by the interconduction band mixing. In contrast, strongly localized states such as E_W and E'_W comprise wave functions with **k** components from the entire Brillouin zone (unlike L_{3c}, they have relatively very little of Γ, L, and X components[11]), leading to a significant asymmetric linewidth broadening of the LO phonon Raman signature for resonance at these localized states. If the two-level interaction of N_X with the CBM at Γ and their resulting hybridization into the E_+ and E_- levels whose consequent level repulsion is the

principal mechanism for the giant band-gap bowing, then one would have expected to observe the asymmetric linewidth broadening phenomenon of the LO phonon under resonance at the E_+ and E_- levels. But this has turned out precisely not to be true for the resonance Raman studies at E_+ as well as at E_-.[17] Instead conventional Raman intensity resonances are observed at E_+ and E_-, whereas asymmetric linewidth broadening resonances are observed at E_W and E'_W, indicating these states are much more delocalized in **k** space. At zero nitrogen doping, both E_W and E'_W extrapolate to a value located below the E_1 transition in GaAs by 1.2 eV which is precisely the energy difference between the valence-band maxima at the Γ and L points. The E_1 transition in GaAs refers to the transition between the conduction- and valence-band extrema that occur at the **k** point located along the [111] direction of the Brillouin zone which is close to the L point. This suggests that both those transitions emerge as a result of the perturbation of the L point conduction-band edge by nitrogen impurities. In electromodulated reflectance studies of dilute $GaAs_{1-x}N_x$ alloys, a transition denoted as E_1 that rises slowly with increased nitrogen, a transition E_+ that rapidly rises with increasing nitrogen, and a transition E_* that falls rapidly with increased nitrogen have been observed.[18] The first transition has also been observed in ellipsometry studies and the last two have been recently corroborated in more precise electromodulated reflectance studies as a function of nitrogen concentration.[15,18,19] At zero nitrogen doping, the data in Fig. 2 indicate that all the transitions originate from near the conduction-band edge at the L point of GaAs. Evidently, the quadruply degenerate E_1 transition in GaAs splits into three levels, E_+, E_W, and E'_W as a result of perturbation by nitrogen impurities.

Since this model explaining the data in Fig. 2 implies a splitting of the $GaAs_{1-x}N_x$ conduction band near the L point that differs from that assumed in the theoretical models discussed earlier,[7,11] we will further elaborate on this. The theoretical models assume that with the origin chosen to be located at the site of a nitrogen impurity, the point-group symmetry remains unchanged from T_d. One then looks for the compatibility of the quadruply degenerate conduction-band states near the L point of GaAs with the irreducible representations of the T_d point group whose point operations are centered on the nitrogen impurity site and obtains $4a_1 \rightarrow a_1 + t_2$. Note, however, that in the presence of an additional nitrogen impurity lying in the vicinity of the first impurity, the point symmetry is no longer T_d but is reduced and depends on the choice of the site for the second impurity. Corresponding to each site m for the second impurity is an NN_m pair state and several of these pairs which generate bound states have been observed in dilute $GaAs_{1-x}N_x$ together with triplet states and larger clusters. Although less abundant than the isolated nitrogen impurity, these states are far more spatially localized. The additional splitting of the triplet state t_2 should therefore not come as a surprise.

In conclusion, we have observed two distinct maxima E_W and E'_W in the resonant Raman scattering profile for the LO phonon asymmetric linewidth broadening in dilute $GaAs_{1-x}N_x$. The data lead to a new interpretation for the splitting of the quadruply degenerate conduction band near the L point. The study also reveals asymmetric linewidth broadening resonances to be a powerful signature for studying strongly localized impurity states in semiconductors.

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