JOURNAL OF APPLIED PHYSICS **103**, 113508 (2008)

Photoluminescence and photoreflectance study of annealing effects on $GaAs_{0.909}Sb_{0.07}N_{0.021}$ layer grown by gas-source molecular beam epitaxy

Hung-Pin Hsu,[1] Yen-Neng Huang,[1] Ying-Sheng Huang,[1,a)] Yang-Ting Lin,[2] Ta-Chun Ma,[2]
Hao-Hsiung Lin,[2] Kwong-Kau Tiong,[3] Piotr Sitarek,[4] and Jan Misiewicz[4]
[1]*Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan*
[2]*Department of Electrical Engineering, National Taiwan University, Taipei 106, Taiwan*
[3]*Department of Electrical Engineering, National Taiwan Ocean University, Keelung 202, Taiwan*
[4]*Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

(Received 22 January 2008; accepted 18 March 2008; published online 9 June 2008)

Thermal annealing effects of a $GaAs_{0.909}Sb_{0.07}N_{0.021}$ film grown on GaAs substrate via gas-source molecular beam epitaxy have been characterized by photoluminescence (PL) and photoreflectance (PR) techniques. PL measurements show the evolution of luminescence feature with the thermal annealing treatment. The conduction to heavy-hole (HH) band and conduction to light-hole (LH) band transitions originated from the strained induced valence band splitting in $GaAs_{0.909}Sb_{0.07}N_{0.021}$ layer have been observed by the PR measurements. The near band edge transition energies are slightly blueshifted, and the splitting of HH and LH bands is reduced with rising annealing temperature. The temperature dependences of near band edge transition energies are analyzed using Varshni and Bose–Einstein expressions in the temperature range from 15 to 300 K. The parameters that describe the temperature variations of the near band edge transition energies are evaluated and discussed. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2927490]

I. INTRODUCTION

The nitride III-V semiconductors alloys such as GaNAs and GaInNAs have attracted a lot of attentions in recent past due to their unique physical properties and potential applications for achieving the telecommunication wavelengths of 1.3–1.55 μm with GaAs-based materials.[1–4] In order to achieve the emission wavelength beyond 1.3 μm, many N atoms must be incorporated into the Ga(In)As alloy which can result in degradation of crystal quality of such materials.[5] In order to guarantee the performance of dilute nitride materials, the N composition in the range of 0%–2%, commonly around 1% for Ga(In)NAs alloys, is suggested.[6] Recently, Ungaro *et al.*[7] proposed an alternative alloy, namely, GaAsSbN which offers capability to achieve longer wavelength with lower N concentration compared to GaInNAs. Their works demonstrate that the GaAsSbN grown on GaAs substrate can be used to prepare optical devices emitting in 1.3–1.5 μm region at room temperature.[8–10] The studies related to GaAsSbN applications in long wavelength optical devices have also been reported.[11–13] However, in spite of their potential applications, very little work has been done on the optical properties related to thermal annealing effects in such a quaternary material. For example, the optical transition features originated from the valence band splitting and their temperature dependent near band edge interband transitions properties is only little known. Hence, further study on the thermal annealing effects of GaAsSbN alloy is not only interesting but also necessary and important.

In this work we present the photoluminescence (PL) and photoreflectance (PR) study of thermal annealing effects on a strained $GaAs_{0.909}Sb_{0.07}N_{0.021}$ layer grown on GaAs substrate by gas-source molecular beam epitaxy (MBE). The conduction to heavy-hole (HH) band and conduction to light-hole (LH) band transitions originated from strain induced valence band splitting have been observed. The temperature dependence behaviors of these transition energies in the range from 15 to 300 K are also studied. The parameters that describe the temperature variations of the near band edge transition energies are evaluated and discussed.

II. EXPERIMENT

The $GaAs_{0.909}Sb_{0.07}N_{0.021}$ layer was grown on (100) semi-insulating GaAs substrate via a VG-V80 gas-source MBE system. An EPI Sb cracking cell was used to provide mixed dimmer and monomer Sb beam. The source of As_2 beam was from a gas cell with a cracking temperature of 1000 °C using AsH_3 as the precursor. Gallium flux, calibrated using an ion gauge to keep the growth rate at 1 μm/h, was provided by an EPI unibulb rf plasma *K*-cell operating at a radio frequency of 13.56 MHz. A shutter was placed in front of the *K*-cell to reduce the ionized species. The thickness of the samples in this study was 1 μm with growth temperature of 490 °C. The composition of the $GaAs_{0.909}Sb_{0.07}N_{0.021}$ was quantified by electron probe x-ray microanalyzer with GaAs, GaN, and GaSb as standards for ZAF (atomic number *Z*, absorption *A*, and fluorescence *F*) correction. The samples were *ex situ* annealed at temperatures of 800 and 850 °C for 300 s in N ambient during the thermal annealing process.

In PL measurements, the signal was collected by a spectrometer and detected by an InGaAs charge coupled device

---

[a)] Author to whom correspondence should be addressed. Electronic mail: ysh@mail.ntust.edu.tw.

0021-8979/2008/103(11)/113508/5/$23.00

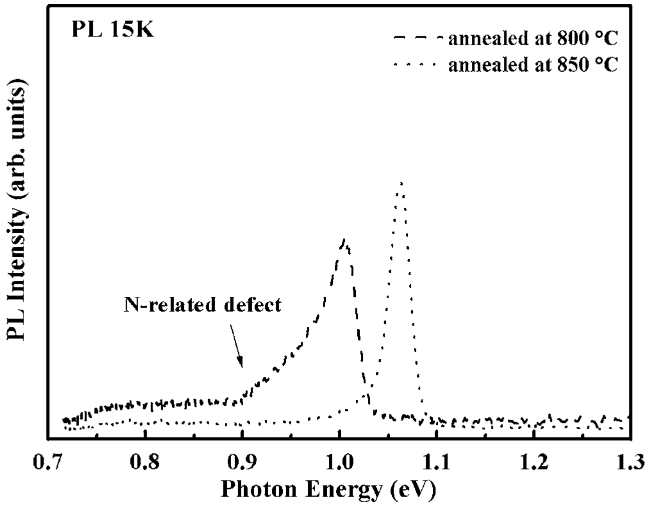

FIG. 1. The PL spectra at 15 K for the $GaAs_{0.909}Sb_{0.07}N_{0.021}$ samples annealed at 800 and 850 °C.

array. A 60 mW double frequency neodymium doped yttrium aluminum garnet 532 nm green laser was employed as the excitation source. For PR measurement, the modulation of the built-in electric field is caused by photoexcited electron-hole pairs created by a mechanically chopped 670 nm line (~3 mW) of a laser diode with a modulating frequency at 200 Hz. The radiation from a 150 W tungsten-halogen lamp filtered by a 0.25 m monochromator provided the monochromatic light. The reflected light was detected by an InGaAs photodetector. The dc output of photodetector was maintained constant by a servomechanism of variable neutral density filter. A dual-phase lock-in amplifier was used to measure the detected signals. Multiple scans over a given photon energy range were programmed until a desired signal-to-noise level has been attained with computer controlled data acquisition procedure. Detailed PR configuration has been described elsewhere.[14,15] For temperature dependent measurements, a closed-cycle cryogenic refrigerator equipped with a digital thermometer controller with a temperature stability better than 0.5 K was used.

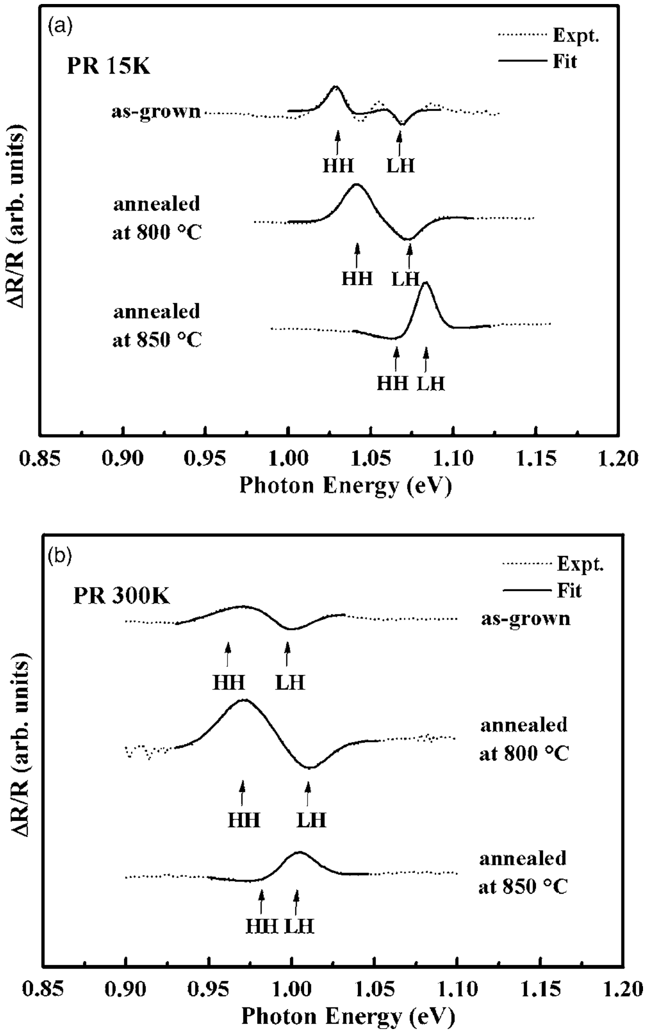

FIG. 2. Experimental PR spectra (dotted curves) for as-grown and two annealed $GaAs_{0.909}Sb_{0.07}N_{0.021}$ samples at (a) 15 and (b) 300 K. The full lines are least-squares fits to Eq. (1). The obtained values of the transition energies are indicated by the arrows.

III. RESULTS AND DISCUSSION

Figure 1 depicts the PL spectra of the annealed $GaAs_{0.909}Sb_{0.07}N_{0.021}$ samples at 15 K. The PL peak energies were determined to be 1.005 and 1.063 eV for samples annealed at 800 and 850 °C, respectively, and no luminescence recorded for the as-grown sample. The PL spectrum for sample annealed at 800 °C revealed a broad signal at lower energy, and the signal quality of this commonly observed feature for dilute nitride compound showed vast improvement via annealing at 850 °C. As shown in Fig. 1, the PL peak position blueshifted together with a narrowing of the full width at half maximum and increases in the intensity with rising thermal annealing temperature. The PL results did imply that the luminescence properties can be improved by thermal annealing. Nevertheless, the PL signal usually affected by the localized clusters due to the alloy disorder in dilute nitride system which may not give us correct information on near band edge transitions. In the following section, we have used PR technique to characterize the near band edge transitions with higher accuracy.

Figure 2 shows PR spectra for the as-grown $GaAs_{0.909}Sb_{0.07}N_{0.021}$ sample and samples annealed at 800 and 850 °C at (a) 15 K and (b) room temperature. The dotted lines are the experimental data and full curves are the least-squares fits to the first-derivative Lorentzian line-shape function of the form[16]

$$\frac{\Delta R}{R} = \mathrm{Re} \sum_{j=1} A_j e^{i\Phi_j}(E - E_j + i\Gamma_j)^{-n}, \tag{1}$$

where A_j and Φ_j are the amplitude and phase of the line shape, E_j and Γ_j are the energy and broadening parameter of the transitions, and the value of n depends on the origin of the transitions. For the derivative functional form, $n=2$ is appropriate for the bound states such as excitons. The obtained near band edge transitions are indicated by vertical arrows and denoted as HH and LH for conduction to HH band and conduction to LH band transitions originated from strain induced valence band splitting. As annealing tempera-

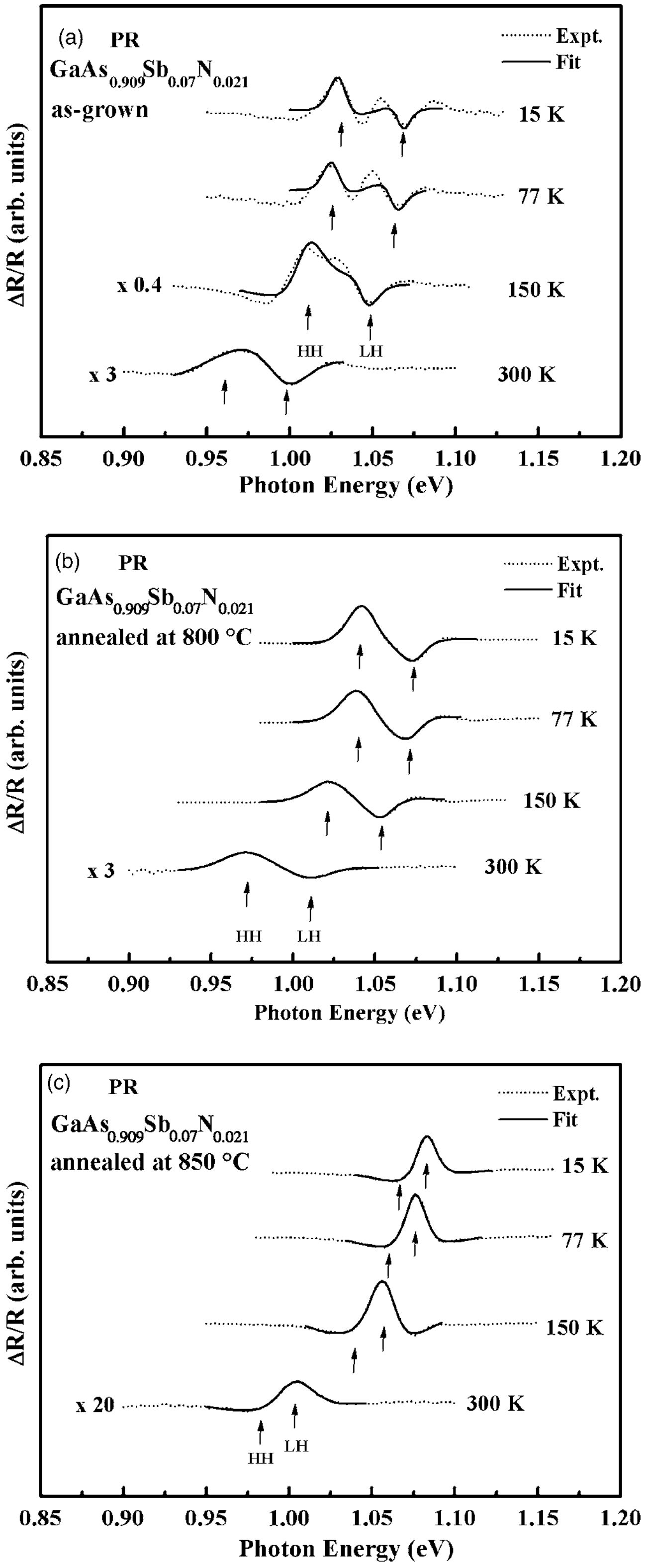

FIG. 3. Experimental PR spectra (dotted curves) of $GaAs_{0.909}Sb_{0.07}N_{0.021}$ (a) as-grown sample and samples annealed at (b) 800 and (c) 850 °C at several temperatures between 15 and 300 K. The full curves are least-squares fits to Eq. (1). The obtained values of the transition energies are indicated by the arrows.

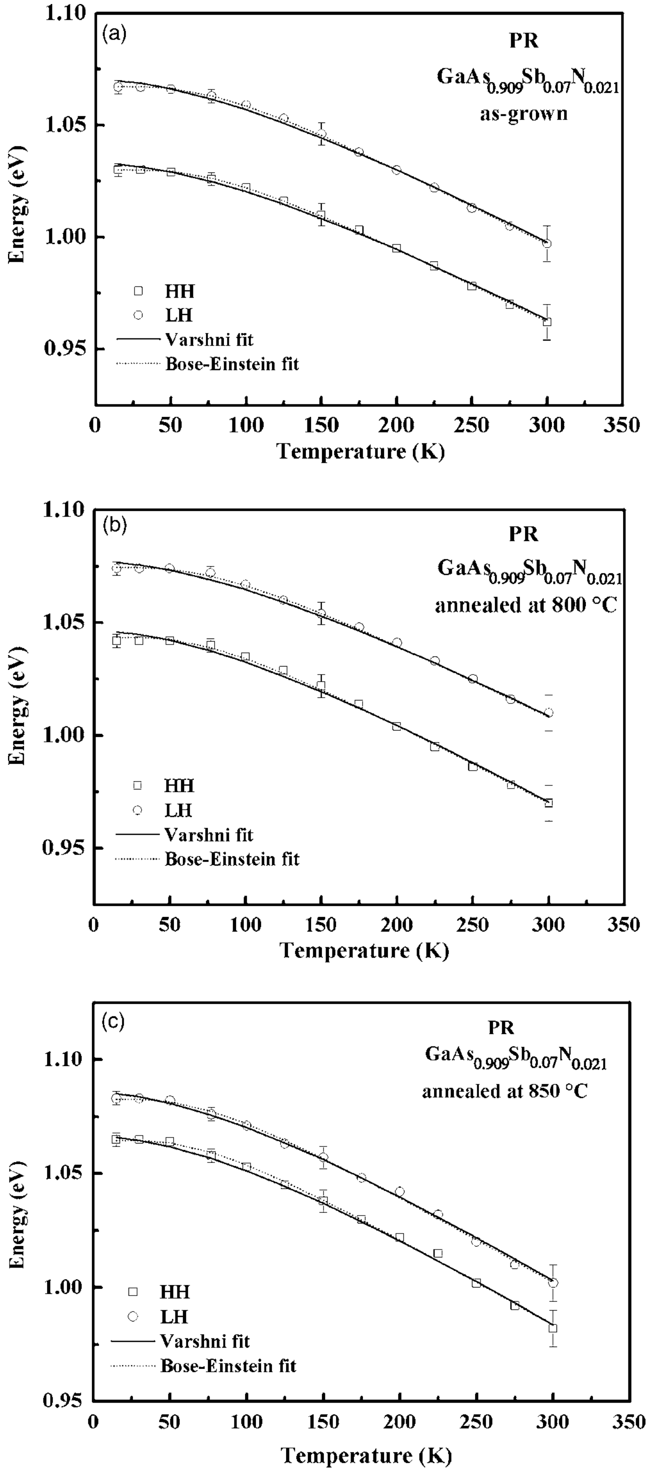

FIG. 4. Temperature variations of the experimental PR values for electron to HH and LH transitions with representative error bars for $GaAs_{0.909}Sb_{0.07}N_{0.021}$ (a) as-grown sample and samples annealed at (b) 800 and (c) 850 °C as open squares and circles, respectively. The full curves are least-squares fits to Eq. (2) and the dotted curves are least-squares fits to Eq. (3).

ture rises, two effects can be noticed: a slight blueshift of the transitions and the reduced separation of HH and LH transitions. The separations between HH and LH transitions are 37, 32, and 19 meV for as-grown sample and samples annealed at 800 and 850 °C, respectively. The results show that strain in GaAsSbN layer can be reduced after thermal annealing treatment.

Displayed by dotted curves in Figs. 3(a)–3(c) are, respectively, the experimental PR spectra of as-grown and samples annealed at 800 and 850 °C, at several temperatures

TABLE I. Values of the Varshni- and Bose–Einstein–type fitting parameters, which describe the temperature dependence of near band edge transition energies for as-grown $GaAs_{0.909}Sb_{0.07}N_{0.021}$ alloy and samples annealed at 800 and 850 °C. The parameters of $GaAs_{0.90}Sb_{0.08}N_{0.02}$, $GaAs_{0.9703}N_{0.0297}$, $GaAs_{1-x}Sb_{x}$, and GaAs are also included for comparison.

Samples	Feature	$E(0)$ (eV)	α (meV/K)	β (K)	a_B (meV)	Θ_B (K)	dE/dT (meV/K)
$GaAs_{0.909}Sb_{0.07}N_{0.021}$[a]	HH	1.032 ± 0.005	0.40 ± 0.05	218 ± 30	43 ± 10	250 ± 30	−0.32
as-grown	LH	1.069 ± 0.005	0.40 ± 0.05	203 ± 30	43 ± 10	240 ± 30	−0.32
$GaAs_{0.909}Sb_{0.07}N_{0.021}$[a]	HH	1.044 ± 0.005	0.43 ± 0.05	215 ± 30	43 ± 10	230 ± 30	−0.35
annealed at 800 °C	LH	1.075 ± 0.005	0.39 ± 0.05	220 ± 30	42 ± 10	245 ± 30	−0.30
$GaAs_{0.909}Sb_{0.07}N_{0.021}$[a]	HH	1.066 ± 0.005	0.46 ± 0.05	200 ± 30	44 ± 10	220 ± 30	−0.37
annealed at 850 °C	LH	1.084 ± 0.005	0.46 ± 0.05	200 ± 30	44 ± 10	220 ± 30	−0.36
$GaAs_{0.90}Sb_{0.08}N_{0.02}$[b]	E_g	1.008	0.44	250			−0.33
$GaAs_{0.9703}N_{0.0297}$[c]	E_g	1.154	0.61	560			−0.31
$GaAs_{1-x}Sb_{x}$[d] (x=0.19–0.67)	E_g		0.42	189			−0.33
GaAs[e]	E_g	1.522	0.58	300			−0.50

[a] Present work (photoreflectance).
[b] Reference 18 (photoluminescence).
[c] Reference 19 (absorption).
[d] Reference 20 (absorption).
[e] Reference 21 (absorption).

between 15 and 300 K. The solid lines are the fitted spectral data to Eq. (1) with $n=2$, which yield transition energies indicated by arrows. As the general property of most semiconductors, when the measuring temperature is increased, the HH and LH transitions in the PR spectra exhibit an energy redshift characteristic.

The temperature variations of the experimental PR values for HH and LH transitions with representative error bars for as-grown $GaAs_{0.909}Sb_{0.07}N_{0.021}$ sample and samples annealed at 800 and 850 °C are depicted in Figs. 4(a)–4(c) as open squares and circles, respectively. The full curves are the temperature dependence of the HH and LH near band edge transition energies fitted by Varshni semiempirical relationship,[17]

$$E_i(T) = E_i(0) - \frac{\alpha_i T^2}{\beta_i + T}, \tag{2}$$

where $E_i(0)$ is the conduction to HH or LH band transition energies at 0 K. The constants α_i is related to the electron (exciton)-average phonon interaction strength and β_i is closely related to the Debye temperature. The values obtained are listed in Table I. For comparison, the parameters for band gap energies of $GaAs_{0.90}Sb_{0.08}N_{0.02}$,[18] $GaAs_{0.9703}N_{0.0297}$,[19] $GaAs_{1-x}Sb_{x}$,[20] and GaAs[21] are also listed in Table I.

The temperature dependence of near band edge transition energies can also be described by a Bose–Einstein expression (dotted curves)[22,23]

$$E_i(T) = E_i(0) - \frac{2a_{iB}}{[\exp(\Theta_{iB}/T) - 1]}, \tag{3}$$

where $E_i(0)$ is the transition energies for the conduction to HH or conduction to LH band transition energies at 0 K, a_{iB} represents the strength of the electron (exciton)-average phonon interaction, and Θ_{iB} corresponds to the average phonon temperature. The values obtained for the various parameters are also presented in Table I, together with that of the parameters for band gap energies of $GaAs_{0.90}Sb_{0.08}N_{0.02}$,[18] $GaAs_{0.9703}N_{0.0297}$,[19] $GaAs_{1-x}Sb_{x}$,[20] and GaAs[21] for comparison.

The parameter α of Eq. (2) can be related to a_B and Θ_B in Eq. (3) by taking the high temperature limit of both expressions. This yields $\alpha=2a_B/\Theta_B$. The comparison of the numbers presented in Table I show that this relation is fairly satisfied. From Eq. (3), it is straightforward to show that high temperature limit of the slope of $E(T)$ versus T curve approaches a value of $-2a_B/\Theta_B$. The calculated value of $-2a_B/\Theta_B$ for conduction to HH (LH) near band edge transition energies equals to −0.34 (−0.35), −0.37 (−0.34), and −0.40 (−0.40) meV/K for as-grown sample and samples annealed at 800 and 850 °C, respectively, which agrees well with the value of $[dE_{\mathrm{HH(LH)}}/dT]=-0.32$ (−0.32), −0.35 (−0.30), and −0.37 (−0.36) meV/K as obtained from the linear extrapolation of the high temperature (150–300 K) PR experimental data.

As shown in Table I, the parameters that describe the temperature variations of near band edge transition energies of $GaAs_{0.909}Sb_{0.07}N_{0.021}$ alloys are quite similar to that reported by Bian *et al.*[18] The values of α and dE/dT for $GaAs_{0.909}Sb_{0.07}N_{0.021}$ are similar to that of $GaAs_{0.9703}N_{0.0297}$ (Ref. 19) and $GaAs_{1-x}Sb_{x}$ (Ref. 20) films and smaller than that of GaAs. The temperature induced shift of the band edge transition energies has been illustrated to be substantially reduced by the presence of nitrogen/antimony.

IV. SUMMARY

In summary, we have studied thermal annealing effects of a dilute nitride $GaAs_{0.909}Sb_{0.07}N_{0.021}$ film grown on GaAs substrate with different thermal annealing temperatures by PL and PR techniques. The PL results show that the luminescence feature blueshifted and the intensity increased together with a narrowing of the feature by thermal annealing at higher temperature. From the PR results, the HH and LH transitions originated from the strained induced valence band splitting in the $GaAs_{0.909}Sb_{0.07}N_{0.021}$ layer have been observed. The near band edge transition energies are slightly blueshifted, and the splitting of HH and LH bands is reduced with rising thermal annealing temperature. The temperature dependences of these near band edge transition energies are analyzed using the Varshni expression and an expression containing the Bose–Einstein occupation factor for phonons. The parameters that describe the temperature dependences of GaAsSbN alloy are similar to that of $GaAs_{0.9703}N_{0.0297}$ and $GaAs_{1-x}Sb_x$ and smaller than that of GaAs. This has been attributed to the incorporation of nitrogen/antimony into the GaAsSbN alloys

ACKNOWLEDGMENTS

The authors acknowledge the supports of National Science Council of Taiwan under Project No. NSC 96-2221-E-011-030 and the project-based personnel exchange programme between the NSC and PAS Project No. NSC96-2911-I-011-003.

[1] M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Wataniki, and Y. Yazama, Jpn. J. Appl. Phys., Part 1 **35**, 1273 (1996).
[2] T. Kitatani, K. Nakahara, M. Kondow, K. Uomi, and T. Kitatani, Jpn. J. Appl. Phys., Part 2 **39**, L86 (2000).
[3] C. W. Tu, J. Phys.: Condens. Matter **13**, 7169 (2001).
[4] K. Uesugi, N. Morooka, and I. Suemune, Appl. Phys. Lett. **74**, 1254 (1999).
[5] L. F. Bian, D. S. Jiang, and S. L. Lu, J. Cryst. Growth **253**, 155 (2003).
[6] M. Fischer, M. Reinhardt, and A. Forchelm, Electron. Lett. **36**, 1208 (2000).
[7] G. Ungaro, G. Le Roux, R. Teissier, and J. C. Harmand, Electron. Lett. **35**, 1246 (1999).
[8] J. C. Harmand, G. Ungaro, L. Largeau, and G. Le Roux, Appl. Phys. Lett. **77**, 2482 (2000).
[9] J. C. Harmand, G. Ungaro, J. Ramos, E. V. K. Rao, G. Saint-Girons, R. Teissier, G. Le Roux, L. Largeau, and G. Patriarche, J. Cryst. Growth **227–228**, 553 (2001).
[10] J. C. Harmand, A. Caliman, E. V. K. Rao, L. Largeau, J. Ramos, R. Teissier, L. Travers, G. Ungaro, B. Theys, and I. F. L. Dias, Semicond. Sci. Technol. **17**, 778 (2002).
[11] S. Wicaksono, S. F. Yoon, W. K. Loke, K. H. Tan, K. L. Lew, M. Zegaoui, J. P. Vilcot, D. Decoster, and J. Chazelas, J. Appl. Phys. **102**, 044505 (2007).
[12] K. H. Tan, S. F. Yoon, W. K. Loke, S. Wicaksono, K. L. Lew, A. Stöhr, O. Ecin, A. Poloczek, A. Malcoci, and D. Jäger, Appl. Phys. Lett. **90**, 183515 (2007).
[13] H. Luo, J. A. Gupta, and H. C. Liu, Appl. Phys. Lett. **86**, 211121 (2005).
[14] Y. S. Huang and F. H. Pollak, Phys. Status Solidi A **202**, 1193 (2005).
[15] F. H. Pollak and H. Shen, Mater. Sci. Eng., R. **10**, xv (1993).
[16] D. E. Aspnes, in *Handbook on Semiconductors*, edited by M. Balkanski (North-Holland, Amsterdam, 1980), Vol. 2, p. 109.
[17] Y. P. Varshni, Physica (Amsterdam) **34**, 149 (1967).
[18] L. F. Bian, D. S. Jiang, P. H. Tan, S. L. Lu, B. Q. Sun, L. H. Li, and J. C. Harmand, Solid State Commun. **132**, 707 (2004).
[19] K. Uesugi, I. Suemune, T. Hasegawa, T. Akutagawa, and T. Nakamura, Appl. Phys. Lett. **76**, 1285 (2000).
[20] R. Lukic-Zrnic, B. P. Gorman, R. J. Cottier, T. D. Golding, C. L. Littler, and A. G. Norman, J. Appl. Phys. **92**, 6939 (2002).
[21] M. B. Panish and H. C. Casey, Jr., J. Appl. Phys. **40**, 163 (1969).
[22] P. Lautenschlager, M. Garriga, and M. Cardona, Phys. Rev. B **36**, 4813 (1987).
[23] P. Lautenschlager, M. Garriga, S. Logothetidis, and M. Cardona, Phys. Rev. B **35**, 9174 (1987).