ANTIMONY ENHANCED HOMOGENEOUS NITROGEN INCORPORATION INTO GaInNAs FILMS GROWN BY ATOMIC HYDROGEN-ASSISTED MOLECULAR BEAM EPITAXY

Naoya Miyashita [1], Nazmul Ahsan [1], and Yoshitaka Okada [1,2]
1. Research Center for Advanced Science and Technology (RCAST), The University of Tokyo, Meguro-ku, Tokyo, Japan.
2. School of Engineering, The University of Tokyo, Meguro-ku, Tokyo, Japan.

ABSTRACT

In this work, we investigated the effect of Sb on N-induced localized states in GaInNAs films. From 77 K photoluminescence (PL) spectra for GaInNAs(Sb) films grown with different Sb fluxes, single band-to-band emissions observed in all samples. The emission wavelength redshifts with increasing Sb flux, which corresponds to an increase in Sb composition. The PL intensity and full-width at half maximum (FWHM) are both improved for a narrow range of Sb flux of 1 − 5×10^{-8} Torr. On the other, higher Sb flux deteriorates the PL characteristics. It can be thought that any higher Sb flux induces some kind of Sb-related defects such as Sb_{Ga} antisites. Further in temperature dependent PL measurements, energy shifts, so-called “S-shaped” curves, were observed in all samples, which indicate a strong carrier localization. Although GaInNAs sample showed a large energy shift of 53 meV, irradiation of Sb decreases the localization energies to 13 − 22 meV. These results show that Sb can enhance the homogeneity of GaInNAs alloy, since the carrier localization is led by inhomogeneous N incorporation. The internal quantum efficiency characteristics for GaInNAsSb solar cell also improved by introducing an optimum amount of Sb and a redshift of fundamental absorption edge into 1 eV range was achieved.

INTRODUCTION

The dilute nitride semiconductor alloy, GaInNAs, has attracted research interest for applications to high-efficiency multi-junction tandem solar cells [1], since the bandgap energy can be ideally tuned to the required 1 eV region while lattice-matched to GaAs and Ge substrates. However, both the optical and electrical characteristics are degraded even if a few percent of N are added to the host Ga(In)As, along with compositional fluctuations and phase separation [2,3].

Recently, use of Sb in molecular beam epitaxy (MBE) is shown to be effective to obtain high-quality GaInNAs(Sb) / GaAs quantum wells (QWs) [3,4]. On the other, validity of Sb irradiation on the growth of “low-strained” GaInNAs films for application to solar cells has not been fully discussed. In addition, Sb is known to be a constituent, and constructs a quinary alloy, GaInNAsSb, which gives a significant difficulty in the compositional control to maintain lattice-matched to GaAs and Ge.

In this work, we investigated the effect of Sb on N-induced localized states by using photoluminescence (PL). Optimal amount of Sb needed to improve the overall optical properties of GaInNAsSb films and solar cells were studied.

EXPERIMENTAL

GaInNAs(Sb) films and solar cells were grown by RF-molecular beam epitaxy (RF-MBE) with atomic hydrogen irradiation [5,6]. The growth conditions were kept identical except for the Sb beam flux, which was varied in the range of 0 ~ 1×10^{-7} Torr in beam equivalent pressure (BEP). Sb and N concentrations were calibrated using secondary ion mass spectroscopy (SIMS). The 0.1 μm-thick $GaIn_{0.076}NAs(Sb)$ layers were grown on GaAs (001) substrate, and the surface was capped by 0.05 μm-thick GaAs. Solar cell samples investigated in this work employed a p-i-n structure, and consisted of a 0.5 μm-thick n-GaAs base, a 0.3 μm-thick undoped i-GaInNAs(Sb), and a 0.15 μm-thick p-GaAs emitter layer. The GaInNAsSb layer was grown under Sb flux of 1×10^{-8} Torr, and this condition gives < 1 % Sb composition.

The secondary ion mass spectroscopy (SIMS) measurements were performed using Cs^+ as the primary ion and detecting Sb, N, and In as the negative secondary ions. The photoluminescence (PL) was measured by using the 532 nm second harmonic line of an $Nd:VO_4$ diode-pumped laser, a 250 mm monochromator, a liquid-nitrogen cooled GaInAs photodetector for PL intensity comparison experiment at 77 K, and a PbS photodetector for temperature dependence measurements. A high-resolution X-ray diffraction (HR-XRD) was used to determine the lattice parameters of GaInNAs(Sb) layer.

RESULTS AND DISCUSSION

Figure 1 show the plots of N and Sb compositions determined by SIMS measurement for $GaIn_{0.076}NAs(Sb)$ control sample grown with different Sb flux of 0, 1×, 5×, and 10×10^{-8} Torr, respectively. The In secondary ion

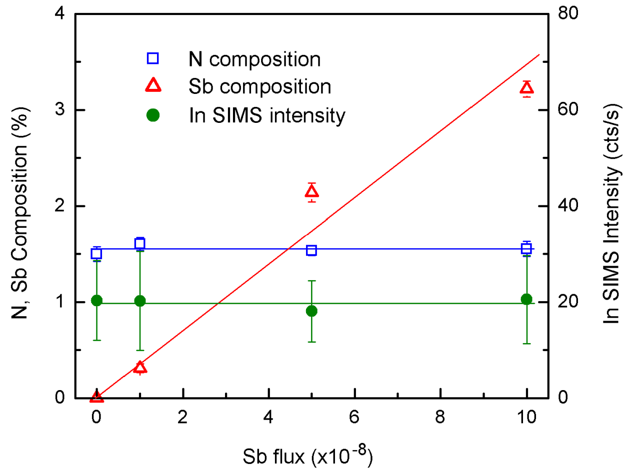

Figure 1 Plots of the N and Sb compositions, and In secondary ion intensity for GaIn$_{0.076}$NAs(Sb) layer grown with different Sb fluxes of 0 (no Sb), 1×10^{-8}, 5×10^{-8}, and 10×10^{-8} Torr, respectively.

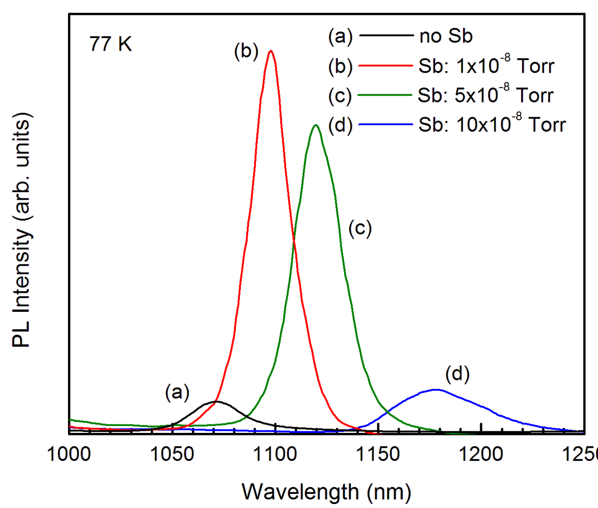

Figure 2 77 K PL spectra for GaIn$_{0.076}$NAs(Sb) films with different Sb fluxes of 0 (no Sb), 1×10^{-8}, 5×10^{-8}, and 10×10^{-8} Torr, respectively.

signals is also plotted in Fig. 1. We can observe that N and In incorporation in GaIn$_{0.076}$NAsSb layers do not show any dependence on Sb beam flux for the given GaInNAs layers studied here. Because the sticking coefficient of In is unity in typical GaInAs growth, all the irradiated In atoms can also be incorporated in GaInNAs(Sb) layers. Our previous experiments reveal that there exists a compositional dependence of N on Sb irradiation in terms of the compositional variation of In [7]. We obtain the same N composition with and without Sb irradiation, if particular In composition range of 7 – 13 % is maintained in GaInNAsSb growth. Meanwhile, Sb composition increases with increasing Sb flux.

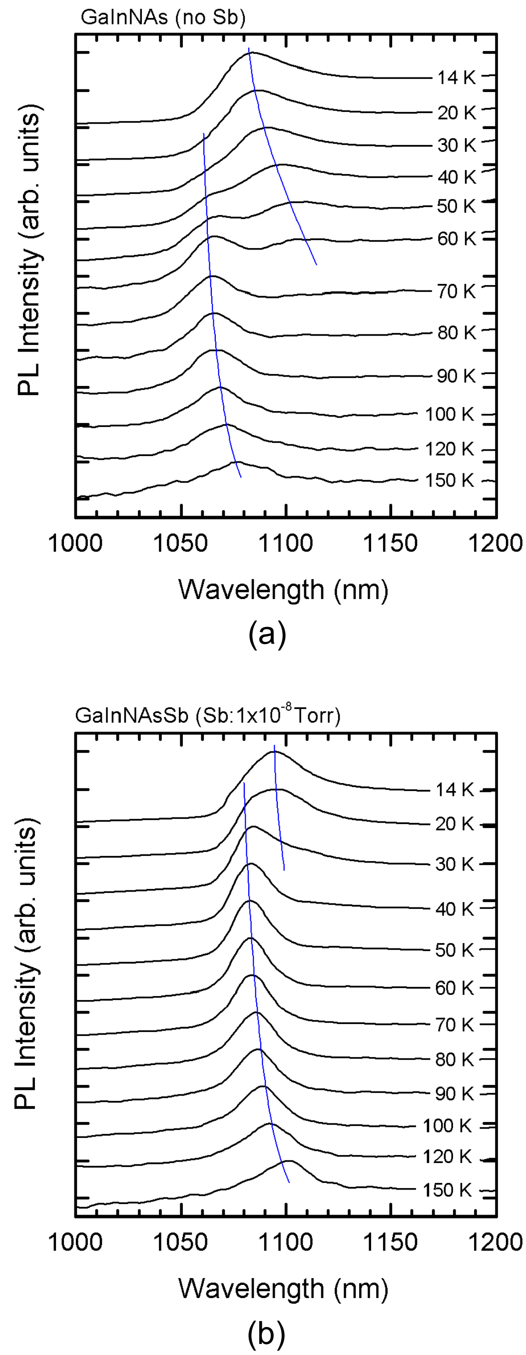

Figure 3 Temperature dependence of PL spectra for (a)GaIn$_{0.076}$NAs (no Sb) and (b)GaIn$_{0.076}$NAsSb (Sb: 1×10^{-8} Torr) films, respectively.

Figure 2 show the 77 K PL spectra of GaIn$_{0.076}$NAs(Sb) films with different Sb fluxes of 0 (no Sb), 1×10^{-8}, 5×10^{-8}, and 10×10^{-8} Torr, respectively. The power of light excitation (λ = 532 nm) used in this analysis was P = 20 W/cm^2. A single band-to-band emission peak is observed in all samples. The emission wavelength redshifts with increasing Sb flux, which corresponds to an increase of Sb composition [8]. The PL intensity and full-width at half maximum (FWHM) are both improved for a narrow range of Sb flux of 1 − 5×10^{-8} Torr. On the other, higher Sb flux decreases the PL intensity, and FWHM is broadened. We think that any higher Sb flux induces some Sb related defects such as Sb_{Ga} antisites [9], which deteriorate the optical characteristics.

In order to investigate the effect of Sb on N-induced localized states, temperature dependent-PL measurements were conducted on our four GaInNAs(Sb) samples. Figures 3(a) and (b) show the temperature dependence of PL spectra measured between 14 – 150 K for $GaIn_{0.076}NAs$ (no Sb) and $GaIn_{0.076}NAsSb$ films (Sb flux = 1×10^{-8} Torr), respectively. The excitation power was reduced to P = 6 W/cm^2 using a ND filter in order to determine detailed conduction band structure.

The energy shifts are observed in all samples; the PL peaks at higher temperatures correspond to the interband transition (E_C – E_V), and the transition between N induced localized states and valence band ($E_{L(N)}$ – E_V) becomes a major origin of luminescence at lower temperatures. The localized states reflect inhomogeneous N incorporation into the host GaInAs(Sb) material, therefore the energy shift indicates uniformity of N distribution in the films.

Figure 4 show the plots of PL peak energies for GaInNAs(Sb) films as a function of temperature. Since two peaks are well separated in GaInNAs sample (no Sb), a large energy shift of 53 meV is observed at around 60 K. On the other hand, samples with Sb irradiation show smaller energy separations, and therefore peak shifts occur over several tens K. Next, peak energy shift, ΔE, as a function of Sb flux is plotted in Fig. 5. The irradiation of Sb reduces the localization energies to 13 − 22 meV. These results show that Sb can enhance the homogeneity of GaInNAs alloy, since the carrier localization is led by inhomogeneous N incorporation.

Finally, the effect of Sb irradiation on the performance of GaInNAs(Sb) solar cells was investigated. Figure 6 shows the schematic structure of p-GaAs / i-$Ga_{0.96}In_{0.04}N_{0.013}As_{0.987}$ or i-$Ga_{0.955}In_{0.045}N_{0.015}As_{0.985-z}Sb_z$ / n-GaAs double heterostructure solar cells fabricated in this work. Both GaInNAs and GaInNAsSb layers were well lattice-matched to GaAs substrate, as can be seen in HR-XRD ω-2θ scans shown in Fig. 7.

Figure 8 show the internal quantum efficiency (IQE) characteristics for GaInNAs and GaInNAsSb solar cells. The IQE in lower wavelength region (< 870nm) remains unchanged and reaches > 90 % at ~700 nm with and without Sb, which suggests that upper p-GaAs emitter layers for both cells maintain good crystalline quality even after growing the GaInNAs(Sb) layers. Although the N composition in $GaIn_{0.045}N_{0.015}AsSb$ cell is slightly higher than that in $GaIn_{0.04}N_{0.013}As$ cell, IQE is improved by introduction of a small amount of Sb (1×10^{-8} Torr), as well as a ~70 nm redshift of the absorption edge. The filtered current density > 870 nm is improved from 4.1 ($GaIn_{0.04}N_{0.013}As$) to 5.6 mA/cm^2 by addition of Sb. Hence, GaInNAsSb is more suitable than GaInNAs sub-cell to improve the performance of future four-junction III-V tandem solar cells.

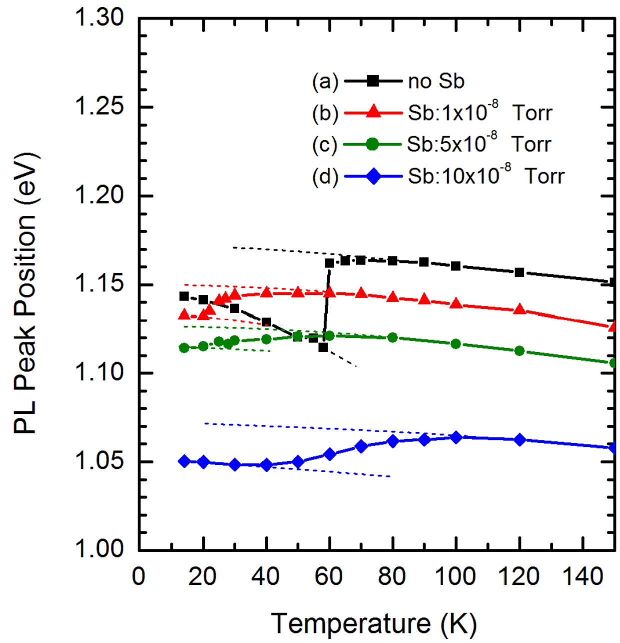

Figure 4 Temperature dependence of the highest PL emission energy for $GaIn_{0.076}NAs(Sb)$ films grown with different Sb fluxes of 0 (no Sb), 1×10^{-8}, 5×10^{-8}, and 10×10^{-8} Torr, respectively.

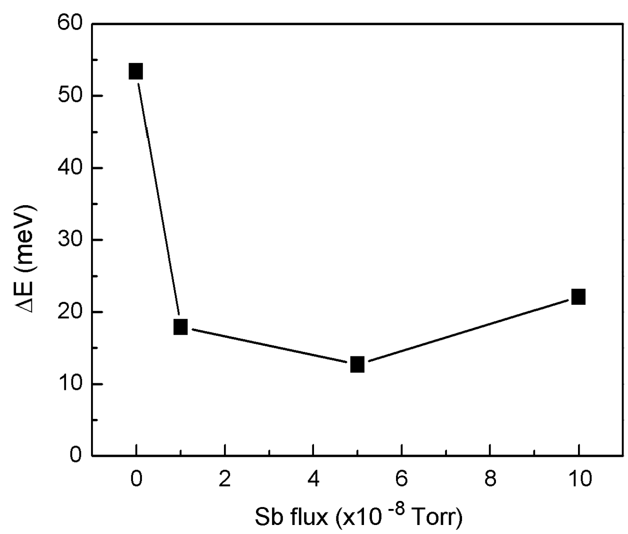

Figure 5 Peak energy shift (ΔE) of $GaIn_{0.076}NAs(Sb)$ film as a function of Sb flux.

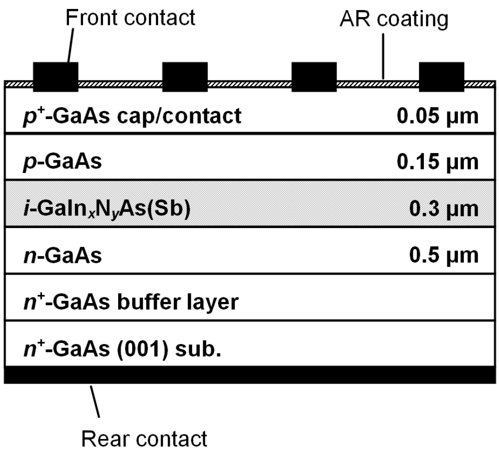

Figure 6 Schematic structure of p-GaAs / i-GaIn$_x$N$_y$As(Sb) / n-GaAs double hetero-structure solar cell samples. In and N compositions (x, y) with and without Sb are (0.045, 0.015) and (0.04, 0.013), respectively.

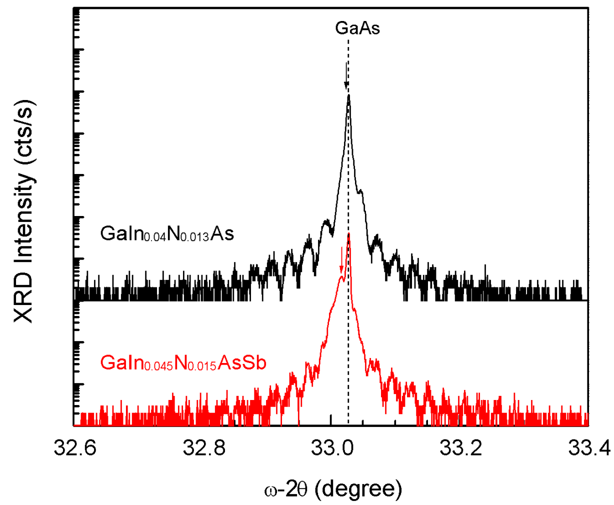

Figure 7 HR-XRD (004) rocking curves of GaIn$_{0.04}$N$_{0.013}$As and GaIn$_{0.045}$N$_{0.015}$AsSb$_z$ double heterostructure solar cells. Arrows indicate the GaInNAs and GaInNAsSb layer peaks.

CONCLUSION

In conclusion, the effect of Sb irradiation on N-induced localized states in our H-MBE grown GaInNAs(Sb) alloys were investigated. Supplying Sb flux in a range of 1 − 10×10^{-8} Torr can enhance homogeneous incorporation of N into host GaInAs material, and reduces the localization energies. Meanwhile, larger amounts of Sb induce degradation of PL characteristics, which suggest that Sb induced defects, such as antisites, were generated. Therefore, small amount of Sb giving < 1% Sb composition is preferred for improvement of GaInNAs crystalline quality and solar cell performance.

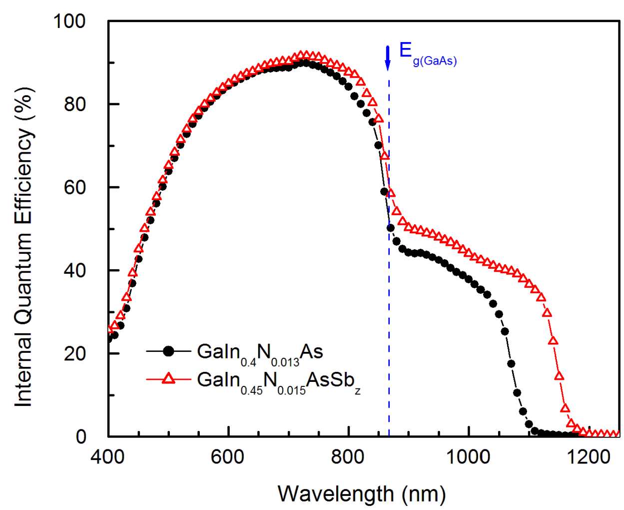

Figure 8 Quantum efficiency spectra for GaInNAs and GaInNAsSb double heterostructure solar cells.

ACKNOWLEDGEMENTS

This work is performed under SOLAR QUEST Project supported by the Incorporated Administrative Agency New Energy and Industrial Technology Development Organization (NEDO) and Ministry of Economy, Trade and Industry (METI), Japan.

REFERENCES

[1] S.R. Kurtz *et al.*, “InGaAsN solar cells with 1.0 eV band gap, lattice matched to GaAs”, *Appl. Phys. Lett.* **74**, 1999, pp. 729-731.

[2] D. Wu *et al.*, “The role of Sb in the molecular beam epitaxy growth of 1.30-1.55 μm wavelength GaInNAs/ GaAs quantum well with high indium content”, *J. Cryst. Growth* **290**, 2006, pp. 494-497.

[3] X. Yang *et al.*, “InGaAsNSb/GaAs quantum wells for 1.55 μm lasers grown by molecular-beam epitaxy”, *Appl. Phys. Lett.* **78**, 2001, pp. 4068-4070.

[4] S.R. Bank *et al.*, “Room-temperature continuous-wave 1.55 μm GaInNAsSb laser on GaAs”, *Electron. Lett.* **42**, 2006, pp. 156-157.

[5] Y. Shimizu *et al.*, “Improvement of crystal quality of GaInNAs films grown by atomic hydrogen-assisted RF-MBE”, *J. Cryst. Growth* **278**, 2005, pp. 553-557.

[6] Y. Shimizu *et al.*, “Effect of growth temperature on the

properties of Ga(In)NAs thin films by atomic hydrogen-assisted RF-MBE", *J. Cryst. Growth* **301-302**, 2007, pp. 579-582.

[7] N. Miyashita *et al.*, "Characteristics of GaInNAsSb solar cells grown by atomic hydrogen-assisted molecular beam epitaxy", *Proc. 18th International Photovoltaic Science and Engineering Conference (PVSEC)*, Kolkata (January 2009), 5-1o-014.

[8] N. Miyashita *et al.*, "Improvement of GaInNAsSb films fabricated by atomic hydrogen-assisted molecular beam epitaxy", *J. Cryst. Growth* **311**, 2009, pp. 3249-3251.

[9] R. Yakimova *et al*., "On the formation of the Sb_{Ga} heteroantisite in metalorganic vapor-phase epitaxial GaAs:Sb", *Appl. Phys. Lett.* **59**, 1991, pp.1323-1325.