

Band gap discontinuity in $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ single quantum wells with $0 \leq x < 0.06$ studied by contactless electroreflectance spectroscopy

R. Kudrawiec,^{a)} M. Motyka, M. Gladysiewicz, and J. Misiewicz

Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

H. B. Yuen, S. R. Bank, H. Bae, M. A. Wistey, and James S. Harris

Solid State and Photonics Laboratory, Department of Electrical Engineering, 126X CISX, Via Ortega, Stanford University, Stanford, California 94305-4075

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Contactless electroreflectance (CER) spectroscopy has been applied to study optical transitions in $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ single quantum well (QW) with antimony content varying from 0% to 5.4%. CER features related to optical transitions between the ground and excited states have been clearly observed. Energies of the QW transitions have been matched with those obtained from theoretical calculations. It has been determined that the conduction band offset decreases from $\sim 55\%$ to $\sim 45\%$ with the increase in Sb content from 0% to 5.4%. This result demonstrates that the band gap discontinuity for $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ system can be simply tuned by a change in antimony content. © 2006 American Institute of Physics. [DOI: 10.1063/1.2208949]

The incorporation of nitrogen atoms into Ga(In)As host material leads to a remarkable band gap reduction (100–150 meV per percent of N), which makes the alloy of technological interest for GaAs-based long-wavelength optoelectronic devices and multijunction high efficiency solar cells.¹ Recent progress on the use of Ga(In)NAs for laser applications has succeeded in producing devices operating at 1.3 and 1.55 μm wavelengths.¹ However, there is still huge interest of these materials because many researchers believe that the parameters of GaInNAs-based lasers can be significantly improved. In general, the growth of high-quality dilute nitrides is quite difficult because incorporation of nitrogen can degrade the optical properties due to ion damage,^{2,3} nonradiative traps,^{4,5} and/or phase segregation.⁶ Thus, a potential for improving the threshold current of GaInNAs-based lasers exists. Recently, it has been shown that the addition of antimony as a surfactant and constituent dramatically improves material and optical quality and also reduces the band gap.^{7–10} It is expected that antimony also influences the band gap discontinuity of GaInNAsSb/GaAs interface. For the indium-free system, i.e., $\text{GaN}_x\text{As}_{1-x}/\text{GaAs}$ quantum wells (QWs), it has been observed that incorporation of antimony atoms into GaNAs decreases the conduction band offset Q_C ,¹¹ which is defined as $Q_C = [\Delta E_C / (\Delta E_C + \Delta E_V)] \times 100\%$, where ΔE_C and ΔE_V are the discontinuities for conduction and valence bands of unstrained materials, respectively. In this letter we report the influence of antimony atoms on the conduction band offset in $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ single QW (SQW) system.

In order to investigate the Q_C in $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ SQWs, contactless electroreflectance (CER) has been applied.^{12–16} Energies of QW

transitions extracted from CER measurements have been matched with those obtained from theoretical calculations performed within the effective mass approximation. Using this method, the antimony-induced change in the conduction band offset has been extracted.

The $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ SQW structures were grown by solid-source molecular beam epitaxy on *n*-type (001) GaAs substrates. Details of the growth conditions can be found in Refs. 2, 3, and 17. Each SQW sample is composed of 300 nm thick GaAs buffer layer, 7 nm thick $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x$ QW, and 50 nm thick GaAs cap layer. Four samples with increasing Sb content from 0% to 6% are investigated in this letter. The composition of QW layer and its thickness were verified on the basis of the secondary ion mass spectroscopy and the high resolution x-ray diffraction (HRXRD) measurements.¹⁷ Since the strain in these QW samples were very small, thicker 100 nm samples of identical composition were grown in order to facilitate strain determination from HRXRD measurements. The HRXRD spectra of these thicker samples are shown in Fig. 1. The HRXRD spectra indicated that the samples had good structural quality and interfaces. In the antimony-free case, the GaInNAs layer had a strain of +0.24%. The strain increases with larger antimony fluxes, up to +0.54% with 1.0

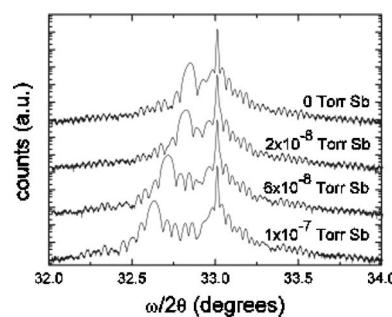


FIG. 1. (004) $\omega/2\theta$ HRXRD spectra of the 100 nm thick GaInNAs(Sb)/GaAs layers.

^{a)}Present address: Solid State and Photonics Laboratory, Department of Electrical Engineering, 311X CISX, Via Ortega, Stanford University, Stanford, California 94305-4075; electronic mails: robert.kudrawiec@pwr.wroc.pl and kudrawiec@snow.stanford.edu

$\times 10^{-7}$ Torr beam equivalent pressure. The verified In, N, and Sb contents into the GaInNASb layer for each of the samples investigated in this letter are summarized in Fig. 2.

A conventional experimental setup with a tungsten halogen lamp (150 W) as a probe light source, a 0.55 m monochromator, and InGaAs *p-i-n* photodiode was applied for obtaining CER spectra. Relevant details of CER setup are described in Ref. 13. Photoreflectance (PR), which is more common than CER, was not applied in this case because the QW samples were grown on *n*-type GaAs substrates. With these substrates, a below GaAs band gap oscillation is observed in PR spectra whereas such an oscillation is not observed in CER spectra.¹³ In order to avoid the “oscillation issue” in this work, CER was applied rather than PR spectroscopy.

Figures 3(a)–3(d) show room temperature CER spectra for $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ SQWs with 0%, 1.3%, 3.7%, and 5.4% of Sb, respectively. All CER spectra are dominated by GaAs band gap bulklike signal at the energy of ~ 1.42 eV. Below the GaAs signal CER features associated with the optical transitions in GaInNASb/GaAs SQW are clearly observed. In order to extract energies of the optical transitions, standard fitting procedure assuming Lorentzian line shape has been applied.^{12,18} The fitting curves are shown by thick solid lines in Fig. 3 together with the moduli of individual resonances (dashed lines). The identification of the resonances was possible on the basis of the calculations performed in the framework of the effective mass approximation. Relevant details of the calculations can be found in our previous papers.^{11,16} All the material parameters for $\text{Ga}_{1-y}\text{In}_y\text{N}_z\text{As}_{1-x-z}\text{Sb}_x$ alloy have been obtained by linear interpolation between the parameters of a relevant binary semiconductor^{19,20} according to Eq. (1),

$$\begin{aligned} Q(x,y,z) = & (1-y)zQ_{\text{GaN}} + (1-y)(1-x-z)Q_{\text{GaAs}} \\ & + (1-y)xQ_{\text{GaSb}} + yzQ_{\text{InN}} + y(1-x-z)Q_{\text{InAs}} \\ & + yxQ_{\text{InSb}}, \end{aligned} \quad (1)$$

where $Q_i = b_i$ or $C12_i$ ($i = \text{GaN}, \text{GaAs}$, etc.). The electron effective mass was assumed as being $0.09m_0$ for each GaInNASb layer. Such an assumption indicates $\sim 50\%$ increase in the electron effective mass in comparison to N-free compounds and is in accordance with band anticrossing (BAC) model²¹ and experimental data obtained for similar compounds.^{22–25} In order to find the band gap energy of the GaInNASb layer we avoid the BAC model, because the knowledge about BAC parameters for GaInNASb is rather poor. We adjusted the band gap energy of GaInNASb to the experimental value of the ground state transition. The Q_C

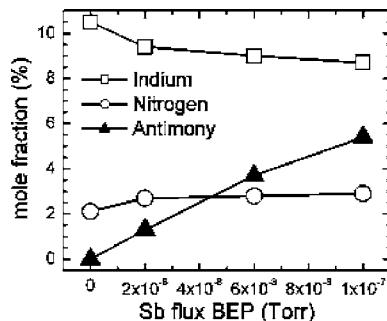


FIG. 2. Indium, nitrogen, and antimony compositions as a function of antimony flux utilized during the QW growth.

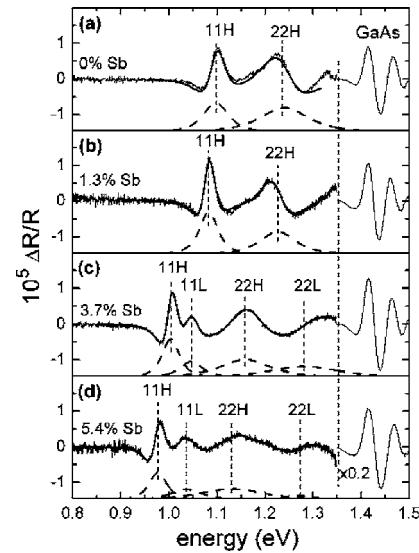


FIG. 3. Room temperature CER spectra of $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ SQWs with (a) 0% Sb, (b) 1.3% Sb, (c) 3.7% Sb, and (d) 5.4% Sb (thin solid lines) together with fitting curves (thick solid lines) and the modulus of the individual lines (dashed lines).

was assumed before including the strain effects. The notation $nm\text{H(L)}$ in Fig. 3 denotes the transition between n th heavy-hole (light-hole) valence subband and m th conduction subband.

For Sb-free SQW [Fig. 3(a)] the CER spectrum below GaAs signal has been fitted by two resonances related to 11H and 22H transitions. The optical transition related to light hole is expected about 50 meV above the 11H transition; however, due to lower intensity of 11L transition and small separation to the 11H transition in comparison to the broadening of CER resonances (~ 40 –50 meV), the 11L transition is not resolved in this spectrum. The incorporation of Sb atoms into $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973}/\text{GaAs}$ SQW redshifts the QW transitions (about 24 meV per 1% Sb). Moreover, the increase in Sb content leads to an increase of the tensile strain in GaInNASb layer that influences the splitting between 11H and 11L transitions. Thereby the 11L transition is resolved for samples with 3.7% and 5.4% of Sb. Moreover, the 22L transition is visible for these samples.

In order to determine the Q_C in this QW system we compared experimental data with theoretical calculations performed for various Q_C , making plots similar to those shown in our previous papers.^{11,16} Note that an analysis of the energy difference between the 22H and 11H transitions is one of the best criteria for matching experimental data with theoretical calculations. Thus, the analysis 22H-11H value is shown in this letter. Figures 4(a)–4(d) show a comparison between experimental data (horizontal dashed lines) and theoretical calculations as a function of Q_C for $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ SQWs with 0%, 1.3%, 3.7%, and 5.4% of Sb, respectively. For Sb-free SQW the best agreement between experimental data and theoretical calculations has been achieved for $Q_C=55\%$ that very well agrees with literature data for this material system.²⁶ The same analysis performed for SQW containing Sb atoms shows that incorporation of Sb atoms into $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973}/\text{GaAs}$ SQW leads to a decrease of the Q_C . According to Fig. 4 it has been found that the Q_C decreases from $\sim 55\%$ to $\sim 45\%$ with the increase in Sb content from 0% to 5.4%. There also exists a contribution to changes

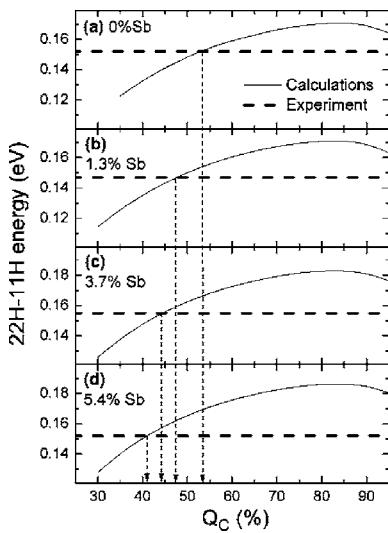


FIG. 4. Method used to determine the Q_C in $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ SQWs with (a) 0% Sb, (b) 1.3% Sb, (c) 3.7% Sb, and (d) 5.4% Sb. The horizontal dashed line corresponds with the energy difference between the 22H and 11H transitions taken from experimental data. Solid curves correspond with the energy difference between the 22H and 11H transitions obtained from the theoretical calculations.

in Q_C related to changes in In and/or N contents observed by XRD. However, this contribution is important in the second order because the increase of Sb content is much bigger than the change in In and Sb contents, as seen in Fig. 2. Thus, almost all changes in the Q_C are attributed to the change in Sb content. In case of $\text{GaInNAsSb}/\text{GaAs}$ QWs with similar N and Sb contents and higher In content ($\sim 34\% - 38\%$), the Q_C is close to 80%,²⁷ i.e., quite different than Q_C found in this letter. This discrepancy is due to higher In incorporation and will be discussed in another paper.

Figure 5 shows the band gap discontinuities for electron (open squares), heavy-hole (open circles), and light-hole (open triangles) QWs obtained on the basis of analysis shown in Fig. 4. It shows that the incorporation of Sb atoms into $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973}/\text{GaAs}$ influences mainly the heavy- (light-) hole QWs while the electron QW is almost unchanged. This result shows that the band gap discontinuity for heavy- (light-) hole QW in $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ system can be simply tuned by a change in Sb content.

In conclusion, the Q_C has been investigated for $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ SQWs with Sb content changing from 0% to 5.4%. It has been found that with the

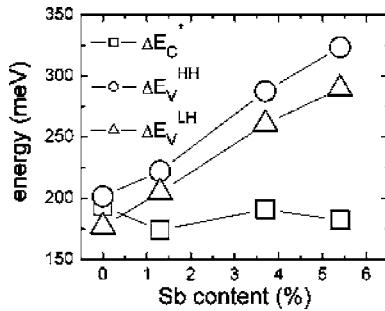


FIG. 5. Calculated variation of the electron, ΔE_C^* , heavy-hole, ΔE_V^{HH} , and light-hole, ΔE_V^{LH} , discontinuities for $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.027}\text{As}_{0.973-x}\text{Sb}_x/\text{GaAs}$ SQWs as a function of Sb composition. Note that ΔE_C^* , ΔE_V^{LH} , and ΔE_V^{HH} include strain induced shift of the band gap energy.

rise of Sb content from 0% to 5.4%, the Q_C decreases from $\sim 55\%$ to $\sim 45\%$. Such a change in Q_C corresponds to $\sim 60\%$ increase in the depth of heavy- (light-) hole QWs and $< 15\%$ change in the depth of electron QW.

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- ¹M. Henini, *Dilute Nitride Semiconductors* (Elsevier, Oxford, 2005).
- ²M. A. Wistey, S. R. Bank, H. B. Yuen, H. P. Bae, and J. S. Harris, Jr., *J. Cryst. Growth* **278**, 229 (2005).
- ³H. B. Yuen, M. A. Wistey, S. R. Bank, H. P. Bae, and J. S. Harris, Jr., *J. Vac. Sci. Technol. B* **23**, 1328 (2005).
- ⁴S. R. Kurtz, A. A. Allerman, C. H. Seager, R. M. Sieg, and E. D. Jones, *Appl. Phys. Lett.* **77**, 400 (2000).
- ⁵A. J. Ptak, S. W. Johnston, S. Kurtz, D. J. Friedman, and W. K. Metzger, *J. Cryst. Growth* **251**, 392 (2003).
- ⁶K. Volz, T. Torunski, and W. Stolz, *J. Appl. Phys.* **97**, 014306 (2005).
- ⁷X. Yang, M. J. Jurkovic, J. B. Heroux, and W. I. Wang, *Appl. Phys. Lett.* **75**, 178 (1999).
- ⁸H. Shimizu, K. Kumada, S. Uchiyama, and A. Kasukawa, *Electron. Lett.* **36**, 1379 (2000).
- ⁹X. Yang, J. B. Heroux, L. F. Mei, and W. I. Wang, *Appl. Phys. Lett.* **78**, 4068 (2001).
- ¹⁰V. Gambin, W. Ha, M. A. Wistey, H. B. Yuen, S. R. Bank, S. M. Kim, and J. S. Harris, Jr., *IEEE J. Sel. Top. Quantum Electron.* **8**, 795 (2002).
- ¹¹R. Kudrawiec, K. Ryczko, J. Misiewicz, H. B. Yuen, S. R. Bank, M. A. Wistey, H. P. Bae, and James S. Harris, Jr., *Appl. Phys. Lett.* **86**, 141908 (2005).
- ¹²F. H. Pollak, in *Modulation Spectroscopy of Semiconductors and Semiconductor Microstructures Handbook on Semiconductors*, edited by T. S. Moss (Elsevier Science, Amsterdam, 1994), Vol. 2, pp. 527–635.
- ¹³R. Kudrawiec, P. Sitarek, J. Misiewicz, S. R. Bank, H. B. Yuen, M. A. Wistey, and James S. Harris, Jr., *Appl. Phys. Lett.* **86**, 091115 (2005).
- ¹⁴R. C. Tu, Y. K. Su, D. Y. Lin, C. F. Li, Y. S. Huang, W. H. Lan, S. L. Tu, S. J. Chang, S. C. Chou, and W. C. Chou, *J. Appl. Phys.* **83**, 1043 (1998).
- ¹⁵M. Munoz, H. Lu, X. Zhou, M. C. Tamargo, and F. H. Pollak, *Appl. Phys. Lett.* **83**, 1995 (2003).
- ¹⁶R. Kudrawiec, M. Motyka, M. Gladysiewicz, J. Misiewicz, J. A. Gupta, and G. C. Aers, *Solid State Commun.* **138**, 365 (2006).
- ¹⁷H. B. Yuen, S. R. Bank, H. P. Bae, M. A. Wistey, and J. S. Harris, Jr., *Appl. Phys.* **99**, 093504 (2006).
- ¹⁸D. E. Aspnes, *Surf. Sci.* **37**, 418 (1973).
- ¹⁹I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, *J. Appl. Phys.* **89**, 5815 (2001).
- ²⁰I. Vurgaftman and J. R. Meyer, *J. Appl. Phys.* **94**, 3675 (2003), and references therein.
- ²¹W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Krutz, *Phys. Rev. Lett.* **82**, 1221 (1999).
- ²²C. Skierbiszewski, P. Perlin, P. Wisniewski, W. Knap, T. Suski, W. Walukiewicz, W. Shan, K. M. Yu, J. W. Ager III, E. E. Haller, J. F. Geisz, and J. M. Olson, *Appl. Phys. Lett.* **76**, 2409 (2000).
- ²³P. N. Hai, W. M. Chen, I. A. Buyanova, H. P. Xin, and C. W. Tu, *Appl. Phys. Lett.* **77**, 1843 (2000).
- ²⁴M. Hetterich, M. D. Dawson, A. Yu. Egorov, D. Bernklau, and H. Riechert, *Appl. Phys. Lett.* **76**, 1030 (2000).
- ²⁵J. Misiewicz, R. Kudrawiec, K. Ryczko, G. Sek, A. Forchel, J. C. Harmand, and M. Hammar, *J. Phys.: Condens. Matter* **16**, 3071 (2004).
- ²⁶J. B. Heroux, X. Yang, and W. I. Wang, *J. Appl. Phys.* **92**, 4361 (2002).
- ²⁷R. Kudrawiec, M. Gladysiewicz, J. Misiewicz, H. B. Yuen, S. R. Bank, M. A. Wistey, H. P. Bae, and James S. Harris, Jr., *Solid State Commun.* **137**, 138 (2006).