Temperature dependence of the optical transitions in $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ multiquantum wells of various widths studied by photoreflectance

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Citation: Journal of Applied Physics **106**, 033507 (2009); doi: 10.1063/1.3187789
View online: http://dx.doi.org/10.1063/1.3187789
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/106/3?ver=pdfcov
Published by the AIP Publishing

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R. Kudrawiec,[1,a)] P. Poloczek,[1] J. Misiewicz,[1] F. Ishikawa,[2,b)] A. Trampert,[2] and K. H. Ploog[2]
[1]*Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*
[2]*Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany*

(Received 21 May 2009; accepted 29 June 2009; published online 7 August 2009)

The temperature dependencies of optical transitions in as-grown $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ multiple quantum wells (QWs) of various widths (ranging from 3.9 to 8.1 nm) grown at the low temperature of 375 °C were studied by photoreflectance (PR). In addition to the 11*H* transition, which is the fundamental transition for this QW, the optical transitions between excited states (22*H* and 33*H* transitions, where the notation *klH* denotes the transition between the *k*th heavy-hole valence subband and the *l*th conduction subband) were clearly observed in the PR spectra. The temperature dependencies of the QW transition energies were analyzed using Varshni and Bose–Einstein expressions. It was found that with increasing temperature, both the ground-state and the excited-state transitions shift to the red without showing S-shape-type behaviors, which are typical for photoluminescence from this system. This shift does not depend on the QW width and amounts to ~80 meV for the 11*H* transition and ~100 meV for the 22*H* and 33*H* transitions in the temperature range of 10–300 K. These shifts are comparable to those of N-free QWs. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3187789]

I. INTRODUCTION

GaInNAs alloy is a promising material for 1.3–1.6 μm telecommunication optoelectronic devices grown on GaAs substrates.[1,2] So far, edge-emitting lasers and vertical cavity surface-emitting lasers with attractive performance around 1.3 μm have been demonstrated using compressively strained GaInNAs/GaAs quantum wells (QWs) as active materials.[2] Pushing the emission wavelength of GaInNAs/GaAs systems to 1.6 μm has gained much interest in the past few years.[3–12] However, when incorporating more than ~2% of nitrogen and ~25% of indium that are required for reaching longer wavelengths, the structural quality of the resulting GaInNAs/GaAs QWs deteriorates due to the large miscibility gap and the phase separation tendency. Recently, in order to avoid the phase separation in GaInNAs, a lower growth temperature than that conventionally employed for the growth of GaInNAs/GaAs QWs has been used, resulting in GaInNAs QWs with a perfect two-dimensional (2D) morphology.[9–11]

In this work, photoreflectance (PR) has been applied to study the temperature dependence of QW transitions for a set of low-temperature grown GaInNAs QWs with high In and N concentrations (36% In and 4.6% N) having a perfect 2D morphology with different QW widths. The aim of this work is to determine the temperature-related band-gap shrinkage and the corresponding Varshni[13] and Bose–Einstein[14] parameters for those QWs. There are numerous reports on the temperature-related band-gap shrinkage in N-containing alloys, which was found to be significantly smaller than that in N-free alloys and QWs.[15] This observation is typical for photoluminescence (PL) studies on this system, since this technique is very sensitive to localized states at low temperatures due to its emissionlike character. In order to avoid the problems stemming from carrier localization effects in PL, the experimental data below ~60 K were often not taken into account, and the results from higher temperatures were extrapolated to low temperatures. As a result, at low temperatures, the accuracy of the energy gap determination from the Varshni fit can be very poor. Moreover, the Varshni parameters can be inaccurate since they were determined in the limited range of temperatures (>60 K). In general, the best solution is to avoid the effect of carrier localization at low temperatures (so-called s-shape behavior), which is a direct measurement of the energy gap by absorptionlike techniques, such as photoreflectance, contactless electroreflectance (CER) or others.[16] So far, PR spectroscopy has been applied to study the temperature dependence of optical transitions in GaInNAs QWs only a few times.[17] GaInNAs QW with high indium and nitrogen content were not studied yet. On the other hand, some studies suggested that the reduction of the temperature-related band-gap shrinkage is associated with nitrogen incorporation.[15] Therefore it is expected that this shrinkage can be stronger for GaInNAs QW with high N concentration. In this context, using PR, we investigate the temperature dependence of direct optical transitions in GaInNAs QWs containing large N and In concentrations.

II. EXPERIMENT

The MQW samples were grown on semi-insulating (001) GaAs substrates by molecular beam epitaxy. Prior to the

[a)]Electronic mail: robert.kudrawiec@pwr.wroc.pl.
[b)]Present address: Graduate School of Engineering, Osaka University, Yamada-oka 2-1, Suita, Osaka 565-0871, Japan.

growth of MQWs, a 300-nm-thick GaAs buffer layer was grown at 560 °C. Then, ten-period GaInNAs/GaNAs multiquantum wells (MQWs) having perfect 2D interfaces were grown at the low substrate temperature of 375 °C and low As pressure. The QW widths were varied for each sample just by changing the respective growth time. Details of the growth as well as the structural characterization are given elsewhere.[10] Transmission electron microscopy (TEM) measurements of these samples showed the regularly stacked 10 QW layers, which remain homogeneous with smooth interfaces throughout the structure.[10] On the basis of the TEM and x-ray diffraction results, the QW widths of these samples were determined to be 3.9, 6.0, 7.0, and 8.1 nm, respectively. The widths of the barrier layers are between 11 and 14 nm, which does not induce any critical difference of the optical transition properties between the four samples. The In and N concentrations in the QWs were determined to be 36% and 4.6%. The GaNAs barriers were grown by closing the shutter of the nitrogen cell. However, a small amount of nitrogen (about 0.6% in our case) was unintentionally incorporated into the layers due to the surpassing active N around the closed shutter, which will be discussed later. These constituents' compositions correspond to 1.69% compressive strain within the QW and 0.12% tensile strain within the barrier. The CER and PR measurements were performed in the so-called "bright configuration,"[18] where the sample is illuminated by white light instead of monochromatic light as it takes place in the standard configuration, i.e. so-called "dark configuration." For CER measurements, the samples were mounted in a capacitor with a semitransparent electrode made from a copper wire mesh. This electrode was kept at a distance of ~0.2 mm from the sample surface while the sample itself was fixed at the bottom copper electrode. A maximum peak-to-peak alternating voltage of ~1.9 kV was applied. The frequency of the ac voltage was 285 Hz. Other relevant details of CER measurements had been described in our previous papers (see Refs. 19 and 20). In the case of PR measurements, the pump beam was provided by the 532 nm line of a yttrium aluminum garnet laser. This beam was chopped by a mechanical chopper at a frequency of 275 Hz. Phase-sensitive detection of the CER and PR signals was made by using a lock-in amplifier.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show room temperature CER and PR spectra for the 8.1-nm-wide $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ MQW, respectively. The strongest CER signal is observed at an energy of ~1.3 eV. This signal has been attributed to the GaNAs barriers grown with the unintentional nitrogen incorporation. According to the band anticrossing (BAC) model,[21] with BAC parameters of $E_N = 1.65$ eV and $C_{NM} = 2.7$ eV, we have determined the nitrogen content in the GaNAs barriers to be ~0.6%. Below the GaNAs signal, the optical transitions in the GaInNAs QW are clearly visible. The notation *klH* in this figure denotes the transition between the *k*th heavy-hole valence subband and the *l*th conduction subband. The identification of CER resonances was accomplished by using standard calculations[20] within the effective mass approximation. The CER spectrum was analyzed in detail in our previous paper,[22] where the experimental QW transition energies were compared with theoretical predictions based on an effective mass formalism model. Good agreement between experimental data and theoretical calculations has been obtained assuming the conduction-band offset at the GaInNAs/GaAs interface of 80% and the electron effective mass of $0.09m_0$.[22]

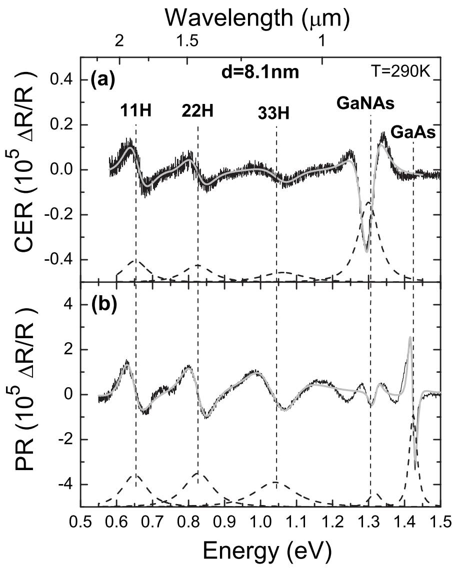

FIG. 1. Room temperature CER (a) and PR (b) spectra of 8.1-nm-wide $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ MQWs (thin solid line) together with fitting curves (thick gray lines) and the modulus of the individual transitions (dashed lines).

In the PR spectra, we observe the interband transitions at the identical energies with the above CER spectra within the experimental error. The significant difference between CER and PR spectra lies in the signal intensity and the sensitivity to detect the optical transition in the GaAs buffer layer. As was discussed in Ref. 20, a higher amplitude of electromodulation is easier to achieve in PR spectroscopy. In the case of PR measurements, which are shown in this paper, the intensity of the probing beam was 20 mW with the spot size of ~4 mm^2, i.e. quite strong as for PR spectroscopy. In addition to the band bending modulation at the sample surface, the laser beam (modulating beam) penetrates to the GaAs buffer layer, generating electron-hole pairs. Hence, the potential is modulated throughout the whole sample between the surface and the substrate interface. In the case of CER spectroscopy, the depth of electromodulation is very small because of different modulation mechanism.[20] This means that the CER signal contains the information mainly close to the sample surface. We have shown in Ref. 20 that the GaAs-related transition was observed in PR whereas no such a transition was detected in CER for uncapped 100-nm-thick GaInNAs layers grown on GaAs. A similar situation is observed in the present case since the cap layer in this sample is GaNAs. The different relative intensities of the GaNAs-related and QW-related signal in the CER and PR spectra are also associated with the different modulation mechanism between these two techniques. Finally, to study the temperature dependence of the optical transitions in this system, we ap-

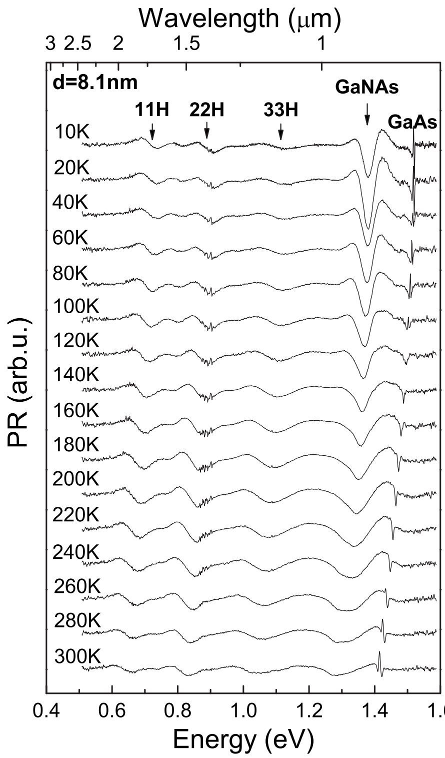

FIG. 2. Temperature dependence of PR spectra of 8.1-nm-wide $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ MQWs.

plied PR spectroscopy because of its stronger signal amplitude of the transitions related to GaInNAs QW, as well as its simpler application in a vacuum cryostat.

Figures 2–5 show the temperature dependence of PR spectra from the $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ MQW samples with

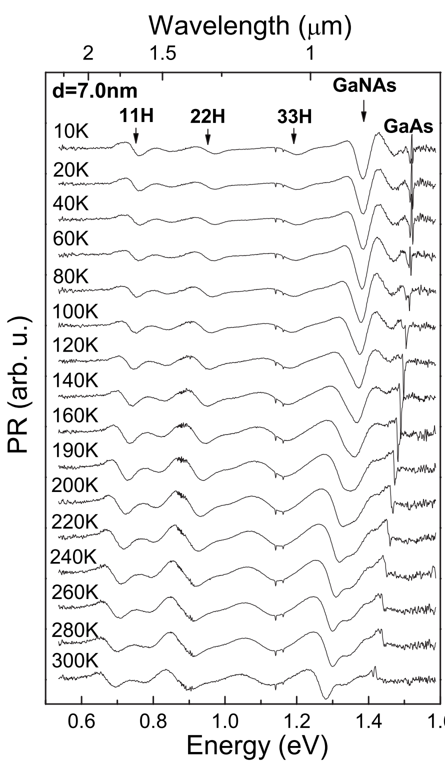

FIG. 3. Temperature dependence of PR spectra of 7.0-nm-wide $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ MQWs.

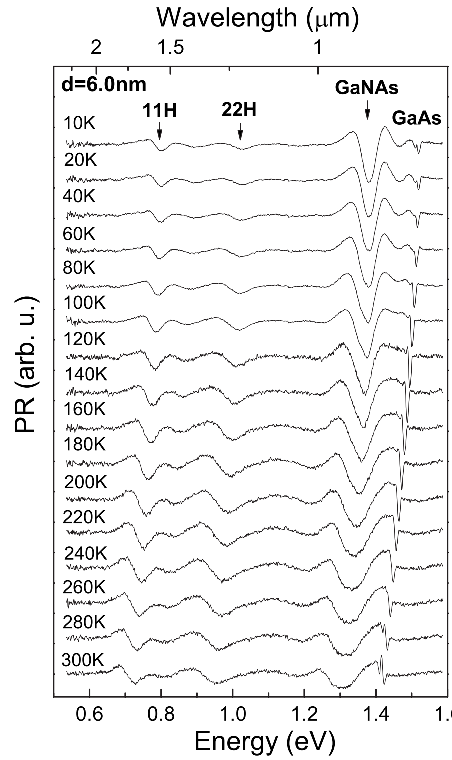

FIG. 4. Temperature dependence of PR spectra of 6.0-nm-wide $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ MQWs.

QW widths of 8.1, 7.0, 6.0, and 3.9 nm, respectively. It is clearly visible that the QW transitions as well as the barrier transitions (GaNAs and GaAs transitions) shift to higher energies when the temperature is decreased.

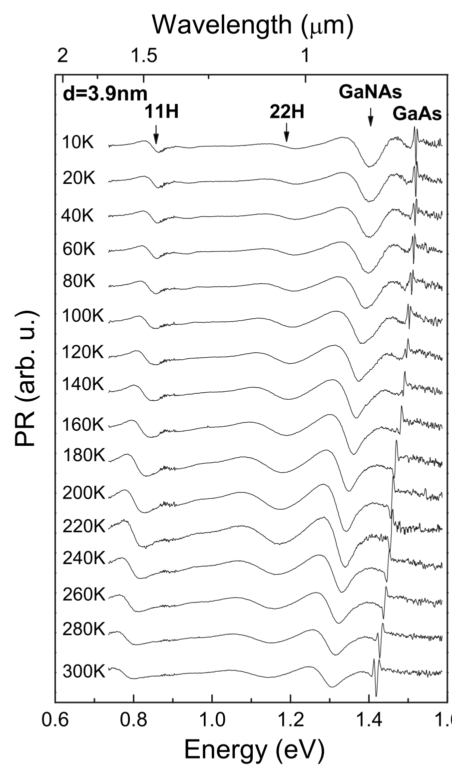

FIG. 5. Temperature dependence of PR spectra of 3.9-nm-wide $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ MQWs.

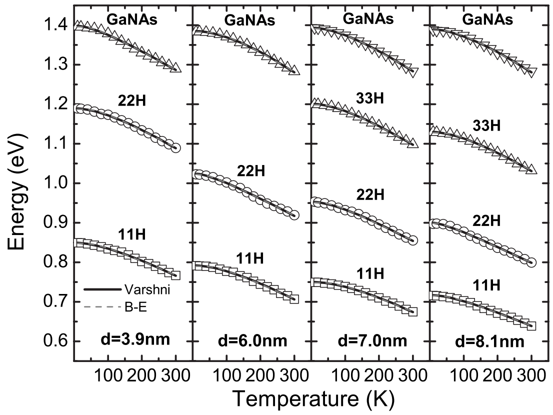

FIG. 6. Temperature dependence of 11H, 22H, 33H, and GaNAs transitions for $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ MQWs of various widths together with Varshni and Bose–Einstein fitting curves.

In order to extract the energies of the optical transitions from the PR spectra, we apply the standard fitting procedure assuming a Lorentzian line shape.[23] According to this model, the spectrum can be fitted using the following formula:

$$\frac{\Delta R}{R}(E) = \mathrm{Re}\left[\sum_{j=1}^{n} C_j \cdot e^{i\cdot\vartheta_j}(E - E_j + i\cdot\Gamma_j)^{-m_j}\right], \tag{1}$$

where n is the number of the optical transitions and spectral functions used in the fitting procedure, C_j and ϑ_j are the amplitude and phase of the line shape, and E_j and Γ_j are the energy and the broadening parameter of the transitions, respectively. The term m refers to the type of optical transitions. In our case we assumed that m equals 3 since this line is very close to the third derivative Gaussian line shape, i.e., the most appropriate line shape for an inhomogeneous system. $m=3$ was also used to fit the GaNAs transition because of an inhomogeneous broadening of this transition. An example of the analysis of experimental data by using Eq. (1) is shown in Fig. 1. The fitting curves are shown by thick gray lines together with the moduli of individual resonances (thin solid lines), obtained by

$$\Delta\rho_j(E) = \frac{|C_j|}{[(E - E_j)^2 + \Gamma_j^2]^{m_j/2}}. \tag{2}$$

Figure 6 plots the extracted energies of the transitions from the above PR spectra. The solid curves in Fig. 6 are least-square fits to the Varshni empirical relationship which can be expressed as[13]

$$E(T) = E(0) - \frac{\alpha T^2}{(\beta + T)}, \tag{3}$$

where $E(0)$ is the exciton energy at $T=0$ K, and α and β are the Varshni coefficients. The temperature dependence of QW and GaNAs transitions also have been fitted by a Bose–Einstein-type expression[14]

$$E(T) = E(0) - \frac{2a_B}{\exp\left(\frac{\Theta_B}{T}\right) - 1}, \tag{4}$$

where $E(0)$ is the transition energy at 0 K, a_B represents the strength of the exciton-average phonon interaction, and Θ_B corresponds to the average phonon temperature. The obtained values of the fitting parameters are summarized in

TABLE I. Values of the Varshni and Bose–Einstein parameters for optical transitions in GaInNAs MQW structures.

Sample optical transition	Varshni E_0 (eV)	Varshni α (meV/K)	Varshni β (K)	Bose–Einstein E_0 (eV)	Bose–Einstein a_B (meV)	Bose–Einstein Θ_B (K)
			$d=8.1$ nm			
GaNAs	1.3898 ± 0.0010	0.73 ± 0.07	299 ± 60	1.3871 ± 0.0005	0.059 ± 0.004	226 ± 9
33H	1.1302 ± 0.0005	0.64 ± 0.03	276 ± 27	1.1281 ± 0.0006	0.048 ± 0.003	209 ± 9
22H	0.9008 ± 0.0012	0.41 ± 0.02	165 ± 56	0.8987 ± 0.0009	0.020 ± 0.003	103 ± 11
11H	0.7169 ± 0.0007	0.40 ± 0.02	159 ± 27	0.7153 ± 0.0006	0.028 ± 0.003	167 ± 11
			$d=7.0$ nm			
GaNAs	1.3936 ± 0.0017	0.69 ± 0.11	265 ± 88	1.3914 ± 0.0008	0.051 ± 0.004	203 ± 11
33H	1.2008 ± 0.0004	0.62 ± 0.02	240 ± 17	1.1987 ± 0.0005	0.047 ± 0.003	197 ± 8
22H	0.9529 ± 0.0008	0.51 ± 0.03	164 ± 25	0.9512 ± 0.0011	0.034 ± 0.005	160 ± 16
11H	0.7601 ± 0.0004	0.56 ± 0.03	355 ± 41	0.7483 ± 0.0005	0.043 ± 0.003	234 ± 11
			$d=6.0$ nm			
GaNAs	1.3852 ± 0.0009	0.9 ± 0.2	477 ± 106	1.3825 ± 0.0005	0.070 ± 0.004	262 ± 9
22H	1.0227 ± 0.0014	0.47 ± 0.03	143 ± 43	1.0223 ± 0.0012	0.028 ± 0.004	128 ± 15
11H	0.7923 ± 0.0007	0.55 ± 0.04	278 ± 46	0.7903 ± 0.0005	0.043 ± 0.003	214 ± 11
			$d=3.9$ nm			
GaNAs	1.399 ± 0.0017	0.53 ± 0.04	123 ± 36	1.3963 ± 0.0012	0.037 ± 0.005	155 ± 16
22H	1.189 ± 0.0006	0.63 ± 0.04	258 ± 33	1.1873 ± 0.0010	0.047 ± 0.005	202 ± 16
11H	0.8500 ± 0.0006	0.49 ± 0.03	230 ± 32	0.8479 ± 0.0007	0.037 ± 0.004	195 ± 15

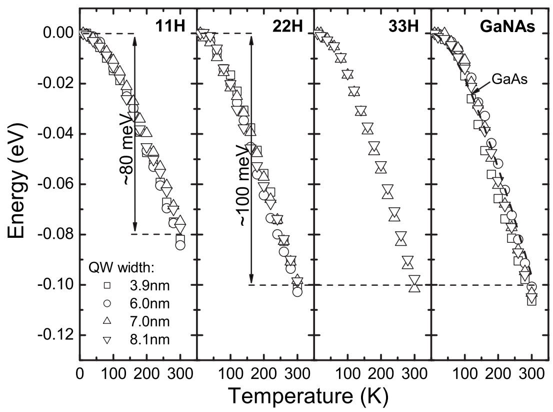

FIG. 7. Temperature-related shift of 11*H*, 22*H*, 33*H*, and GaNAs transitions for $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ MQWs of various widths. The dashed line corresponds to the temperature dependence of the energy gap in GaAs.

Table I. The obtained Varshni and Bose–Einstein parameters are consistent with parameters reported for low nitrogen and indium content GaInNAs QWs.[17] This means that the large nitrogen concentration significantly influences the energy of QW transitions (in this case this shift amounts to ~400 meV for 4.6% nitrogen). However, their temperature dependencies are only weakly sensitive to the nitrogen content (i.e., the Varshni and Bose–Einstein parameters are very similar for N-containing and N-free QWs). The temperature-induced shift of the transition energies is compared between the four MQW samples in Fig. 7. First, it is clearly visible that this shift does not depend on the QW width within the experimental error. Second, the shift is about 20 meV smaller for the ground state transition but its amount of 80 meV is still large in comparison to the reported values of 60–70 meV (see, e.g., in Ref. 9), where the shift was derived from PL with the correction of carrier localization at low temperatures. We believe that this difference is due to an inaccuracy in the estimate of the carrier localization from PL measurements. This estimate is especially difficult if the localized emission is observed up to the higher temperature regime, e.g., up to 150 K. In this case, the application of absorption-like techniques (e.g., PR) is the best approach to determine the temperature dependence of QW transitions.

IV. SUMMARY

In summary, PR has been applied to study the temperature dependence of optical transitions between the ground and excited states of $Ga_{0.64}In_{0.36}N_{0.046}As_{0.954}$ MQWs of four different well widths having high nitrogen contents. The 11*H*, 22*H*, and 33*H* QW transitions as well as the GaNAs barrier transition were clearly resolved at temperatures between 10 and 300 K. All the transitions shift to the red with increasing temperature, which can be well fitted by the Varshni and Bose–Einstein formulas. The Varshni and Bose–Einstein parameters have been determined for all QW transitions as well as the GaNAs barrier transition. In addition, the temperature-induced shift of the transition energies has been compared for the four MQW samples with various QW widths.

ACKNOWLEDGMENTS

This work was supported by the MNiSW Grant no. N N515 074 31/3896. In addition, R.K. acknowledges the support from the Foundation for Polish Science.

[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* (Elsevier, Oxford, 2005).
[3] M. Fischer, M. Reinhardt, and A. Forchel, Electron. Lett. **36**, 1208 (2000).
[4] E. Tournie, M. A. Pinault, S. Vezian, J. Massies, and O. Tottereau, Appl. Phys. Lett. **77**, 2189 (2000).
[5] E. Tournie, M.-A. Pinault, M. Laugt, J.-M. Chauveau, A. Trampert, and K. H. Ploog, Appl. Phys. Lett. **82**, 1845 (2003).
[6] H. L. Liu, M. Hopkinson, P. Navaretti, M. Gutierrez, J. S. Ng, and J. P. R. David, Appl. Phys. Lett. **83**, 4951 (2003).
[7] A. Trampert, J.-M. Chauveau, K. H. Ploog, E. Tournie, and A. Guzman, J. Vac. Sci. Technol. B **22**, 2195 (2004).
[8] M. Hugues, B. Damilano, J.-Y. Duboz, and J. Massies, Appl. Phys. Lett. **88**, 091111 (2006).
[9] G. Jaschke, R. Averbeck, L. Geelhaar, and H. Riechert, J. Cryst. Growth **278**, 224 (2005).
[10] F. Ishikawa, M. Horicke, U. Jahn, A. Trampert, and K. H. Ploog, Appl. Phys. Lett. **88**, 191115 (2006).
[11] H. Y. Liu, C. M. Tey, C. Y. Jin, S. L. Liew, P. Navaretti, M. Hopkinson, and A. G. Cullis, Appl. Phys. Lett. **88**, 191907 (2006).
[12] F.-I. Lai, S. Y. Kuo, J. S. Wang, R. S. Hsiao, H. C. Kuo, J. Chi, S. C. Wang, H. S. Wang, C. T. Liang, and Y. F. Chen, J. Cryst. Growth **291**, 27 (2006).
[13] Y. P. Varshni, Physica (Amsterdam) **34**, 149 (1967).
[14] P. Lautenschlager, M. Garriga, S. Logothetidis, and M. Cardona, Phys. Rev. B **34**, 2458 (1986).
[15] I. Suemune, K. Uesugi, and W. Walukiewicz, Appl. Phys. Lett. **77**, 3021 (2000).
[16] R. Kudrawiec, G. Sek, J. Misiewicz, F. Ishikawa, A. Trampert, and K. H. Ploog, Appl. Phys. Lett. **94**, 011907 (2009).
[17] B. Q. Sun, D. S. Jiang, Z. Pan, L. H. Li, and R. H. Wu, Appl. Phys. Lett. **77**, 4148 (2000); S. Shirakata, M. Kondow, and T. Kitatani, *ibid.* **79**, 54 (2001); M. M. E. Fahmi, A. Khan, J. A. Griffin, G. L. Harris, L. H. Robins, A. G. Birdwell, Y.-S. Kang, D. J. Smith, T. Steiner, and S. N. Mohammad, J. Appl. Phys. **94**, 7576 (2003); T. H. Chen, Y. S. Huang, D. Y. Lin, and K. K. Tiong, *ibid.* **96**, 6298 (2004).
[18] R. Kudrawiec and J. Misiewicz, Appl. Surf. Sci. **253**, 80 (2006).
[19] R. Kudrawiec, M. Gladysiewicz, J. Misiewicz, H. B. Yuen, S. R. Bank, M. A. Wistey, H. P. Bae, and J. S. Harris, Phys. Rev. B **73**, 245413 (2006).
[20] M. Motyka, R. Kudrawiec, and J. Misiewicz, Phys. Status Solidi A **204**, 354 (2006).
[21] 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).
[22] R. Kudrawiec, M. Gladysiewicz, J. Misiewicz, F. Ishikawa, and K. H. Ploog, Appl. Phys. Lett. **90**, 041916 (2007).
[23] D. E. Aspnes, Surf. Sci. **37**, 418 (1973).