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Interpretation of an anomalous peak in low-temperature photoluminescence measurements of bulk $\text{GaAs}_{1-x}\text{N}_x$ on GaAs

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Low-temperature (10 K) photoluminescence measurements of $\text{GaAs}_{1-x}\text{N}_x$ epitaxial layers grown on GaAs reveal an anomalous second peak in solid-source molecular beam epitaxy. Rapid thermal annealing (RTA) of a specific GaAsN sample reveals a lower energy peak (γ) which redshifts and a higher energy peak (α) which blueshifts under increasing annealing temperature. The band-anticrossing model is used to identify the origins of the two peaks and we propose a model to explain the RTA observations by the concept of increased confinement in areas of higher N concentrations by trapped N localized states. The γ peak is due to the accumulation of N content near the GaAs/GaAsN interface. Hence, this abnormal annealing behavior occurs in layers with nonuniform N concentration at the GaAsN/GaAs interface. © 2006 American Institute of Physics. [DOI: 10.1063/1.2199976]

I. INTRODUCTION

Dilute III–V nitrides such as (In)GaAsN have attracted much attention due to the potential for optoelectronic device applications operating at the 1.3 and 1.55 μm wavelengths on the GaAs substrate. The conventional choices of active regions for lasers at the wavelengths mentioned are InGaAsP or InGaAs on InP substrates. However, these material systems exhibit poor temperature characteristics due to a shallow conduction band potential as compared with the III–V–N material system. The incorporation of N into (In)GaAs causes a redshift with increasing N composition, due to the large band gap bowing factor (in the order of ~ 10 eV) between the GaN and the GaAs binaries. One of the most well-known models used to explain this redshift phenomenon is the band-anticrossing model, which is based on the repulsive behavior between the conduction band edge (CBE) and the localized N resonant states.¹ Despite these positive attributes, the fluctuation of N introduces a strong modification to the band structure of (In)GaAs. The large electronegativity of N atoms as compared with As significantly alters the III–As–N epilayer from that of an ideal random alloy. N atoms tend to incorporate into nonsubstitutional lattice sites and form defect complexes due to the small covalent radii of nitrogen. Besides that, dilute nitride growth also heralds a host of associated defects such as Ga vacancies, As_{Ga} antisites which lead to the deterioration of the optical and electrical characteristics.² Rapid thermal annealing (RTA) can be used to improve the epitaxial quality by eliminating the impurity-related radiative and nonradiative recombination centers. The common observations from RTA include the blueshift of the PL peak position and the improvement of the PL efficiency

by more than one order of magnitude. The blueshift has been claimed to be caused by nitrogen outdiffusion at the interfaces.³ However, in recent research, it is unanimously agreed that the blueshift is caused by the homogenization of the bulk N composition, driven by strain relief during the RTA process.^{4,5} In contradictory to the above mentioned work, Francoeur *et al.* report that annealing causes a redshift for $\text{GaAsN}_{0.019}$.⁶ To further complicate matters, two energy peaks in low-temperature (LT) photoluminescence (PL) measurements have been reported in GaAsN_x ($0.5\% \leq x \leq 1.5\%$) grown by solid-source molecular beam epitaxy (SSMBE).^{7–9} The two emission peaks are claimed to be originated from spatial carrier localization and from regions of varying N composition, which blueshift with increasing annealing temperature. In this paper, our group also reports that two peaks are observed from the bulk GaAsN epitaxial layer from LT PL measurements. The most unique phenomenon is that the high energy peak (denoted by α) blueshifts and the lower energy peak in the PL spectra (denoted by γ) redshifts when subjected to increasing annealing temperature during RTA. Amid the confusion shrouding this issue, we attempt to interpret the origins of these peaks and the abnormality behind the red/blueshift using a model and substantiate it with secondary-ion-mass spectroscopy (SIMS) measurements.

II. EXPERIMENTAL DETAILS

An ~ 1000 Å GaAsN epilayer was grown at 490 °C on a 3000 Å GaAs buffer and subsequently capped with ~ 200 Å GaAs (580 °C) on semi-insulating (100) orientated GaAs substrates. The rf power in high brightness mode is kept at about 100 W to allow an N composition of $\sim 1.3\%$. Rapid thermal annealing at temperature intervals between 600 and 800 °C is then performed under nitrogen ambient for a fixed

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FIG. 1. Low-temperature (LT) 10 K photoluminescence (PL) measurements of the as-grown and the annealed GaAsN_{1.3%} sample vs annealing temperature (°C) in steps of 50 °C.

interval of 10 min. GaAs wafer proximity capping was used to prevent As desorption at elevated temperatures. LT PL measurements were performed at 10 K using the 5145 Å line of an Ar⁺ laser as the exciting source and a liquid nitrogen cooled Ge detector as the detection source with a standard lock-in technique. SIMS measurements were performed using a Cameca IMS 6f magnetic sector ion microprobe. MCs⁺ secondary ions ($M=^{69}\text{Ga}$, ^{75}As , and ^{14}N) were used for the depth profiling to minimize dependence on the matrix effect in III–V semiconductor compound matrix elements. With a primary accelerating voltage of 4.00 kV and 2.00 kV for the secondary, producing an effective primary voltage of 2 keV, the primary beam was rastered over a square region of 250 μm^2 on one side, and the secondary ions were collected from the central region of the sputtered crater, using a physical aperture of 30 μm in diameter.

III. RESULTS AND DISCUSSION

A. Photoluminescence peak spectra of annealed GaAsN

Figure 1 depicts the LT PL measurements of the as-grown and the annealed GaAsN_{1.3%} sample. The annealed samples are plotted in 50 °C intervals from 600 to 800 °C. We observe two peaks in the LT PL spectra. First, we introduce the lower energy peak in the PL spectra (denoted by γ) which exhibits an asymmetric line shape with a low energy tail. The γ peak blueshifts by ~ 6 meV from the as-grown to 600 °C and gradually redshifts by ~ 31 meV from 600 to 750 °C. The redshift observed is primarily caused by interstitial N entering substitutional sites at ~ 750 °C.^{6,10} Our

observations for the γ peak fully support the trend that RTA at LT of ~ 650 °C can only remove the defects which originate from the dilute-N/GaAs interfaces, causing blueshift.¹¹ Defects originating from the bulk, however, can only be eradicated by high-temperature (HT) RTA, ~ 750 °C. The PL intensity improves with increasing annealing temperature and peaks at 750 °C, giving the near-band-gap radiative recombination originating from excitons localized by GaAsN when most of the impurity-related recombination centers are eradicated. Beyond 750 °C, a drastic blueshift results from the overannealing and the N–As interdiffusion occurs at the interfaces at the elevated temperatures. At this juncture, the linewidth broadens and the PL intensity decreases rapidly due to the RTA induced defects. On the high energy side, the second weaker peak (denoted by α) is observed for annealing temperatures between 650 and 750 °C at ~ 1.267 eV. The α peak is observed to slightly blueshift (~ 13 meV) with increasing annealing temperature. In order to understand the two peaks, SIMS measurements are carried out. The SIMS profiles of the (a) as-grown and (b) annealed samples at 750 °C are shown in Fig. 2. The interfaces are shown to be abrupt before and after annealing which supports the trend that the dominant peak shifting is bulk induced rather than interface induced interdiffusion. The substrate temperature of 490 °C (higher than the optimized temperature of dilute N at 460 °C) may increase the tendency of forming three-dimensional growth and create composition modulation which perturbs the local microstructure.^{4,7} In Fig. 2(a), we find signatures of higher N concentration at ~ 98 and 123 nm from the surface, which are close to the position of the GaAsN/GaAs interface. One possible interpretation of the observation is the enhancement of the N incorporation due to the enrichment of the active N species between the transients involved such as the N plasma ignition and the tuning of the coupling in the rf power input to the actual epitaxial deposition, which in our case is approximately 5 min. Even when the main shutter is closed, it is unlikely to be 100% efficient in preventing nitridation, although it is minimized. After annealing at 750 °C [Fig. 2(b)], the inhomogeneous elemental N distribution has been reduced and the bulk N concentration is homogenized. From the discussions, a physical model of the observed PL is proposed in Fig. 3. The transition from the areas of higher N compositions in the as-grown sample is denoted by T_1 . The more homogeneous areas with lower N compositions give rise to a higher energy transition, denoted by T_2 . The localized state with higher N has a greater amount of interstitial N (N_i) as compared with that with lower N. Under an *ex situ* thermal treatment of 10 min, the mobile interstitial N enters an As site to form substitutional N via a kick out mechanism.³ Hence, the low energy transition (T_1) decreases into energy (T'_1), leading to greater confinement which allows more carriers to recombine radiatively under laser excitation. This explains the higher PL intensity of the γ transition as compared with the α peak from the bulk. The decrease of N_i in the higher N areas with increasing annealing temperature leads to greater PL intensities at the γ peak transition until 750 °C. As for the T_2 transition which arises from the lower N regions, there is less N_i generated; T'_2 transition becomes higher than the T_2 transition from the profile

FIG. 2. SIMS measurements of the (a) as-grown and the (b) annealed GaAsN_{1.3%} sample at 750 °C with the nitrogen concentration (atm/cm³) vs the sputtering depth (nm).

homogenization and causes blueshift during the *ex situ* annealing.^{4,5} This is used to explain the observed photoluminescence trend in Fig. 1, where the dominant low energy peak (γ) redshifts and the weaker high energy peak (α) blueshifts with the annealing temperature.

B. Identification of the photoluminescence peaks using the BAC model

The origins of the peaks can be confirmed by means of the fundamental energy transition peak derived from the band-anticrossing (BAC) model including the strain effect. The effective band gap from tensile strained GaAs_{1-x}N_x epilayers is formulated as

$$E_{g(\text{strained})} = E_g(x) + 2a\left(1 - \frac{C_{12}}{C_{11}}\right)\varepsilon + b\left(1 + \frac{2C_{12}}{C_{11}}\right)\varepsilon, \quad (1)$$

where $E_g(x)$ is the unstrained fundamental band gap energy, the second component lowers the conduction band (CB), and

FIG. 3. A proposed model of the better confinement of localized N states at higher N concentrations. The solid line denotes the as-grown energy levels and the dotted line denotes the annealed energy levels. The transitions are not drawn to scale.

the third component raises the valence band (VB) due to the tensile strain.¹² The strain ε is denoted as $[a_0 - a(x)]/a_0$. The GaAsN parameters are assumed to be the interpolation of the GaAs and GaN parameters as tabulated in Table I. The unstrained fundamental band gap can be derived from the BAC model,¹⁴

$$E_g(x) = \frac{1}{2}[E_M(T) + E_N - \sqrt{(E_M(T) - E_N)^2 + 4V_{MN}^2}], \quad (2)$$

where $E_M(T)$ is the energy of the unperturbed conduction band edge of the semiconductor matrix and E_N is the energy of the N-related level relative to the top of the valence band. E_N is constant for small N values and the acceptable range of E_N is 1.65–1.71 eV.¹³ The V_{MN} is the matrix element describing the interaction and the hybridization between the localized N states and the extended states. $V_{MN}^2 = C_{MN}^2 x$, where C_{MN} is assumed to be a temperature independent, constant value and x is the mole fraction of N, for randomly distributed N atoms ($x < 5\%$). The range of C_{MN} is from 2.3 to 2.7 eV.¹³ Skierbiszewski *et al.*¹⁵ and Shan *et al.*¹⁶ use $E_N = 1.65$ eV and $C_{MN} = 2.7$ eV in their dilute nitride work. Klar *et al.*, however, list E_N to be 1.71 eV and $C_{MN} = 2.5$ eV for $T < 20$ K.¹⁷ We fitted E_N to be 1.67 eV and $C_{MN} = 2.6$ eV for our calculations for $T = 10$ K. It is found that Kudrawiec *et al.* state E_N to be 1.67 eV for their annealed GaAsN_{0.02} samples at 750 °C for 10 min and their

TABLE I. Data parameters of GaAs and GaN (zinc blende).^{a,b}

	GaAs	GaN
a_0 (Å)	5.6533	4.5
a (eV)	-8.33	-7.4
b (eV)	-1.7	-2
C_{11} (GPa)	118.79	293
C_{12} (GPa)	53.76	159

^aReference 12.

^bReference 13.

FIG. 4. The SIMS measurements of the as-grown GaAsN_{1.89%} and the annealed sample at 750 °C (10 min) with the nitrogen concentration (atom/cm³) vs the sputtering depth (nm).

$C_{MN}=2.6$ eV for photon energies ~ 1.15 eV,¹⁸ which are in very good agreement with our results. The temperature dependence of the GaAs host matrix is determined by the well-known Varshni function,

$$E_M(T) = E_{g(\text{GaAs})} - \frac{\alpha T^2}{\beta + T}, \quad (3)$$

and using the GaAs parameters, $\alpha=5.408 \times 10^{-4}$ eV/K, $\beta=204$ K, and $T=10$ K, we find $E_M(T=10 \text{ K})$ to be ~ 1.5118 eV using $E_{g(\text{GaAs})}$ of 1.512 eV at 0 K.¹⁹ We have the energy band gap in terms of the N composition (x) which is comparable with the experimental data of the mentioned groups.^{16,17,20} The unstrained fundamental band gap energy can then be used to calculate the strained energy band gap in Eq. (1) with the data parameters in Table I to determine the origins of the PL peaks in Fig. 1. The as-grown SIMS data [Fig. 2(a)] reveal the lower N content of 1.3% and the higher N concentration of $\sim 1.9\%$. This corresponds to the 1.251 and 1.176 eV PL peak positions, respectively, which unsurprisingly show that the higher energy peak (α) is from the lower N of 1.3% and that the lower energy peak (γ) comes from the higher N concentration of 1.9%. The straight dashed and dotted lines in Fig. 1 serve as a guide to the eye, the position of the strained N composition. The curved lines show the imaginary peak shift position in relation to annealing temperature. The SIMS measurements reveal the total concentration of N regardless of the site locality. In PL measurements, only the N situated at substitutional site contributes to redshift. At the optimized annealing temperature of 750 °C, most of the interstitial N enter substitutional sites, contributing to the maximum PL redshift. Hence, the redshift of the low energy γ peak does not exceed 1.176 eV (corresponding to the total N of 1.9% measured by the SIMS).

The PL peak blueshifting with annealing temperature in GaAsN is widely reported.²¹ We also find the normal PL peak blueshifting in our uniformly (see Fig. 4) grown GaAsN_{1.89%} in Fig. 5. After annealing for 10 min at 750 °C, the N profile is further homogenized (Fig. 4). The 10 K PL measurement of the bulk GaAsN_{1.89%} sample (Fig. 5) shows a single PL peak blueshifting ~ 50 meV from 1116 (as grown) to 1165.4 meV when the annealing temperature reaches 800 °C. This again is in good agreement with the

FIG. 5. The low-temperature (LT) 10 K photoluminescence (PL) measurements of the as-grown and the annealed GaAsN_{1.89%} sample vs annealing temperature (°C) in steps of 100 °C.

BAC model and the SIMS measurements. The dominant mechanism present in the GaAsN_{1.89%} sample during annealing is the homogenization of the N profile which leads to the PL peak blueshifting.²¹

IV. CONCLUSIONS

In conclusion, two peaks of LT PL measurements of GaAsN grown on GaAs are found and explained by using RTA, SIMS, and BAC model. The γ peak confines carriers more efficiently (T_1) in the as-grown sample. As more N_i become substitutional, the confinement increases (T_1'), leading to a greater PL intensity from 600 to 750 °C. The as-grown sample does not show a α PL peak until ~ 650 °C due to the inherent quality of as-grown dilute N and the trapping of carriers in T_1 . The α peak from the lower N regions blueshifts with increasing annealing temperature due to the homogenization of the N profile. However, as the confinement increases in T_1' , T_2' has less carriers and hence the PL intensity of the α peak decreases.

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¹W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 1221 (1999).

²J. Toivonen, T. Hakkarainen, M. Sopanen, H. Lipsanen, J. Oila, and K. Saarinen, Appl. Phys. Lett. **82**, 40 (2003).

³S. G. Spruytte, C. W. Coldren, A. F. Marshall, and J. S. Harris, 2000 MRS Spring Meeting, San Francisco (Materials Research Society, Pittsburgh, 2000), Paper No. K9-1.

⁴A. Trampert, J.-M. Chauveau, K. H. Ploog, E. Tournié, and A. Guzmán, J.

- Vac. Sci. Technol. B **22**, 2195 (2004).
- ⁵E. Tournié, M.-A. Pinault, and A. Guzmán, Appl. Phys. Lett. **80**, 4148 (2002).
- ⁶S. Francoeur, G. Sivaraman, Y. Qiu, S. Nikishin, and H. Temkin, Appl. Phys. Lett. **72**, 1857 (1998).
- ⁷A. R. Kovsh, J. S. Wang, L. Wei, R. S. Shiao, J. Y. Chi, B. V. Volovik, A. F. Tsatsul'nikov, and V. M. Ustinov, J. Vac. Sci. Technol. B **20**, 1158 (2002).
- ⁸X. D. Luo, P. H. Tan, Z. Y. Xu, and W. K. Ge, J. Appl. Phys. **94**, 4863 (2003).
- ⁹G. Mussler, L. Däweritz, K. H. Ploog, J. W. Tamm, and V. Talalaev, Appl. Phys. Lett. **83**, 1343 (2003).
- ¹⁰T. Ahlgren, E. Vainonen-Ahlgren, J. Likonen, W. Li, and M. Pessa, Appl. Phys. Lett. **80**, 2314 (2002).
- ¹¹Z. Pan, L. H. Li, W. Zhang, Y. W. Lin, R. H. Wu, and W. Ge, Appl. Phys. Lett. **77**, 1280 (2000).
- ¹²S. L. Chuang, *Physics of Optoelectronic Devices* (Wiley, New York, 1995), p. 441, and references therein.
- ¹³I. Vurgaftman and J. R. Meyer, J. Appl. Phys. **94**, 3675 (2003).
- ¹⁴W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, J. Appl. Phys. **86**, 2349 (1999).
- ¹⁵C. Skierbiszewski *et al.*, Phys. Rev. B **65**, 035207 (2001).
- ¹⁶W. Shan, K. M. Yu, W. Walukiewicz, J. W. Ager III, E. E. Haller, and M. C. Ridgway, Appl. Phys. Lett. **75**, 1410 (1999).
- ¹⁷J. P. Klar, H. Grüning, W. Heimbrod, J. Kock, F. Höhnsdorf, W. Stolz, P. M. A. Vicente, and J. Camassel, Appl. Phys. Lett. **76**, 3439 (2000).
- ¹⁸R. Kudrawiec, G. Sek, J. Misiewicz, L. H. Li, and J. C. Harmand, Solid State Commun. **129**, 353 (2004).
- ¹⁹Y. P. Varshni, Physica (Utrecht) **39**, 149 (1967).
- ²⁰R. Chtourou, F. Bousbih, S. Ben Bouzid, F. F. Charfi, J. C. Harmand, G. Ungaro, and L. Largeau, Appl. Phys. Lett. **80**, 2075 (2002).
- ²¹L. Grenouillet, C. Bru-Chevallier, G. Guillot, P. Gilet, P. Ballet, P. Duvaut, G. Rolland, and A. Million, J. Appl. Phys. **91**, 5902 (2002).