Interpretation of Anomalous Photoluminescence Peak in $GaAs_{1-x}N_x$ Grown by Molecular Beam Epitaxy

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ABSTRACT

Low-temperature (10K) photoluminescence (PL) measurements of $GaAs_{1-x}N_x$ epitaxial layers grown on GaAs by solid-source molecular beam epitaxy (SSMBE) reveal an anomalous second peak. 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 when 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.

***Keywords**:* GaAsN; MBE; PL; SIMS;

1. INTRODUCTION

GaAs-based III-V-N such as (In)GaAsN have attracted much attention due to the potential for optoelectronic device applications operating at the 1.3 and 1.55μm wavelengths. The incorporation of N into (In)GaAs causes a redshift with increasing N composition, due to the large band gap bowing factor. However, the fluctuation of N introduces a strong modification to the band structure of (In)GaAs. The large electronegativity of N atoms as compared to As significantly alters the III-As-N epilayer from that of an ideal random alloy. N atoms are easier to incorporate into non-substitutional 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 [1]. RTA can be used to improve the epitaxial quality by eliminating the above impurity-related radiative and nonradiative recombination centres. 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. The blueshift has been claimed to be caused by nitrogen outdiffusion at the interfaces [2]. 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 [3,4]. In contradictory to the above mentioned work, Francoeur *et. al.* reports that annealing causes a redshift for $GaAsN_{0.019}$ [5]. To further complicate matters, two energy peaks in LT PL measurements have been reported in bulk layers of $GaAsN_x$ $(0.5\% \le x \le 1.5\%)$ grown by SSMBE [6-8]. 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 2 peaks are observed in the bulk GaAsN epitaxial layer from low temperature (LT) photoluminescence (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 increasing annealing temperature. Amid the confusion shrouding this issue, we attempt to interpret the origins of these peaks and the abnormality behind the red/blue-shift using a model and substantiate it with secondary-ion mass spectroscopy (SIMS) measurements.

2. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

A ~1000Å GaAsN epilayer was grown at 490ºC on a 3000Å GaAs buffer and subsequently capped with ~200Å GaAs (580ºC) on semi insulating (100) orientated GaAs substrates. The rf power in high brightness mode is kept at about 100W to allow an N composition of ~1.3%. Rapid thermal annealing (RTA) at temperature intervals between 600ºC to 800ºC is then performed under nitrogen ambient for a fixed interval of 10min. GaAs wafer proximity capping was used to prevent As desorption at elevated temperatures. LT PL measurements were performed at 10K using the 5145Å 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 6*f* magnetic sector ion microprobe. MCs^+ secondary ions (M = ^{69}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 4.00kV and 2.00kV for the secondary, producing an effective primary voltage of 2kV, the primary beam was rastered over a square region of 250μm^2 on one side, and the secondary ions were collected from the central region of the sputtered crater, using a physical aperture of 30μm in diameter.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the LT PL measurement of the as-grown and the annealed $GaAsN_{1.3\%}$ sample. The annealed samples are plotted in 50ºC intervals from 600 to 800ºC. The γ peak blueshifts by ~6meV from the as-grown to 600ºC and gradually redshifts by ~31meV from 600 to 750ºC. The redshift observed is primarily caused by interstitial N entering substitutional sites at ~750ºC

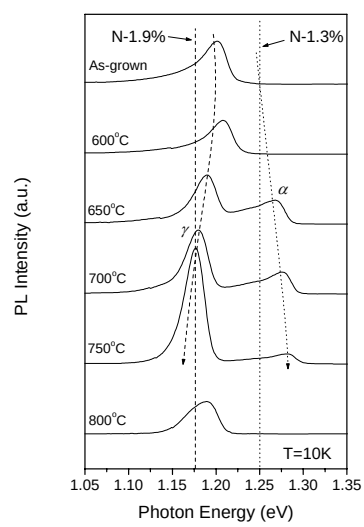

Figure 1: 10K PL measurement of the as-grown and the annealed $GaAsN_{1.3\%}$ sample vs annealing temperature (ºC) in steps of 50ºC.

[5,9]. Our observations for the γ peak support that RTA at a low annealing temperature of ~650ºC can only remove the defects which originates from the dilute-N/GaAs interfaces, causing

blueshift [10]. Beyond 750ºC, a drastic blueshift results from the over-annealing. At this juncture, the linewidth broadens and the PL intensity decreases rapidly due to the over-annealing induced defects. On the high energy side, the second weaker peak (denoted by α) is observed for annealing temperatures between 650 - 750ºC at ~1.267eV. The α peak is observed to slightly blueshift (~13meV) with increasing annealing temperature. In order to understand the two peaks, SIMS measurements are carried out.

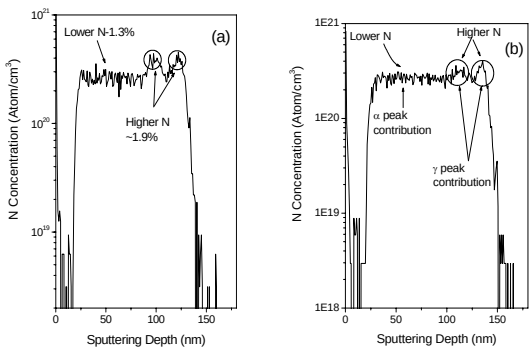

Figure 2: SIMS measurement of the (a) as-grown and the (b) annealed $GaAsN_{1.3\%}$ sample at 750ºC with the nitrogen concentration (atm/cm^3) vs the sputtering depth (nm).

The SIMS profile of the (a) as-grown and (b) annealed sample at 750ºC is shown in Figure 2. The interface 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 490ºC (higher than the optimized temperature of dilute N at 460ºC) may increase the tendency of forming three-dimensional growth and create composition modulation which perturbs the local microstructure [3,6]. In Figure 2(a), we find signatures of higher N concentration at ~98 and 123nm 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 like 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 750ºC [Figure 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 to that with lower N. Under an *ex-situ* thermal treatment of 10min, the mobile interstitial N enters a As site to form substitutional N via a kick out mechanism [2]. 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 to 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 till 750ºC. 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 homogenization and causes blueshift during the *ex-situ* annealing [4-5]. This is used to explain the observed photoluminescence trend in Figure 1, where the dominant low energy

peak (γ) redshifts and the weaker high energy peak (α) blueshifts with the annealing temperature.

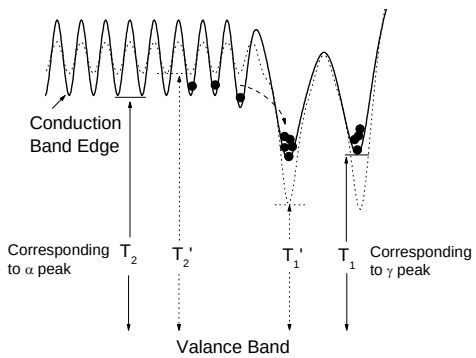

Figure 3: A proposed model of the better confinement of localized N states at higher N concentrations. The solid line denotes the as-grown energy levels and the dotted line denotes the annealed energy levels. The transitions are not drawn to scale.

4. CONCLUSIONS

In conclusion, two peaks of LT PL measurements of GaAsN grown on GaAs are found and explained by using RTA, SIMS. 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 - 750ºC. The as-grown sample does not show a *α* PL peak until ~650ºC 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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