NRC Publications Archive
Archives des publications du CNRC

Contactless electroreflectance of GaN0.025As0.975-xSbx/GaAs quantum wells with high Sb content (0.27 <= x <= 0.33): the determination of band gap discontinuity

Kudrawiec, R.; Gupta, J. A.; Wu, X.

This publication could be one of several versions: author’s original, accepted manuscript or the publisher’s version. / La version de cette publication peut être l’une des suivantes : la version prépublication de l’auteur, la version acceptée du manuscrit ou la version de l’éditeur.
For the publisher’s version, please access the DOI link below./ Pour consulter la version de l’éditeur, utilisez le lien DOI ci-dessous.

Publisher’s version / Version de l'éditeur:
http://doi.org/10.1063/1.2370506
Applied physics letters, 89, 2006

NRC Publications Record / Notice d'Archives des publications de CNRC:
http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/ctrl?lang=en
http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/ctrl?lang=fr

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at
http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/jsp/nparc_cp.jsp?lang=en
READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L’accès à ce site Web et l’utilisation de son contenu sont assujettis aux conditions présentées dans le site
http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/jsp/nparc_cp.jsp?lang=fr
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D’UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at
PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n’arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research Council Canada
Conseil national de recherches Canada

Canada

APPLIED PHYSICS LETTERS **89**, 171914 (2006)

Contactless electroreflectance of $GaN_{0.025}As_{0.975-x}Sb_x$/GaAs quantum wells with high Sb content ($0.27 \leqslant x \leqslant 0.33$): The determination of band gap discontinuity

R. Kudrawiec[a)]
Institute of Physics, Wrocław University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wrocław, Poland

J. A. Gupta[b)]
Institute for Microstructural Sciences, National Research Council of Canada, Ottawa K1A 0R6, Canada

M. Motyka, M. Gladysiewicz, and J. Misiewicz
Institute of Physics, Wrocław University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wrocław, Poland

X. Wu
Institute for Microstructural Sciences, National Research Council of Canada, Ottawa K1A 0R6, Canada

(Received 2 May 2006; accepted 15 September 2006; published online 26 October 2006)

$GaN_{0.025}As_{0.975-x}Sb_x$/GaAs quantum wells (QWs) with $x=0.27$ and $x=0.33$ were investigated by contactless electroreflectance (CER) spectroscopy. CER features related to optical transitions between the ground and excited states were clearly observed, indicating that these QWs have type-I structures. By matching the QW transition energies with those obtained from theoretical calculations performed within the electron effective mass approximation the conduction band offset in these QWs is found to be close to 40%. The resulting conduction band discontinuities were found to be ~200 and ~150 meV for the QWs with $x=0.27$ and $x=0.33$, respectively. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2370506]

The demonstration of band gap narrowing in GaInAs with the introduction of nitrogen by Kondow *et al.*[1] has promoted intense research towards high-performance GaInAs quantum well (QW) lasers for the fiber optic telecommunication windows (1.3 and 1.55 μm).[2] Another promising material for 1.3 and 1.53–1.6 μm lasers is GaNAsSb.[3–8] It is well known that the bowing parameter for GaAsSb is three times higher than for GaInAs [1.43 vs 0.48 (Ref. 9)]. Assuming the same influence of N atoms on the band gap energy, it is thus expected that the GaNAsSb band gap will be significantly narrower than the band gap of GaInNAs with the same strain, e.g., $GaN_{0.025}As_{0.645}Sb_{0.33}$ should have smaller band gap energy than $Ga_{0.64}In_{0.36}N_{0.025}As_{0.975}$ (the strain for the two compounds is ~2%). Moreover, recent investigations suggest that the N-related redshift is higher for GaNSb than for GaNAs.[10,11] Such a tendency has indeed been observed for bulklike layers with low In and Sb contents.[12] Thus emission at 1.55 μm is easer to achieve in GaNAsSb/GaAs than in the GaInNAs/GaAs system. However, for a long time, GaNAsSb was not considered for laser applications since it was expected that GaNAsSb/GaAs QWs are type-II structures. According to the band anticrossing model (BAC),[13] which has been applied to Ga(In)NAs system,[2] it is expected that N in GaNAsSb influences the conduction band only. Note that within this model some conclusions on the band gap discontinuity in GaNAsSb/GaAs QWs appear automatically and they have been discussed by some authors.[14,15] However, these results cannot be treated as an investigation of the conduction band offset in GaNAsSb/GaAs QWs. Recently, photoreflectance and contactless electroreflectance (CER) spectroscopies have been applied to study the conduction band offset in GaNAsSb/GaAs QWs.[16,17] It has been shown that GaNAsSb/GaAs QWs with ~2% N and <11% Sb provide a confinement potential for both electrons and holes. However, for 1.5 μm emission the Sb content has to be increased up to 30%–35%. Several reports suggest that GaAsSb/GaAs QWs with high Sb content are type-II structures above a critical composition.[18,19] Therefore, a key question emerges: Is the electron confinement in highly strained GaNAsSb/GaAs QWs appropriate for laser applications? The aim of this letter is to answer this question since no experimental investigations on this issue can be found in the literature. Also, extrapolations of previous results[16,17] may not be valid for Sb-rich systems since it is well known that the dilute nitrides are an unusual system whose properties cannot be easily extrapolated from the constituent binary materials. Moreover, the crossover in the conduction band behavior of GaAsSb films on GaAs substrates is a subject of some debate.[18,19] The present sample with Sb=33% is thus in a regime where the band alignment may change rapidly with composition. In addition, the N-related redshift can be distributed between both the conduction and valence bands. Thus direct investigations are necessary to determine how the band gap discontinuity is distributed in highly strained GaNAsSb/GaAs QWs.

GaNAsSb/GaAs QW samples were grown by molecular beam epitaxy on *n*-type (100) GaAs substrates in a custom V90 system using Ga and Al thermal effusion cells and valved cracker cells for As_2 and Sb_2. Active nitrogen was provided by Veeco Unibulb™ radio frequency plasma source using N_2/Ar dynamic gas switching, as described in Ref. 23. Two $GaN_{0.025}As_{0.975-x}Sb_x$/GaAs double QWs with different

[a)]Electronic mail: robert.kudrawiec@pwr.wroc.pl
[b)]Electromic mail: james.gupta@nrc-cnrc.ge.ca

 © 2006 American Institute of Physics
Downloaded 20 Nov 2006 to 132.246.2.19. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

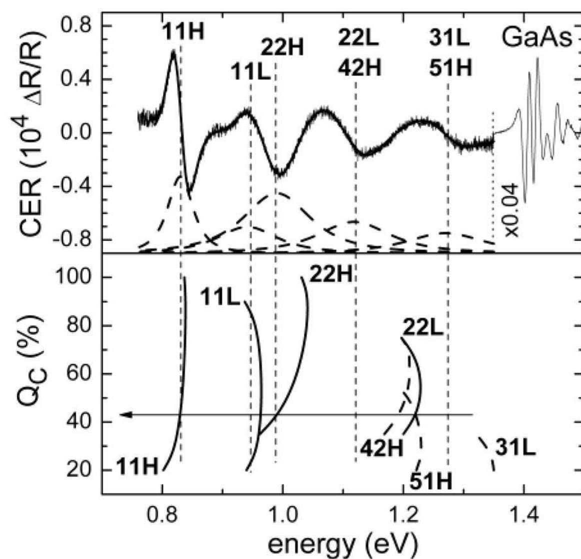

FIG. 1. Top panel: the room temperature CER spectrum of the $GaN_{0.025}As_{0.705}Sb_{0.27}/GaAs$ QW (solid line) together with the fitting curve (thick line) and the moduli of individual CER resonances (dashes lines). Bottom panel: theoretical calculations performed for various Q_C.

Sb contents ($x=0.27$ and $x=0.33$) and the same thickness of 7 nm were grown for this study. The QW active regions in the samples with $x=0.27$ and $x=0.33$ were grown at 450 and 465 °C, respectively. The samples were characterized by x-ray diffraction measurements which yielded experimental data in excellent agreement with dynamical simulations of the ideal structures. After growth the samples with $x=0.27$ and $x=0.33$ were processed by rapid thermal annealing for 5 min under flowing N_2 at 750 and 775 °C, respectively.

The top panels in Figs. 1 and 2 show the room temperature CER spectra for the GaNAsSb/GaAs QWs with $x=0.27$ and $x=0.33$, respectively. The strongest CER signal is observed at an energy of ~1.42 eV originating from the band-to-band absorption in the GaAs barrier and cap layers. The CER features observed below the GaAs signal are associated with the QW optical transitions. There is clearly more than one visible CER resonance indicating that these QWs have a type-I structure. The observed CER features were analyzed using the low-field electromodulation Lorentzian line shape functional form[20] used previously.[17,21,22] The notation $klH(L)$ in Figs. 1 and 2 denotes the transition between the kth heavy-hole (light-hole) valence subband and the lth conduction subband. The identification of CER resonances was accomplished using standard calculations within the electron effective mass approximation. Relevant details of the calculations were reported previously.[17,21,22] For the present samples the value of electron effective mass was taken to be $0.09m_0$ after Ref. 24. This represents an increase of the electron effective mass in comparison with N-free alloys, in accordance with BAC model predictions.[13] The GaNAsSb band gap energy was adjusted using the experimental value of the ground state transition as in Refs. [17,21,22] since BAC parameters are not well known for GaNAsSb alloys. Note that in our calculations the value of Q_C was deduced before including strain effects using the definition $Q_C = [\Delta E_C/(\Delta E_C+\Delta E_V)]\times 100\%$, where ΔE_C and ΔE_V are the conduction and valence band heterojunction discontinuities for unstrained materials. For QW laser design, the relevant parameters are the band gap discontinuities in the strained system, namely, the values of ΔE_C^*, ΔE_V^{HH}, and ΔE_V^{LH} for the conduction, heavy-hole, and light-hole QWs, respectively. These values are determined in the following.

Calculations for various values of Q_C are shown in the bottom panels of Figs. 1 and 2. In general, such a plot allows individual CER resonances to be attributed to specific QW transitions. In order to determine the value of Q_C for a QW system, the best approach is to analyze the energy difference between QW transitions as follows. The lowest energy resonance in Figs. 1 and 2 originates from the 11H transition, which is a fundamental transition for the two QW samples. In addition to the 11H transition, the CER spectra show a 11L transition (i.e., the lowest energy transition for light holes) and transitions between excited QW states such as 22H and 22L. Unfortunately, for the QW with $x=0.33$ the 11L transition interferes with the 22H transition and hence this part of CER spectrum is fitted by one resonance which is attributed to both 11L and 22H transitions. In addition to the allowed transitions, the partially forbidden transitions, such as the 31H, 51H, 24H, and 31L transitions, were also considered for our QW samples. In general, the partially forbidden transitions are weaker than the allowed transitions. However, the intensity of the allowed transitions observed in CER decreases with an increase in the number of energy levels. Thus the intensity of an allowed higher level transition can be comparable with the intensity of a partially forbidden transition with a significant electron-hole overlap. It should also be noted that built-in electric fields or deviations from a perfectly abrupt QW profile can also influence the transition intensities. For the samples discussed here, a weak intermixing of Sb or N atoms at the QW interfaces due to thermal annealing cannot be excluded. All these considerations lead to the conclusion that some of the partially forbidden transitions should appear in our analysis. It was established that the partially forbidden transitions are important in the spectral region related to the 22L transition (1.15–1.3 eV). The theoretical predictions for the 51H, 24H, and 31L QW transitions in this spectral region are shown in the bottom panels of Figs. 1 and 2. It is likely that several optical transitions

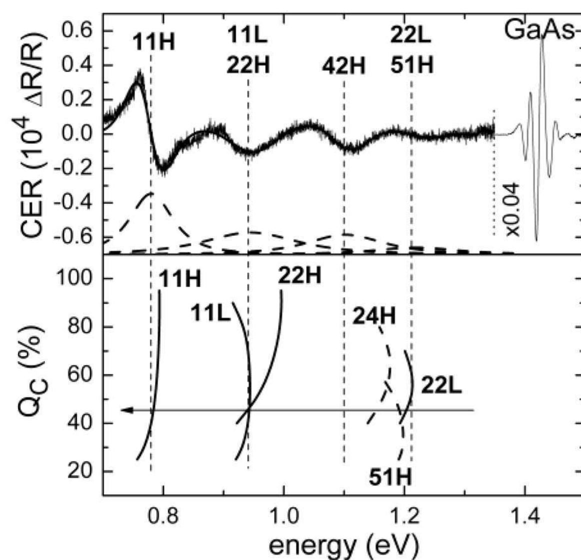

FIG. 2. Top panel: the room temperature CER spectrum of the $GaN_{0.025}As_{0.645}Sb_{0.33}/GaAs$ QW (solid line) together with the fitting curve (thick line) and the moduli of individual CER resonances (dashes lines). Bottom panel: theoretical calculations performed for various Q_C.

Downloaded 20 Nov 2006 to 132.246.2.19. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

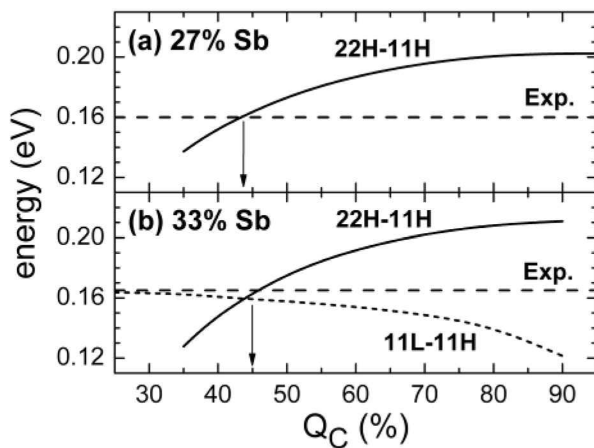

FIG. 3. Method used to analyze the Q_C in GaNAsSb/GaAs QWs with (a) $x=0.27$ and (b) $x=0.33$. The horizontal dashed lines correspond to the energy difference between the 22H and 11H transitions taken from experimental data. The solid curves correspond to the energy difference between the 22H and 11H transitions obtained from the theoretical calculations. The short dashed curve in panel (b) corresponds to the energy difference between the 11L and 11H transitions obtained from the theoretical calculations.

have similar intensities in this spectral region which limits the agreement between the theoretical calculations and the measured spectra. On the other hand the introduction of more than two CER resonances in this spectral region could be controversial due to the large broadening of these resonances. In order to determine the Q_C in these QWs we ultimately focused on the 11H and 22H transitions.

Figures 3(a) and 3(b) show the energy differences between the 22H and 11H transitions taken from experimental data (horizontal dashed lines) and from theoretical predictions (solid lines) for GaNAsSb/GaAs QWs with $x=0.27$ and $x=0.33$, respectively. In the case of the QW with $x=0.27$ the best agreement between the experimental data and theoretical calculations is obtained with $Q_C \approx 40\%$. This corresponds to values of $\Delta E_C^* \approx 200$ meV, $\Delta E_V^{HH} \approx 455$ meV, and $\Delta E_V^{LH} \approx 385$ meV. In the case of the QW with $x=0.33$ the best agreement is obtained with the value $Q_C \approx 45\%$. However, in this QW the 11L and 22H transitions interfere with one another. Therefore, the theoretical prediction for the energy difference between the 11L and 11H transitions is also plotted in Fig. 3(b). Taking into account the possible 11L-related contribution to the 22H resonance, it has been concluded that Q_C may be overestimated in this case. Finally, it has been concluded that for the GaNAsSb/GaAs QWs with $x=0.33$ the Q_C is also close to 40%. This value of Q_C leads to the values $\Delta E_C^* \approx 150$ meV, $\Delta E_V^{HH} \approx 555$ meV, and $\Delta E_V^{LH} \approx 430$ meV.

The results obtained in this letter are consistent with our previous investigations,[15,16] where it was shown that the incorporation of Sb atoms into a GaNAs/GaAs QW with 2% of N changes Q_C (the Q_C decreases from 80% to 50% with the increase in Sb content from 0% to 11%). The GaNAsSb/GaAs QWs studied in the present work have similar N content but much higher Sb content and hence the conduction band offset is smaller. On the other hand assuming that the highly strained GaAsSb/GaAs QWs are nearly type II it can be concluded that the incorporation of 2.5% of N leads to an increase in the value of Q_C and forces the QW to have a type-I structure. This suggests that GaNAsSb is a very promising compound for band gap engineering since the band gap discontinuity can be tuned in a broad range by both N and Sb contents.

In conclusion, it has been shown that $GaN_{0.025}As_{0.975-x}Sb_x$/GaAs QWs with $x=0.27$ and 0.33 are type-I structures with Q_C values close to 40%. This leads to values of $\Delta E_C^*=200$ meV, $\Delta E_V^{HH}=455$ meV, and $\Delta E_V^{LH}=385$ meV for the GaNAsSb/GaAs QW with $x=0.27$ and $\Delta E_C^*=150$ meV, $\Delta E_V^{HH}=555$ meV, and $\Delta E_V^{LH}=430$ meV for the GaNAsSb/GaAs QW with $x=0.33$. This indicates that highly strained GaNAsSb/GaAs QWs are promising for GaAs-based lasers operated in 1.3 and 1.55 μm windows from the viewpoint of electron confinement.

[1] M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, Jpn. J. Appl. Phys., Part 1 **35**, 1273 (1996).
[2] M. Henini, *Dilute Nitride Semiconductors*, edited by M. Henini (Elsevier, New York, 2005).
[3] G. Ungaro, G. Le Roux, R. Teissier, and J. C. Harmand, Electron. Lett. **35**, 15 (1999).
[4] 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).
[5] G. M. Peake, K. E. Waldrip, T. W. Hargett, N. A. Modine, and D. K. Serkland, J. Cryst. Growth **261**, 398 (2004).
[6] S. Wicaksono, S. F. Yoon, K. H. Tan, and W. K. Cheah, J. Cryst. Growth **274**, 355 (2005).
[7] L. Wu, S. Iyer, K. Nunna, J. Li, S. Bharatan, W. Collis, and K. Matney, J. Cryst. Growth **279**, 293 (2005).
[8] H. B. Yuen, S. R. Bank, M. A. Wistey, J. S. Harris, M.-J. Seong, S. Yoon, R. Kudrawiec, and J. Misiewicz, J. Appl. Phys. **97**, 113510 (2005).
[9] T. D. Veal, L. F. J. Piper, S. Jollands, B. R. Bennett, P. H. Jefferson, P. A. Thomas, C. F. McConville, B. N. Murdin, L. Buckle, G. W. Smith, and T. Ashley, Appl. Phys. Lett. **87**, 132101 (2005).
[10] A. Belabbes, M. Ferhat, and A. Zaoui, Appl. Phys. Lett. **88**, 152109 (2006).
[11] I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, J. Appl. Phys. **89**, 5815 (2001).
[12] R. Kudrawiec, G. Sek, J. Misiewicz, L. H. Li, and J. C. Harmand, Eur. Phys. J.: Appl. Phys. **27**, 313 (2004).
[13] W. 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).
[14] J. C. Harmand, A. Caliman, E. V. K. Rao, L. Largeau, J. Ramos, R. Teisser, L. Travers, G. Ungaro, B. Theys, and I. F. L. Dias, Semicond. Sci. Technol. **17**, 778 (2002).
[15] F. Bousbih, S. Ben Bouzid, R. Chtourou, F. F. Charfi, J. C. Harmand, and G. Ungaro, Mater. Sci. Eng., C **21**, 251 (2002).
[16] R. Kudrawiec, K. Ryczko, J. Misiewicz, H. B. Yuen, S. R. Bank, M. A. Wistey, H. P. Bae, and J. S. Harris, jr., Appl. Phys. Lett. **86**, 141908 (2005).
[17] R. Kudrawiec, M. Gladysiewicz, J. Misiewicz, H. B. Yuen, S. R. Bank, M. A. Wistey, H. P. Bae, and J. S. Harris, Jr., Phys. Rev. B **73**, 245413 (2006).
[18] R. Teissier, D. Sicault, J. C. Harmand, G. Ungaro, G. Le Roux, and L. Largeau, J. Appl. Phys. **89**, 5473 (2001), and references therein.
[19] J. B. Wang, S. R. Johnson, S. A. Chaparro, D. Ding, Y. Cao, Yu. G. Sadofyev, Y.-H. Zhang, J. A. Gupta, and C. Z. Guo, Phys. Rev. B **70**, 195339 (2004), and references therein.
[20] F. H. Pollak, in *Modulation Spectroscopy of Semiconductors and Semiconductor Microstructures Handbook on Semiconductors*, edited by T. S. Moss (Elsevier, Amsterdam, 1994), Vol. 2, pp. 527–635.
[21] R. Kudrawiec, M. Motyka, M. Gladysiewicz, J. Misiewicz, H. B. Yuen, S. R. Bank, H. Bae, M. A. Wistey, and J. S. Harris, Appl. Phys. Lett. **88**, 221113 (2006).
[22] R. Kudrawiec, M. Gladysiewicz, M. Motyka, J. Misiewicz, J. A. Gupta, and G. C. Aers, Solid State Commun. **138**, 365 (2006).
[23] J. A. Gupta, Z. R. Wasilewski, B. J. Riel, J. Ramsey, G. C. Aers, R. L. Williams, G. I. Sproule, A. Perovic, D. D. Perovic, T. Garanzotis, and A. J. Spring Thorpe, J. Cryst. Growth **242**, 141 (2002).
[24] R. T. Senger, K. K. Bajaj, E. D. Jones, N. A. Modine, K. E. Waldrip, F. Jalali, J. F. Klem, G. M. Peake, X. Wei, and S. W. Tozer, Appl. Phys. Lett. **83**, 5425 (2003).

Downloaded 20 Nov 2006 to 132.246.2.19. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp