

Resonant Raman Scattering and Photoluminescence Emissions from Above Bandgap Levels in Dilute GaAsN Alloys *

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Abstract: The transitions of E_0 , $E_0 + \delta$, and E_+ in dilute GaAs_{1-x}N_x alloys with $x = 0.10\%$, 0.22% , 0.36% , and 0.62% are observed by micro-photoluminescence. Resonant Raman scattering results further confirm that they are from the intrinsic emissions in the studied dilute GaAsN alloys rather than some localized exciton emissions in the GaAsN alloys. The results show that the nitrogen-induced E_+ and $E_0 + \delta$ transitions in GaAsN alloys intersect at a nitrogen content of about 0.16% . It is demonstrated that a small amount of isoelectronic doping combined with micro-photoluminescence allows direct observation of above band gap transitions that are not usually accessible in photoluminescence.

Key words: GaAsN; resonant Raman scattering; photoluminescence; bandgap; isoelectronic doping

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1 Introduction

Ga(In)AsN semiconductor alloys containing small concentrations of nitrogen have attracted much attention due to their unusual physical properties^[1-4]. A nitrogen isoelectronic substitution in GaAs of only 1% can introduce a reduction of the fundamental band gap (E_0) by about 200meV ^[1]. The large bowing parameters in Ga(In)AsN alloys make it easy to realize long-wavelength semiconductor lasers with higher temperature stability for optical-fiber communications on GaAs substrate^[5]. A nitrogen-induced level (E_+) above the conduction-band minimum has been observed experimentally for GaInNAs samples^[3,4]. Whereas E_0 undergoes a red shift and the spin-orbit split-off transition ($E_0 + \delta$) appears with the increase of nitro-

gen concentration ($< 3\%$), E_+ increases with increasing nitrogen content^[3,6,7]. Up to now, many mechanisms have been proposed to explain the unexpected nitrogen-induced changes on the band structures of Ga(In)AsN alloys^[4,7-10]. The origin and nature of the E_+ level are not completely clear yet. The E_+ level in GaAsN alloys has been directly probed by modulated reflectance spectra, and E_+ has been clearly resolved only for nitrogen concentrations down to about 0.8% ^[3]. Obtaining well-resolved E_+ levels in dilute Ga(In)AsN alloys is very important for understanding their unusual physical properties and the mechanisms behind them. The much lower nitrogen content in GaAsN alloys, however, results in unresolved spectral features of $E_0 + \delta$ and E_+ , and these features are always interrupted by the $E_0 + \delta$ signal from

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the GaAs substrate in modulated reflectance measurements^[7]. To the best of our knowledge, there has been no report on the photoluminescence emission from the $E_0 + \epsilon_0$ and E_+ transitions in $\text{GaAs}_{1-x}\text{N}_x$ alloys. In this paper, we report the emission from the above band-gap states in the energy region relevant to E_+ and $E_0 + \epsilon_0$, even into the composition region of $x = 0.1$ from their micro-photoluminescence (μ -PL) spectra. The observation of these transitions in dilute GaAsN alloys from PL spectra is very useful in studying the mechanisms responsible for their unusual physical properties.

2 Experiment

The $\text{GaAs}_{1-x}\text{N}_x$ samples investigated here were grown by gas-source molecular beam epitaxy on semi-insulating (001) GaAs substrates at 420 °C at a growth rate of 0.8 nm/h using an RF nitrogen radical beam source with a mixture of N_2 and Ar in a ratio of 1 : 9. The epilayer thickness of the samples is nominally 400 nm. Four samples (No. 2658 ($x = 0.10\%$), No. 2846 ($x = 0.22\%$), No. 2847 ($x = 0.36\%$), and No. 2848 ($x = 0.62\%$)) were used in this study. The detailed growth process has been described elsewhere^[11]. The nitrogen concentration was determined by high-resolution X-ray rocking curve measurements and theoretical dynamical simulations. The PL and Raman spectra of the GaAsN samples were recorded by two micro-Raman systems (Dilor Super Labram and Dilor HR) in a back-scattering geometry. The systems consist of holographic notch filters for Rayleigh rejection and a long-working-distance microscope with a 50 \times objective lens, allowing a high signal-to-noise ratio and a spatial resolution of $\sim 1.0 \mu\text{m}$. The laser excitation wavelengths are 514.5 nm for an Ar^+ laser, 632.8 nm for a He-Ne laser, and 671.0 nm for a diode pumped solid-state red laser. The sample temperature was controlled by a programmable hot-stage THMS 600 from Linkam Scientific Instruments Ltd.

3 Results and discussion

Figure 1 shows the PL spectra of $\text{GaAs}_{1-x}\text{N}_x$ samples ($x = 0, 0.1\%, 0.22\%, 0.36\%$, and 0.62%) at 80 K, which were excited by a 632.8 nm He-Ne

laser. For the GaAs reference sample, the PL peak at 822.8 nm is from the recombination near its fundamental band gap E_0 . A broad peak is located at 669 nm, whose energy is 0.346 eV higher than that of E_0 . The energy of 0.346 eV is very close to the spin-orbit splitting ϵ_0 in bulk GaAs^[7], and thus the peak at 669 nm is assigned as the transition from the spin-orbit split-off valence band ($E_0 + \epsilon_0$). Two sharp peaks in the PL spectra of the GaAs reference sample correspond to the first- and second-order longitudinal optical (LO) modes of bulk GaAs at 295 and 589 cm^{-1} , respectively. The 2LO mode in bulk GaAs is very weak under other excitations, such as an excitation of 514.5 nm. It is, however, apparent that it is resonantly enhanced by the observed $E_0 + \epsilon_0$ transition in the PL spectra.

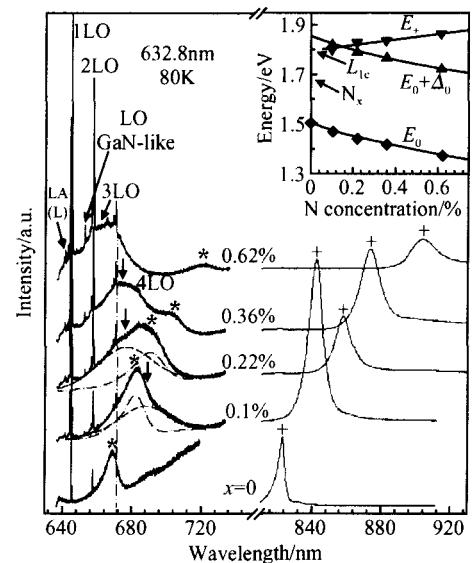


Fig. 1 PL spectra of $\text{GaAs}_{1-x}\text{N}_x$ samples ($x = 0, 0.1\%, 0.22\%, 0.36\%$, and 0.62%) excited by a 632.8 nm laser at 80 K in the range from 635 to 940 nm. The arrows, stars and crosses indicate the observed PL peaks. The inset shows the nitrogen-induced levels in GaAsN as a function of nitrogen concentration and the fitting results. The dashed lines give the peak fitting results for $x = 0.1\%$ and 0.22% . The spectra are vertically shifted for clarity. The vertical dash-dotted line indicates the wavelength of 671.0 nm.

For $\text{GaAs}_{1-x}\text{N}_x$ samples ($x = 0$), as shown in Fig. 1, the PL peaks above 800 nm labeled with crosses (+) are from the emission of their fundamental band gaps E_0 , which were observed by Luo et al. under short pulse excitation^[12]. Here, it shows that the micro-PL technique is very power-

ful in investigating the alloy states in dilute GaAs_{1-x}N_x alloys, because the localized states from some defect centers will be saturated due to the limited number of localization centers under a high power density of about 100kW/cm². We do not observe significant blue-shift (< 1meV) of the PL peaks under different excitation powers at 80K. These peaks decrease in energy with the increase of nitrogen content from 0.1% to 0.62%. From the energy of the E₀ transition, we can deduce that the bowing coefficients are 37.7, 31.0, 25.9, and 23.7eV, respectively, for the dilute GaAs_{1-x}N_x alloys with x = 0.1%, 0.22%, 0.36%, and 0.62% after assuming a bandgap energy of 3.29eV for cubic GaN at 80K^[13]. This is well known as the giant and composition-dependent optical bowing coefficient in GaAs_{1-x}N_x alloys^[1,2]. In the spectral range from 640 to 740nm, two broad peaks were observed in the PL spectra of GaAs_{1-x}N_x samples with x of 0.10%, 0.36%, and 0.62%. The two peaks are so close for the sample with a nitrogen content of 0.22% that it is hard to distinguish them. Two peaks with a line shape like the E₀ + σ peak in bulk GaAs are used to fit the high-energy peaks of 0.10% and 0.22% alloys, and the fitting peaks are shown in Fig. 1 as dashed lines. The energies of all the observed PL peaks are summarized in the inset of Fig. 1. The data clearly show that the PL peaks at 682.1, 691.0, 701.2, and 719nm observed in GaAs_{1-x}N_x samples closely track the nitrogen content dependent E₀ energy with a constant blue-shift of 0.348eV, which is equal to the spin-orbit splitting σ in bulk GaAs. This indicates, therefore, that these PL peaks are the transition from the spin-orbit split-off valence band (E₀ + σ) in GaAs_{1-x}N_x. They are labelled with stars (*) in Fig. 1.

More importantly, besides the PL peaks of E₀ and E₀ + σ , the other PL peaks indicated in Fig. 1 by arrows increase in peak energy with increasing nitrogen content, a behavior which is similar to that of the E₊ energy observed by modulated reflectance in GaAsN alloys^[3,7]. The energy of these peaks is encompassed by the reported E₀ + σ and well-known nitrogen-induced level (E₊). For example, the energy 1.865eV (1.838eV) of the PL peak at 664.7nm (674.1nm) for the x = 0.62% (0.36%) GaAs_{1-x}N_x sample is very close to that of the nitrogen-induced E₊ level observed by

modulated reflectance measurement at 80K^[7]. Therefore, we believe that the other PL peaks are the expected optical transitions related to the nitrogen-induced E₊ states. In addition to the above broad PL peaks, many sharp peaks close to the laser line are also observed for all dilute GaAs_{1-x}N_x samples. These sharp peaks are Raman peaks of dilute GaAs_{1-x}N_x, including GaAs-like LO, 2LO, 3LO, and 4LO phonons at about $x \times 295\text{cm}^{-1}$ and a GaN-like LO phonon at $\sim 473\text{cm}^{-1}$. Referring to the Raman spectra of bulk GaAs, we see clearly that the Raman modes are resonantly enhanced in intensity by the observed high-energy PL peaks. For example, the intensities of the GaN-like LO and GaAs-like 2LO and 3LO phonon modes located near the broad high-energy PL peak in the GaAs_{1-x}N_x sample with x of 0.62% are much stronger than those in the GaAs_{1-x}N_x samples with x of 0.1% and 0.22%. The previous results show that the out-going resonance, rather than the incoming resonance, dominates the Raman light-scattering process in GaAsN alloys^[15]. As shown in Fig. 1, the zone-boundary phonons LA (L) (= 207cm⁻¹), LO (L) (= 243cm⁻¹), and TO (X) (= 207cm⁻¹) to the left of the GaAs-like LO phonon modes in GaAsN alloys become stronger as the PL peaks approach the Raman modes for GaAs_{1-x}N_x samples with larger nitrogen content, such as x = 0.36% and 0.62%. This is a typical resonant Raman behavior related to the E₊ transition in GaAsN alloys^[14,15]. The resonant behavior of the Raman modes further suggests that the PL peaks labeled with arrows are from the intrinsic transitions with the E₊ level in our GaAs_{1-x}N_x samples.

For dilute GaAs_{1-x}N_x samples (0.1% < x < 0.62%), as shown in the inset of Fig. 1, the observed levels of E₀ and E₀ + σ exhibit a nonlinear dependence on the nitrogen content, which indicates that the bowing coefficients are strongly dependent on the composition of the GaAs_{1-x}N_x alloys. E₊ increases with increasing nitrogen content in GaAsN alloys, whereas E₀ and the spin-orbit split-off transition (E₀ + σ) decrease with the increase of nitrogen concentration. E₊ intersects E₀ + σ at a nitrogen content of about 0.16%. For the x = 0.1% sample, the E₊ transition is lower in energy than the E₀ + σ transition. It is also found that the intensity of the E₊ transition is much stronger than that of the E₀ + σ transition for the

$x = 0.22\%$ samples, whereas the $E_0 + \epsilon_0$ transition exceeds the E_+ transition in intensity for the $x = 0.1\%$ sample.

In a small range of nitrogen concentration between 0.10% and 0.62% , it is found that the energies of E_+ are almost linear versus the nitrogen composition of alloys. Linear extrapolation to the dilute limit of the E_+ transition in $\text{GaAs}_{1-x}\text{N}_x$ yields the energy $E_+(x=0^+)$ of 1.797eV . The identification of the E_+ PL peak as a localized resonant N level is very unlikely because the linear extrapolation energy 1.797eV of $E_+(x=0^+)$ at 80K is even much larger than the N_x transition^[16] of 1.68eV below 10K , and previous works also show that the shift of N_x is rather small in a dilute nitrogen limit^[17,18]. Because the PL peaks associated with $E_0 + \epsilon_0$ are very weak, the electronic transition from the conduction band extremum to the spin-orbit split valence band is not a possible candidate for the E_+ peak. The nitrogen incorporation into GaAs breaks the translational symmetry of the lattice, and the impurity potential splits the L_{1c} -derived quadruplet into an $a_1(L_{1c})$ singlet and a $t_2(L_{1c})$ doublet and the ϵ_{1c} state becomes a $a_1(\epsilon_{1c})$ singlet^[18-10]. Considering that the derived $E_+(x=0^+)$ is almost equal to the energy 1.8eV of L_{1c}^c conduction band minimum of GaAs related to the top ($\frac{v}{8}$) of the valence band at 77K ^[13], we ascribe the observed E_+ peak to transitions between the top of the valence band and high lying conduction band states near the L point, which have been strongly perturbed by the nitrogen doping.

In bulk GaAs, optical transitions from L_{1c} and X_{1c} to the valence maximum are forbidden. In an ordered structure (one N in a supercell), the L point is folded to the Γ point and obtains some component due to coupling to the Γ point^[10]. In the real sample, being disordered, optical transitions from the degenerated $a_1(L_{1c})$ to the valence maximum become partially allowed due to the relaxation in the selection rule related to the translation symmetry^[10]. Previous pseudopotential calculations have indicated that the GaAs host states will be quite strongly perturbed by the incorporation of nitrogen by the $-L-X$ mixing effect, which results in all levels containing a significant admixture of ϵ -like character^[18-10]. The optical transition probability is defined by their charac-

ter. This may be the main reason that optical transitions from the top of the valence band to the perturbed $a_1(L_{1c})$ become allowed.

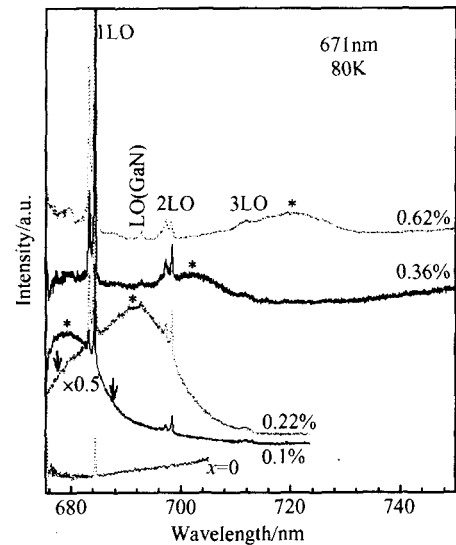


Fig. 2 PL and Raman spectra of $\text{GaAs}_{1-x}\text{N}_x$ samples excited by 671nm laser at 80K in the range from 677 to 750nm . The stars indicate the observed PL peaks. The spectra are vertically shifted for clarity.

Figure 2 shows PL spectra of $\text{GaAs}_{1-x}\text{N}_x$ samples ($x=0, 0.1\%, 0.22\%, 0.36\%$, and 0.62%) at 80K excited by a laser line of 671nm . The broad PL peaks were also observed for each $\text{GaAs}_{1-x}\text{N}_x$ sample as marked with stars and arrows. These peaks are from the $E_0 + \epsilon_0$ (star marked) or E_+ (arrow marked) transitions in these GaAsN alloys. Because of the condition of near resonant excitation, the PL peak of the $E_0 + \epsilon_0$ transition shows stronger intensity than those excited with the 632.8nm excitation. The 514.5nm laser line of an Ar^+ laser is also used as an excitation (results not shown), and the relative intensity of the $E_0 + \epsilon_0$ transition to the E_+ transition is about ten times weaker than that excited with the 632.8nm laser for the $x=0.62\%$ alloys. The sharp peaks in Fig. 2 are Raman peaks of dilute $\text{GaAs}_{1-x}\text{N}_x$ alloys. For bulk GaAs, only one Raman peak of 1LO phonon is observed. However, GaAs-like 2LO and 3LO phonon modes are observed in the Raman spectrum of each GaAsN alloy. The vertical dash-dotted line in Fig. 1 shows the wavelength position of the 671.0nm laser. One can see that the energy of the E_+ transition of a $\text{GaAs}_{1-x}\text{N}_x$ alloy with $x=0.36\%$ is slightly lower than that of the 671.0nm laser line whereas that of a $\text{GaAs}_{1-x}\text{N}_x$

alloy with $x = 0.62\%$ is larger than that of the 671.0nm laser line. That the 3LO phonon mode in the $x = 0.62\%$ alloy is stronger than the that of the $x = 0.36\%$ alloy indicates that the 3LO phonon mode in the $x = 0.62\%$ alloy is resonantly enhanced by its $E_0 + \omega_0$ transition, because the outgoing resonance dominates the light-scattering process in GaAsN alloys^[15]. Using a low excitation power, a GaAs-like 4LO phonon mode was also observed in the $x = 0.62\%$ alloy. Therefore, the results of resonant Raman scattering further verify the intrinsic feature of band gap emission from the observed $E_0 + \omega_0$ transition in GaAs_{1-x}N_x alloys. For the 0.1% alloy, its $E_0 + \omega_0$ transition is very close to the excitation energy. However, we still observe the GaAs-like 3LO phonon peak in this alloy. This suggests that the other level of E_+ observed by 633nm excitation should resonantly enhance this high order Raman peak, where the PL signal of E_+ transition is enshrouded in the strong resonantly-excited PL signal of the $E_0 + \omega_0$ transition.

4 Conclusion

In summary, we have observed three groups of PL peaks in dilute GaAs_{1-x}N_x alloys with $x = 0.10\%$, 0.22% , 0.36% , and 0.62% by micro-photoluminescence measurements. Using these and resonant Raman scattering measurements, the three groups of PL peaks are confirmed to be the intrinsic transitions of E_0 , $E_0 + \omega_0$ and E_+ in the studied dilute GaAsN alloys. The bowing coefficients are deduced as 37.7, 31.0, 25.9, and 23.7eV at 80K, respectively, for the dilute GaAs_{1-x}N_x alloys with $x = 0.1\%$, 0.22% , 0.36% , and 0.62% . Our results show that the near-resonant excitation of the micro-PL spectra is very important in observing the optical transitions above the fundamental band gap of semiconductor materials.

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低 N 含量 GaAsN 材料的共振喇曼散射及其带边以上的光致发光光谱*

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摘要: 利用显微光致发光技术, 观测到了 N 含量为 0.1%, 0.22%, 0.36% 和 0.62% 的 GaAsN 合金的 E_0 , $E_0 + \epsilon_0$ 和 E_+ 能级的光致发光峰. 共振喇曼散射谱进一步证实了这些发光峰来源于所研究材料的本征能级, 而不是来源于 GaAsN 合金中的一些局域激子发射. 随着 N 组分的增加, $E_0 + \epsilon_0$ 和 E_+ 能级分别向低能和高能方向移动并在 N 组分为 0.16% 时发生交错. 文中提出了一种少量等电子掺杂和显微光致发光谱相结合的方法来直接观测半导体材料带边以上的跃迁能级, 尽管光致发光谱通常没有用来观测这些能级位置.

关键词: GaAsN; 共振喇曼散射; 光致发光; 带隙; 等电子掺杂

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