Annealing Ambient Effects on Optical Properties in the GaInNAs Epitaxial Growth

Takashi ISHIZUKA*, Hideyuki DOI, Mitsuru SHIMAZU, Shigenori TAKAGISHI, Akira YAMAGUCHI, Ryuta YAGINUMA and Masaaki NAKAYAMA

Sumitomo Electric Industries have studied annealing ambient effects on optical properties of GaInNAs/GaAs single quantum wells by utilizing photoluminescence (PL) spectroscopy and photoreflectance (PR) spectroscopy to investigate carrier localization and intrinsic band-edge transition, respectively. By the systematic analysis of PL and PR spectra, the authors have revealed that the annealing conditions in the GaInNAs epitaxial growth greatly effected improvements in the optical properties. In the study, two annealing ambient sequences were examined: tertiarybutylarsine and hydrogen (H_2) in the annealing process. The PL efficiency at room temperature is markedly improved in the H_2 ambient annealing process. The authors found from systematic results of PL and PR spectra that the PL efficiency at room temperature is in connection with the Stokes shift at 10 K, which is a measure of carrier localization, and the broadening factor of the band-edge transitions.

Keywords: GaInNAs, annealing, photoluminescence, photoreflectance, carrier localization

1. Introduction

The recent progress of optical communication networks demands the development of low power consumption and low cost optical devices. GaInNAs quantum-well (QW) systems are one of the good candidates for optical devices in a near-infrared light region such as vertical cavity surface emitting lasers because relatively strong confinement of electrons in the QW, which mainly originates from nitrogen alloying, leads to temperature-stable and low threshold-current operations [(1)-(5)]. However, it is difficult to obtain high quality GaInNAs QW grown by either metalorganic vapor phase epitaxy (MOVPE) or molecular beam epitaxy because the growth needs extreme non-equilibrium conditions [(6)]. Moreover, an incorporation of nitrogen into GaInNAs usually produces localized states, so-called band-tail states shown in **Fig. 1**, since nitrogen has large electron affinity [(7)-(13)].

In order to improve the optical properties of GaInNAs/GaAs QWs, it is essential to be annealed at a higher temperature than the growth temperature. However, it is not easy to do annealing in the fabrication of GaInNAs laser diodes because the optimization of annealing conditions strongly depends on not only post-growth annealing sequences but also structures of epitaxitial layers of GaInNAs devices. Since the annealing process directly influences to photoluminescence (PL) efficiency and optoelectronic device properties such as threshold-current and reliability, it is very interesting and important to investigate details of annealing effects.

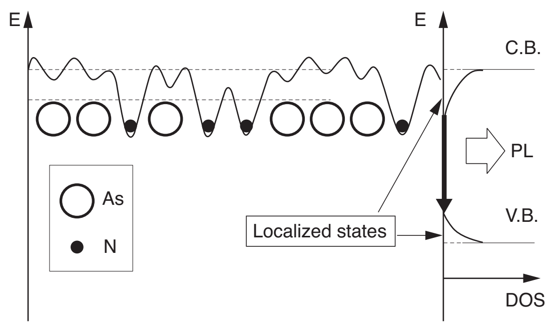

Fig. 1. Localized states of GaInNAs/GaAs SQWs.

Many studies have suggested that post-growth annealing can improve the optical properties [(9),(14)-(17)]; however, there is little understanding of what causes the effects of annealing. Volz *et al.* reported an influence of annealing ambience on optical and structural properties of GaInNAs/GaAs QWs [(18)]. They attributed the increase of PL efficiency of GaInNAs annealed in hydrogen (H_2) ambience to the removal of nonradiative defects. Moreover, Shirakata *et al.* reported a decrease of localized states by annealing of GaInNAs/GaAs QWs [(9)]. From an aspect of the annealing conditions (ambience, annealing temperature, etc.), however, little has been known about optical properties and carrier localization of GaInNAs/GaAs QWs.

In this work, we have investigated annealing ambient effects on the optical properties of GaInNAs/GaAs single QWs (SQWs) with use of two spectroscopic methods of photoluminescence (PL) and photoreflectance (PR). It is noted that the PL spectroscopy is sensitive to carrier localization and the PR spectroscopy is sensitive to intrinsic band-edge transition. The systematic spectroscopic characterizations reveal that the PL efficiency at room temperature (RT) is related to the carrier localization and the broadening factor of the band-edge transition.

2. Experimental Procedure

$Ga_{1-x}In_xN_yAs_{1-y}$/GaAs SQWs with $x = 0.35$ and $y = 0.005$ were grown by MOVPE using triethylgallium (TEGa), trimethylindium (TMIn), tertiarybutylarsine (TBAs) and

1,1-dimethylhydrazine (UDMHy). The surface orientation of Si-doped GaAs (001) substrates was 2 degrees toward (111)A. The growth temperature and growth rate were 540 °C and 1.0 µm/hr, respectively. During the MOVPE growth, the reactor pressure and As/III ratio, [TBAs]/([TEGa]+[TMIn]), were kept at 10 kPa and 5, respectively. A 200 nm-thick GaAs buffer layer was first grown on the substrate, and then a 7 nm-thick GaInNAs QW layer and a 100 nm-thick GaAs cap layer were grown.

After the MOVPE growth, the samples were thermally annealed by two kinds of sequences (A and B) under different ambient conditions shown in **Fig. 2**. In the sequence (A), the sample was annealed for 10 minutes under TBAs ambience and cooled to RT under H_2 ambience. In the sequence (B), the sample was annealed for 10 minutes under H_2 ambience and cooled to RT under H_2 ambience. The annealing temperature was systematically changed.

For optical characterizations, PL spectra at 10 K and RT, and PR spectra at 10 K were measured. The excitation light for the PL was the 514.5 nm line of an Ar^+ laser. The typical spectral resolution of PL was 1.5 nm. In PR measurements, the probe light was produced by combination of a halogen lamp and a single monochromator with a resolution of 1.5 nm. The pump light for reflectance modulation was the 514.5 nm line of an Ar^+ laser chopped at 210 Hz. The PR signal was detected with a conventional lock-in technique.

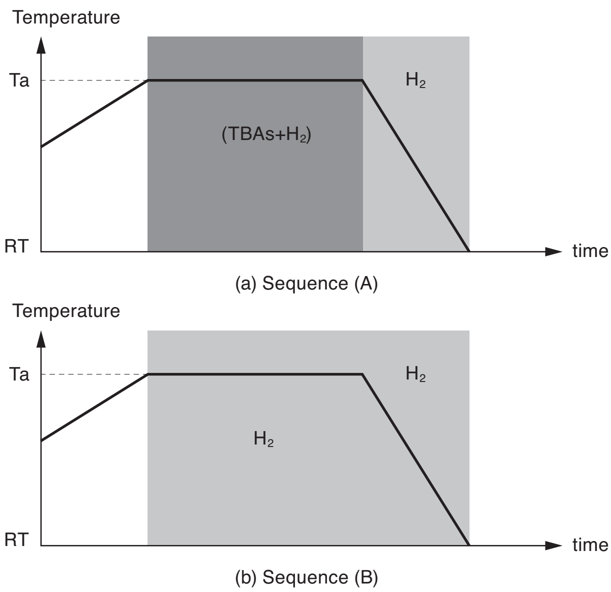

Fig. 2. Two annealing sequences of GaInNAs/GaAs SQWs, (a) (TBAs+H_2) ambience and (b) H_2 ambience, respectively.

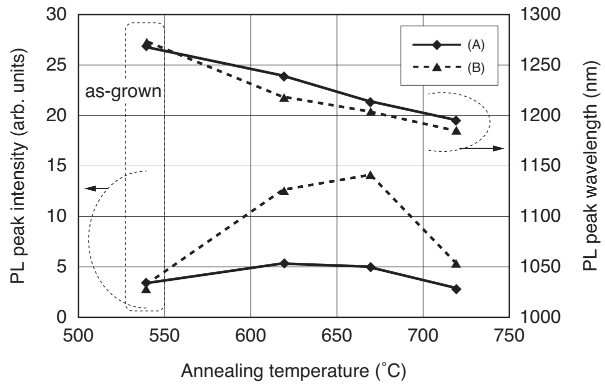

Fig. 3. PL peak intensity and peak wavelength of GaInNAs/GaAs SQWs as a function of annealing temperature under the two annealing sequences, where the results in the sequences (A) (TBAs+H_2 ambience) and (B) (H_2 ambience) are depicted by closed diamonds and triangles, respectively.

3. Results and Discussion

Figure 3 shows the annealing temperature dependence of PL peak intensity and peak wavelength in GaInNAs/GaAs SQWs at RT, where the results in the annealing sequences (A) and (B) are depicted by closed diamonds and triangles, respectively. It is evident that the PL peak wavelength becomes shorter with increasing annealing temperature, indicating a well-known blue-shift of the band gap energy after annealing. The difference of the magnitudes of the blue-shift in the two annealing sequences was small. On the other hand, the PL intensity in the 670 °C annealing under H_2 [sequence (B)] is about three times stronger than that under the TBAs [sequence (A)]. This fact indicates that the annealing in H_2 ambience considerably improves the PL efficiency.

In order to discuss band-edge transition properties, the PR spectra at 10 K in GaInNAs/GaAs SQWs in as-grown and three annealing temperatures under the two annealing sequences (A) and (B) are shown in **Fig. 4**. It is well known that PR spectroscopy is sensitive to the optical transitions at critical points of density of states, especially for the band-edge transition. From a line-shape analysis of the PR signal based on the third derivative functional form [19] that is a conventional analysis model, we evaluated the transition energy at the intrinsic band edge (E_g) and the broadening factor (Γ) that reflects disorders of density of states of the band edge [11], [20]. The values of E_g and Γ obtained from the line-shape analysis are denoted on **Fig. 4**. It is obvious that the value of E_g increases with increasing annealing temperature, indicating the blue-shift of the band gap energy after annealing. The value of Γ considerably depends on the annealing temperature and the sequence. For optical properties of GaInNAs/GaAs SQWs, the broadening factor is one of key factors. The detail of the broadening factor will be discussed below with **Fig. 6**.

Next, we evaluated the Stokes shift (ΔE_s) that is a measure of carrier localization. **Fig. 5** shows PR spectra and the excitation power dependence of PL spectra at 10 K in GaInNAs/GaAs SQWs at 670 °C annealing under the two sequences (A) and (B), where the fitted line shapes of the PR spectra are indicated by the solid curves. The excitation power was widely varied to confirm the carrier

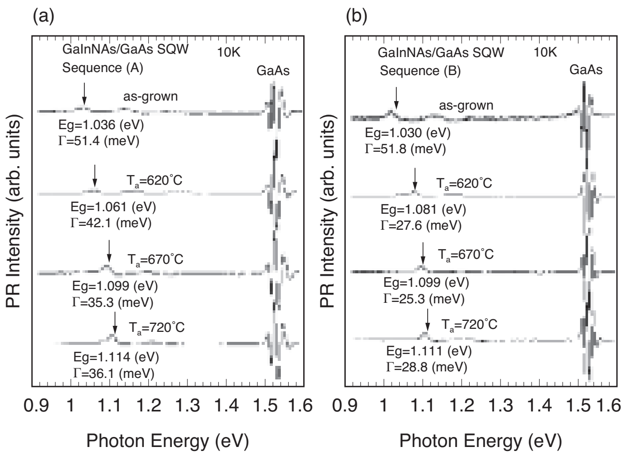

Fig. 4. PR spectra at 10 K in the GaInNAs/GaAs SQWs with in as-grown and three annealing temperatures under the two annealing sequences: (a) the sequence (A) (TBAs+H_2 ambience) and (b) the sequence (B) (H_2 ambience), where the fitted values of E_g and Γ for the band-edge transition are denoted.

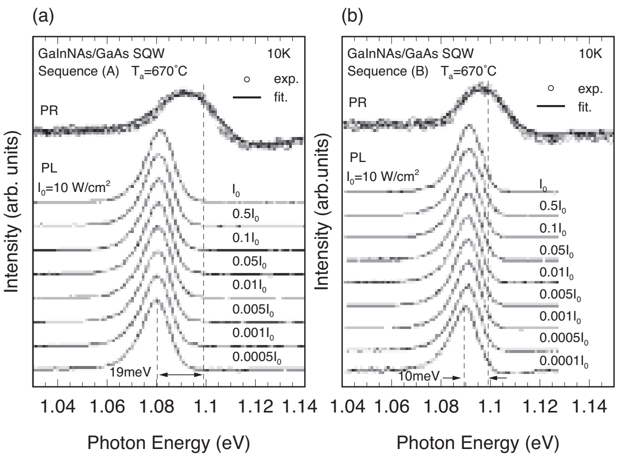

Fig. 5. PR spectra (open circles) and the excitation-power dependence of PL spectra at 10 K in the GaInNAs/GaAs SQWs in 670 ˚C annealing under the two annealing sequences: (a) sequence (A) (TBAs ambience), (b) sequence (B) (H_2 ambience). The fitted line shapes of the PR spectra are indicated by the solid curves, and the long dashed lines represent the band-edge energies.

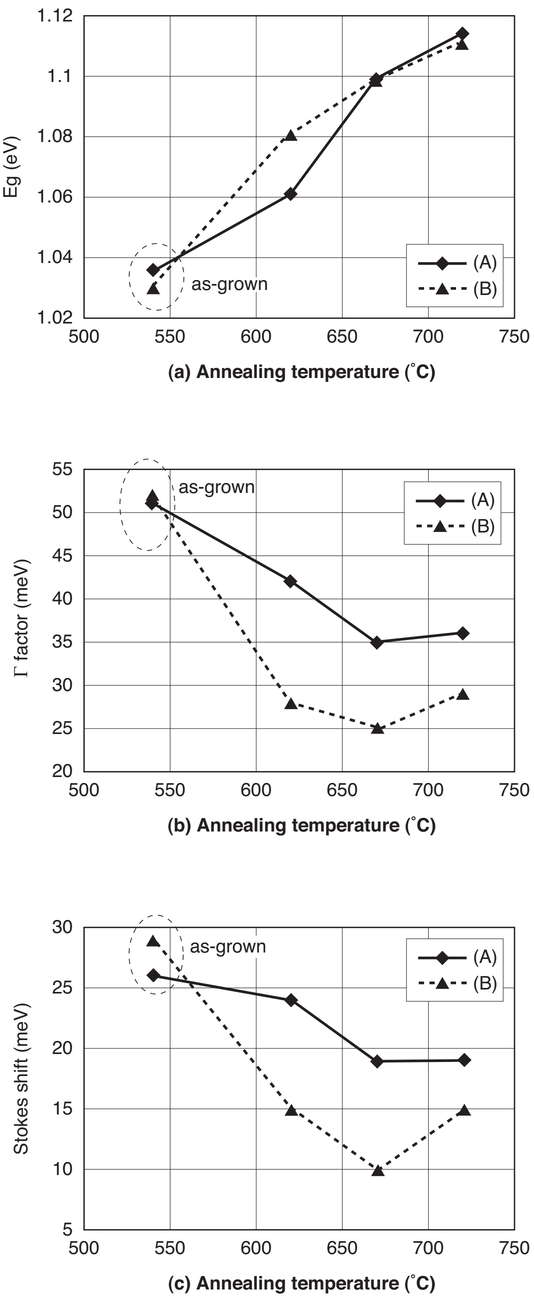

Fig. 6. Annealing temperature dependence of (a) band-edge energy (E_g), (b) broadening factor (Γ), and (c) Stokes shift (ΔE_S) evaluated from PL and PR spectra of GaInNAs/GaAs SQWs at 10 K under the two annealing sequences (A) (TBAs ambience) and (B) (H_2 ambience).

localization. The Stokes shift corresponds to the energy spacing between the band-edge energy, indicated by the long dashed line estimated from the line-shape analysis of the PR signal, and the PL peak energy at the lowest excitation power. We note that the PL peak energy was unchanged by a further decrease of excitation power. In 670 °C annealing, the Stokes shifts are 19 meV under the annealing sequence (A) and 10 meV under the annealing sequence (B), respectively. Although the values of E_g under both ambient conditions are almost equivalent, it is obvious that the value of ΔE_S under the H_2 ambient condition is considerably smaller than that under the TBAs ambient condition. This means that the carrier localization is reduced under the H_2 ambient condition.

Figure 6 summarizes the annealing temperature dependence of the values of (a) E_g, (b) Γ, and (c) ΔE_S at 10 K, where the results of the two annealing sequences (A) and (B) are depicted. The difference of E_g values under the TBAs and H_2 ambient conditions is not so large. On the other hand, it is evident from the values of Γ and ΔE_S that the optical properties are remarkably improved under the H_2 ambient condition in every annealing temperature; namely, the band-edge disorder and carrier localization are remarkably reduced. As shown in **Fig. 3**, the

PL efficiency at RT under the sequence (B) is markedly higher than that under the sequence (A), which is in connection with the reduction of the band-edge disorder and carrier localization. Therefore, the systematic spectroscopic characterizations demonstrate that the H_2 ambient condition in annealing is advantageous to improve the optical properties.

Finally, we briefly discuss the process in which the annealing effect is generated from two kinds of viewpoints. One is a change in the N-H stretch, and the other is a phase separation of the alloy GaInNAs. It was reported the N-H stretch in the alloy GaInNAs grown by MOVPE was changed from NH to NH_2 after annealing [16]. It is probable that the active atomic hydrogen produced by the pyrolysis of TBAs in the annealing ambience is related the change of the N-H stretch, though it is not concluded in our results described. From a slightly different point of view, GaInNAs/GaAs QW systems have a tendency of phase separation due to a large miscibility gap resulting in compositional fluctuation [21]. The compositional fluctuation usually causes band-edge disorders producing localized states and nonradiative centers, which leads to the performance degradation of optical devices. It seems that the annealing process reduces a degree of the compositional inhomogeneity by the rearrangements of local nitrogen environments and/or migration of constituent atoms. Our result phenomenologically suggests that the less As-stabilized annealing condition under the H_2 ambience is effective to enhance the annealing effects.

4. Conclusions

In conclusion, we have found that the ambience of thermal annealing remarkably influences the optical properties of GaInNAs/GaAs SQWs from the systematic measurements of PL and PR spectra. The H_2 ambience in the annealing process reduces the band-edge disorder and the localization of carriers effectively, resulting in the considerable improvement of the PL efficiency at RT. Thus, the ambience in the annealing process plays a role to improve the optical properties of GaInNAs QW systems.

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Contributors (The lead author is indicated by an asterisk (*)).

T. ISHIZUKA*

• Assistant Manager
Semiconductor Technologies R&D Laboratories
He is engaged in the research and development of compound semiconductor epitaxial growth for laser diodes and photo detectors.

H. DOI

• Assistant General Manager
New Energy and Industrial Technology Development Organization (NEDO)

M. SHIMAZU

• Senior Assistant General Manager
New Energy and Industrial Technology Development Organization (NEDO)

S. TAKAGISHI

• Dr. Eng.
Senior Assistant General Manager
R&D General Planning Division

A. YAMAGUCHI

• Senior Specialist
Dr. Eng.
General Manager
Semiconductor Technologies R&D Laboratories

R. YAGINUMA
- Department of Applied Physics, Graduate School of Engineering, Osaka City University

M. NAKAYAMA
- Professor
  Department of Applied Physics, Graduate School of Engineering, Osaka City University