

Resonant Raman scattering with the E_+ band in a dilute $\text{GaAs}_{1-x}\text{N}_x$ alloy ($x=0.1\%$)

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Resonant Raman scattering has been applied to a dilute $\text{GaAs}_{1-x}\text{N}_x$ alloy with 0.1% N. The Raman lines of GaAs and GaN related modes, their combinations, and multiple order replicas of GaAs-like longitudinal-optical modes have been observed with a lower N composition than those studied previously. All these Raman features are found to be strongly enhanced with excitations in resonance with a broad photoluminescence band that is associated with the so-called E_+ transition. This study provides additional insights into how the GaAs host conduction band states are perturbed and thus the electron-phonon interaction is affected by the N doping. © 2006 American Institute of Physics. [DOI: 10.1063/1.2345605]

Heavily nitrogen (N)-doped GaAs, often referred to as dilute $\text{GaAs}_{1-x}\text{N}_x$ alloys, have attracted much attention in recent studies due to their promising applications in the optoelectronic fields.^{1,2} Small amount of N incorporated into GaAs will produce a large reduction of the fundamental band gap (E_0).^{1,3-5} The band gap reduction has been shown to be observable even at a doping level as low as 0.0015% or $3 \times 10^{17} \text{ cm}^{-3}$,⁶ which indicates that the N-induced perturbation to the electronic band structure is unusually strong, comparing to other types of doping. In addition to the band gap reduction in dilute $\text{GaAs}_{1-x}\text{N}_x$ alloy, a nitrogen-induced optical transition (E_+) above E_0 has been observed experimentally for $\text{GaAs}_{1-x}\text{N}_x$ with $x \geq 0.2\% - 0.3\%$.^{3,4,7,8} However, the effects of N doping on the bulk of the conduction band are not yet clearly understood. Raman scattering has been shown to be a very informative tool to give important insights into the vibrational and electronic properties of $\text{GaAs}_{1-x}\text{N}_x$.⁹⁻¹⁴ In this letter, we apply a micro-Raman (and microphotoluminescence) technique to a low composition $\text{GaAs}_{1-x}\text{N}_x$ sample of $x=0.1\%$. We observe not only a broad PL peak with its peak position matching the extrapolated value of the E_+ transition but also strongly enhanced multiple order Raman features that do not exist in materials such as GaAs with very weak ionicity.

The $\text{GaAs}_{1-x}\text{N}_x$ sample ($x=0.10\%$) investigated here was grown by a gas-source molecular beam epitaxy on semi-insulating (001) GaAs substrates with an epilayer thickness of 400 nm. The detailed growth process has been described elsewhere.⁵ An undoped GaAs substrate is used as a reference sample ($x=0$). Micro-Raman or microphotoluminescence (μ -PL) is measured by a Raman system of Dilor SuperLabram in a backscattering geometry at 80 K. The system consists of holographic notch filters for Rayleigh rejection, a

LN_2 cooled Si charge-coupled detector, and a long-working-distance microscope with $50\times$ objective lens. The laser excitation energies are 1.959 eV of a He-Ne laser and 2.621, 2.089, and 1.848 eV of three diode pumped solid-state lasers, respectively. The typical excitation density is about 100 kW cm^{-2} .

Figure 1 shows the Raman spectra from the $\text{GaAs}_{1-x}\text{N}_x$ alloy with $x=0.1\%$ where the subtraction of the weak luminescence background from the measured spectra and the logarithmic intensity were used to magnify the weak Raman signal. All Raman spectra show the distinct Raman peaks of GaAs-like longitudinal-optical (LO) and transverse-optical (TO) zone-center phonons [$\text{LO}(\Gamma)$, $\sim 295 \text{ cm}^{-1}$; $\text{TO}(\Gamma)$, $\sim 271 \text{ cm}^{-1}$] and GaN-like LO phonons (LO_{GaN} ,

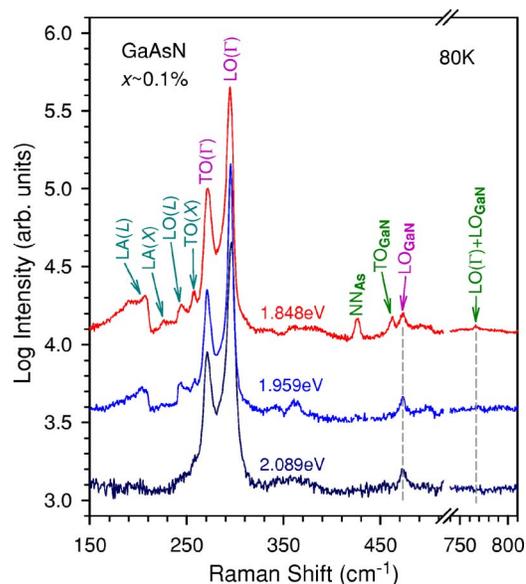


FIG. 1. (Color online) Normalized Raman spectra with the $\text{LO}(\Gamma)$ phonon in $\text{GaAs}_{1-x}\text{N}_x$ for $x=0.1\%$ by 2.089, 1.959, and 1.848 eV excitations at 80 K.

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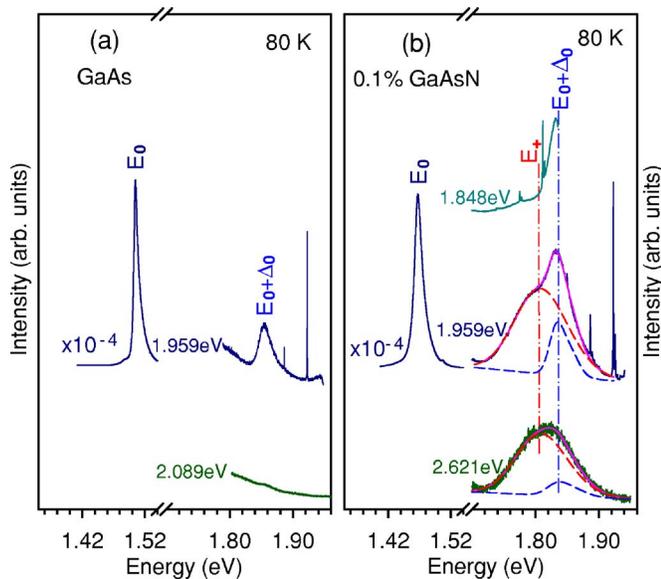


FIG. 2. (Color online) (a) E_0 and $E_0+\Delta_0$ emissions from the GaAs reference. (b) The excitation energy dependence of the μ -PL spectra of $\text{GaAs}_{1-x}\text{N}_x$ with 0.1% N. The dashed curves give the fitted results for the above-band-gap transitions (see the text).

$\sim 473 \text{ cm}^{-1}$). In comparison with the off-resonance spectrum excited by 2.089 eV, the one excited by 1.848 eV at near resonance exhibits three groups of distinguishable spectral features. Firstly, several weak Raman peaks appear at the low-frequency side of GaAs-like $\text{TO}(\Gamma)$ phonons, which are Raman scattering from the first-order-zone-boundary phonons and have been observed for higher N composition samples,¹¹ such as $\text{LA}(L)$ ($\sim 206 \text{ cm}^{-1}$), $\text{LA}(X)$ ($\sim 225 \text{ cm}^{-1}$), $\text{LO}(L)$ ($\sim 244 \text{ cm}^{-1}$), and $\text{TO}(X)$ ($\sim 258 \text{ cm}^{-1}$). The appearance of first-order-zone-boundary phonons in Raman spectra indicates that only 0.1% of nitrogen isoelectronic substitution in GaAs has already strongly perturbed the host band state far above the band gap. Secondly, two sharp Raman features at 426 and 462 cm^{-1} are observed and are, respectively, attributed to scattering by N dimers on As sites (NN_{As}) and GaN-like $\text{TO}(\text{TO}_{\text{GaN}})$ phonons, which had been reported by Ramsteiner *et al.* in GaAsN alloys with nominal N concentrations of 1.5% and 0.6%.¹⁴ Thirdly, an additional peak is located at 767 cm^{-1} , which can be assigned as a combination of the GaAs-like $\text{LO}(\Gamma)$ phonon and LO_{GaN} phonon because its frequency is equal to the frequency sum of the two phonons. This peak had been observed in GaAsN alloys with 0.7% N where the frequencies of the three modes also satisfy the frequency match,¹² which supports our above assignment.

Figure 1 clearly shows that the zone-boundary phonons, N dimer local mode (NN_{As}), TO_{GaN} , and $\text{LO}(\Gamma)+\text{LO}_{\text{GaN}}$ phonon exhibit more significant resonant Raman behavior than $\text{LO}(\Gamma)$ and LO_{GaN} phonons, similar to the case for higher N alloys.¹⁴ One would like to question how N doping at a level as low as 0.1% in a $\text{GaAs}_{1-x}\text{N}_x$ alloy could affect electronic structure and thus the Raman features. If applying linear extrapolations to the measured $E_0+\Delta_0$ and E_+ data for $x \geq 0.3\%$,⁷ one will find that the E_+ level falls below the $E_0+\Delta_0$ level for $x < 0.2\%$, should the E_+ transition still exist in GaAsN alloys with such low N composition? To reveal the origin of the resonant Raman scattering, μ -PL technique has been applied to both the 0.1% alloy sample and a referent undoped GaAs sample. Figure 2 depicts the μ -PL spectra of

the undoped GaAs (a) and 0.1% GaAsN alloy (b). The low-energy PL peaks at 1.507 and 1.472 eV are from the recombination near the fundamental band gap E_0 of GaAs and the 0.1% alloy, respectively. In the high-energy spectral region, a weak PL peak at 1.853 eV is observed from GaAs, whose energy exactly matches that of $E_0+\Delta_0$,⁷ with $\Delta_0=0.346 \text{ eV}$. In addition to the E_0 peak, a broad luminescence band that extends a few hundred meV above E_0 is observed in the GaAsN alloy whose intensity is only 10^{-4} of E_0 . The emission band can clearly be seen to have two features: one (E_{high}) at $\sim 1.83 \text{ eV}$ and the other (E_{low}) at $\sim 1.80 \text{ eV}$.

An asymmetrical PL line shape with a high-energy tail, a typical spectral feature from band gap emission, is observed for the E_0 emission in the 0.1% alloy as well as in GaAs. It is interesting to note that the $E_0+\Delta_0$ emission in GaAs and the E_{high} feature in the 0.1% alloy also exhibit such an asymmetric spectral shape. To further explore the physical properties of the above-band-gap luminescence in the GaAsN alloy, its excitation energy dependence is examined by other two excitation energies as shown in Fig. 2(b). Two asymmetrical line shape functions similar to that of the $E_0+\Delta_0$ peak in GaAs are used for fitting the above-band-gap PL spectra of the 0.1% sample. The deconvoluted spectra are shown in Fig. 2(b) with dashed curves, which give $E_{\text{high}}=1.833 \text{ eV}$ and $E_{\text{low}}=1.802 \text{ eV}$. It is clear that the relative intensity of the two peaks is quite sensitive to the excitation energy. For the 1.848 eV excitation, the E_{high} transition is resonantly excited and dominates the spectrum. With increasing excitation energy, E_{high} becomes weaker while E_{low} appears, and the latter becomes stronger and even prominent for the 2.621 eV excitation. A similar resonant effect for $E_0+\Delta_0$ is also observed in GaAs, where only a very weak $E_0+\Delta_0$ peak is observed for the 2.089 eV off-resonance excitation, as shown in Fig. 2(a). The similarity between the excitation energy dependence of the high-energy peak in the 0.1% alloy and the $E_0+\Delta_0$ peak in bulk GaAs suggests that the high-energy peak E_{high} at about 1.833 eV should also be identified as $E_0+\Delta_0$ in the 0.1% alloy. The other peak, E_{low} , at 1.802 eV is found to agree with the extrapolated value of E_+ at $x=0.1\%$,⁷ and is attributed to the E_+ transition that has never been reported at such a low composition. In fact, a similar PL band with its peak position matching the energy of E_+ transition has been observed for x from 0.22% to 1.1% (to be discussed in detail elsewhere⁸), which further supports the association of E_{low} to E_+ for this sample.

Figure 3 shows the Raman spectra of $\text{GaAs}_{1-x}\text{N}_x$ with 0.1% N and GaAs reference excited by three excitation energies of 1.848, 1.959, and 2.089 eV. For the GaAs reference, only $\text{LO}(\Gamma)$ and very weak $2\text{LO}(\Gamma)$ phonons are observed for 1.848 and 2.089 eV excitations, even though Raman scattering of these phonons nearly satisfies the condition of incoming resonance with its $E_0+\Delta_0$ transition for the 1.848 eV excitation. The $3\text{LO}(\Gamma)$ phonon can only be observed under the 1.959 eV excitation because of its outgoing resonant condition. However, for the 0.1% alloy, multiple phonon Raman GaAs-like $n\text{LO}(\Gamma)$ peaks are observed at frequency shift of $(n)295 \text{ cm}^{-1}$, for example, the observation of GaAs-like 4LO and 5LO modes for the 1.959 eV laser excitation and the strong intensity enhancement of the GaAs-like $\text{LO}(\Gamma)$ multiple phonons for the 1.848 eV excitation. The light-scattering process is dominated by the outgoing resonance, rather than the incoming resonance which dominates in GaAsN alloys.^{11,13} Compared to the Raman spectra of

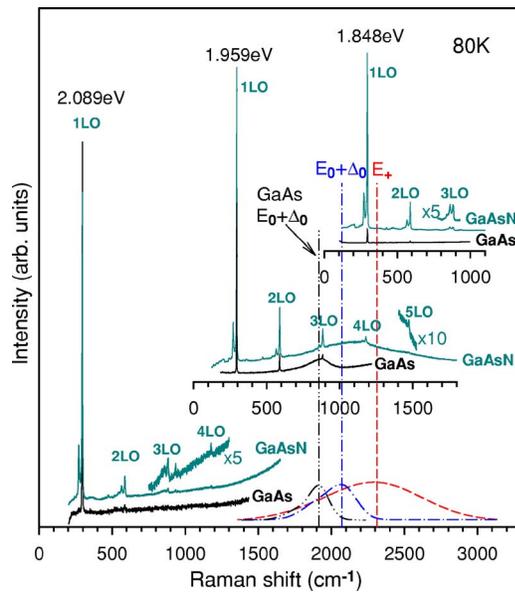


FIG. 3. (Color online) (Resonant) Raman scattering from the 0.1% GaAsN and the GaAs reference. The normalized curves of $E_0+\Delta_0$ in GaAs and $E_0+\Delta_0$ and E_+ in GaAsN used to fit the μ -PL spectra are shown at the bottom of figure.

GaAs reference, it is evident that the Raman features of the 0.1% GaAsN alloy are resonantly enhanced in intensity with the appearance of the E_+ transition, as no enhancement of high-order LO peaks is observed in GaAs. This is also consistent with the fact that the $E_0+\Delta_0$ transition contributes little to the intensity enhancement of various longitudinal and transverse phonon modes for higher N alloys.¹¹ It should be noted that the observed bandwidth of E_+ in the 0.1% GaAsN alloy is surprisingly large, being more than 100 meV, which is significantly greater than that of E_0 . Its higher energy portion covers the whole bandwidth of the $E_0+\Delta_0$ transition in the GaAsN alloy. Therefore, we can conclude that GaAs-like LO(Γ) feature and its multiple replicas are resonantly enhanced with the states in the E_+ band that is comprised of perturbed GaAs host states by N doping. The enhancement of the first-order-zone-boundary phonons by 1.848 eV excitation is indeed a clear fingerprint of the resonant behavior from the E_+ transition for the GaAsN alloy with N composition as low as 0.1%, similar to the case for higher N alloys.¹¹

Because the resonant Raman scattering is mainly determined by the outgoing resonance condition in GaAs and GaAsN, the $E_0+\Delta_0$ transition which does not have much resonant excitation effect for Raman scattering in GaAs is also not expected either to contribute significantly to the resonant observation of NN_{As} , TO_{GaN} and $LO(\Gamma)+LO_{GaN}$ phonons in the 0.1% GaAsN alloy. One can see from Fig. 3 that for the 1.848 eV excitation, the NN_{As} , TO_{GaN} , and $LO(\Gamma)+LO_{GaN}$ phonons are far from the outgoing resonance with the $E_0+\Delta_0$ transition; however, they are just in outgoing resonance with the E_+ transition. This accords with no observation of these phonons by the 1.959 eV excitation where they are far from the outgoing resonance condition with the E_+ transition for the NN_{As} , TO_{GaN} , and $LO(\Gamma)+LO_{GaN}$ phonons.

From the above discussions, it is obvious that the observation of the multiple order GaAs-like $nLO(\Gamma)$ features in a wide energy range of excitation benefits from the surprisingly large bandwidth of the E_+ transition, as shown in Figs.

2(b) and 3 of the μ -PL and μ -Raman results. Note that such zone-center multiple resonant Raman lines are typically observed in a strongly ionic semiconductor (e.g., CdS, GaN and ZnO),^{15–17} especially under resonant excitation with a critical point. It appears that the incorporation of even a small amount of N has drastically changed some characters of the GaAs states.

In conclusion, resonant Raman scattering from a GaAs_{1-x}N_x sample with $x=0.1\%$ has been investigated in detail, in order to reveal the nitrogen-perturbed band E_+ states and their interaction with phonons. The incorporation of only 0.1% nitrogen into GaAs has already strongly perturbed the host band states far above the band gap, which is evidenced by the observations of a broad photoluminescence band related to the so-called E_+ transition, the activation of zone-boundary and strong enhancement of the zone-center GaAs phonons, and the observation of the high-order $nLO(\Gamma)$ (with n up to 5) phonon replicas. The last finding is of particular interest, since a small amount of N has surprisingly led to drastical changes in the characters of GaAs states such that they exhibit the typical characters of bulk states in strongly ionic semiconductors. This study shows that resonant Raman scattering is a very sensitive tool to probe the effects of isoelectronic doping at the levels close to the dilute doping limit.

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