Optica Applicata, Vol. XLVI, No. 2, 2016
DOI: 10.5277/oa160210

Role of nitrogen in carrier confinement potential engineering and optical properties of GaAs-based quantum wells heterostructures

DAMIAN PUCICKI*, KATARZYNA BIELAK, WOJCIECH DAWIDOWSKI, BEATA ŚCIANA, MAREK TŁACZAŁA

Faculty of Microsystem Electronics and Photonics, Wrocław University of Science and Technology, Janiszewskiego 11/17, 50-372 Wrocław, Poland

*Corresponding author: Damian.Pucicki@pwr.edu.pl

In this work, the authors present the results of optical characterization of GaAs-based multiple quantum well heterostructures, together with energy band structure analysis. The optical properties were investigated by applying photoluminescence spectroscopy. Structures with GaInNAs, GaInAs and GaNAs multiple quantum wells emitting around 1 μm, grown by atmospheric pressure metal-organic vapor phase epitaxy, were compared in this work. The role of nitrogen in quantum well carriers confinement potential was analysed. The photoluminescence intensities of the samples were correlated with the analysis of energy band structures and the overlaps of the carriers' wave functions. In addition, the main carrier activation energies were estimated based on photoluminescence temperature dependence and the Arrhenius plots analysis. It was deduced that the thermal photoluminescence decay is most probably related to the escape of electrons whereas the holes, independently of the potential well depth, are additionally confined by the local inhomogeneities or by the Coulomb interaction with the confined electrons.

Keywords: dilute nitrides, optical properties, carrier confinement, photoluminescence.

1. Introduction

Significant progress in the development of multicomponent semiconductors like GaInNAs(Sb) allows to extend the working optical wavelength range of GaAs-based structures [1–5]. Optimization of growth conditions and better understanding of the characteristics of this material system have resulted in many laser constructions with dilute nitride quantum wells (QWs). GaInNAs/GaAs structures are good candidates for high power telecom lasers and room-temperature ultra-low threshold current lasers based on exciton-polariton Bose–Einstein condensate due to huge conduction band offset results in strong electrons confinement and good thermal stability [6, 7]. In addition, the unique properties of quaternary dilute nitrides alloys, especially GaInNAs, make possible to tune the electrons and holes band offsets almost separately. It means

that it is possible to tune the conduction (CBO) and valence (VBO) bands offsets ratio of the GaInNAs QWs keeping at the same time the energy gap of the alloy constant. Those changes have an incredible impact on the carriers wave functions and thus change the wave functions overlap integral. According to Fermi's golden rule that the intensity of an optical transition is proportional to the square of the overlap integral between the wave functions of the carriers that are involved in the transition [8], those changes allow to tune the photoluminescence (PL) intensities of the GaInNAs-based samples.

It can be found in the literature that the improvement of the QWs-based optoelectronic devices leads often to higher complicity of the active parts of the devices. One of the ideas is to modify the QW by introducing additional sublayers increasing confinement potential of holes or electrons. Another approach is to modify the surrounding barrier layers. In both of these approaches, the interlayer stresses and heavy-light holes subbands splitting must be taken into consideration. In the case of dilute nitrides GaInNAs QWs it is proposed to introduce the side or even central GaAsSbN QW sublayer which increases the confinement potential of holes and modifies the wave function of electrons by forming W-type QW [9]. We also proposed to use GaAsP as a direct barrier for GaInNAs QWs or to reinforce the band offsets created by GaAs direct barrier [10]. That solution slightly changes the energy states of GaInNAs QWs in contrast to introducing QWs sublayer. Nevertheless both of these solutions lead to better carriers confinement, better overlap of wave functions and thus higher efficiency of the devices.

The motivation of our research was to examine the impact of the energy structure of the nitrogen containing QWs on the optical properties of multiple quantum well (MQW) heterostructure. For the purpose of this study, three structures were chosen. All structures contain QWs with comparable thicknesses and emit nearly the same wavelength, although they differ in material composition. Changing the composition of the QWs allows to modify the VBO and CBO and to tune the carrier confinement potential, interlayer stresses and heavy-light hole splitting. The chosen structures were also compared with two additional structures.

2. Experimental details

In the experiments, the MQW samples were grown by atmospheric pressure metalorganic vapor phase epitaxy (AP-MOVPE) in AIX200 R&D AIXTRON horizontal reactor. The investigated structures consist of 450 nm thick GaAs buffer and three QWs sandwiched between 30 nm thick GaAs barriers capped by 40–50 nm thick GaAs. (100)-oriented semi-insulating (SI) GaAs wafers were used as substrates. Trimethylgallium (TMGa), trimethylindium (TMIn), tertiarybutylhydrazine (TBHy) and arsine (AsH_3: 10% mixture in H_2) were used as the growth precursors. The main goal was to fabricate the MQW structures with comparable thicknesses of the QWs and energies of the QWs main transitions despite the fact that the samples differ in QWs CBOs and VBOs. Wherefore, three structures were grown: #A – with GaInAs QWs, #B – with

GaInNAs QWs, and #C – with GaNAs QWs. The chosen structures were compared with two samples with different QWs thicknesses and band offsets: #D – with GaInNAs and #E – with GaInAs QWs.

High resolution X-ray diffractometry (HRXRD) was applied to study the structural properties of the grown structures. The X-ray diffraction curves of the (004) symmetrical reflexes were analysed using a dynamical diffraction theory and in agreement with the algorithm presented by the authors elsewhere [11]. The structures were optically investigated by using room and high temperature PL spectroscopy, before and after rapid optical annealing (ROA). Annealing was carried out in order to improve the op-

T a b l e 1. Estimated structural parameters of the quantum wells embedded in GaAs barrier with the energy of the RT PL peak.

Structure	In [%]	N [%]	d_{QW} [nm]	$E_{PL,\,RT}$ [eV]
#A	**13.4**	**0**	**10.5**	**1.274**
#B	**9.3**	**0.3**	**11**	**1.274**
#C	**0**	**1**	**8.7**	**1.257**
#D	6.2	0.69	16.5	1.245
#E	9	0	5	1.357

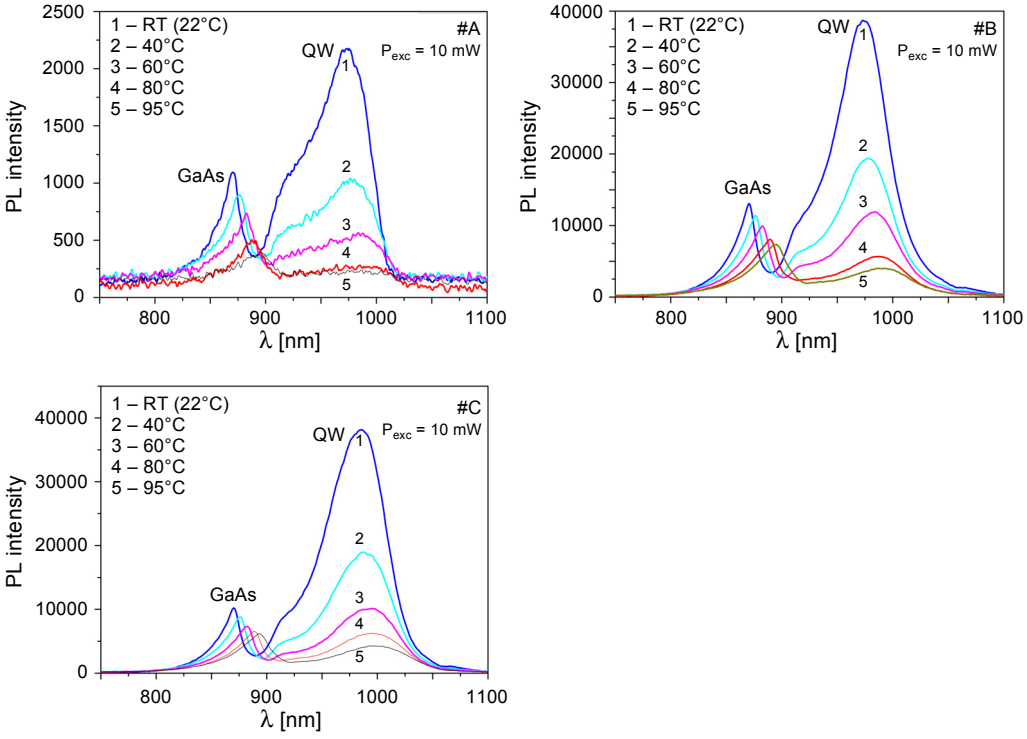

Fig. 1. PL spectra of Ga(In)(N)As/GaAs MQW structures #A, #B and #C measured after rapid optical annealing at room and higher temperature.

tical performance of the nitrogen containing samples, what is also often reported in the literature [12]. The calculations of QWs energy band structure were performed within the framework of the usual envelope function approximation, on the basis of the Pikus–Bir Hamiltonian calculations and including hydrostatic and shear stresses. The band anticrossing (BAC) model was applied in the case of nitrogen containing QWs. The numerical matrix methods were applied in order to solve Schrödinger's equation and to calculate eigenvalues and eigenvectors.

The structural parameters of the investigated MQW samples, determined by HRXRD curves simulations, are collected in Table 1. There are specified: the thicknesses of the QWs, indium and nitrogen average contents and energy of PL peaks measured at room temperature. In Figure 1 there are presented the PL spectra of the considered structures: #A, #B and #C, measured after ROA. The QWs PL emissions at 973.5, 973.0 and 986.0 nm are observed for the structures #A, #B and #C, respectively. The GaAs-related peaks are also visible on the spectral characteristics. From the presented spectra, one can clearly see a decrease in the PL intensity with an increase in temperature and much weaker PL intensity in the sample #A with GaInAs/GaAs QWs.

3. Results and discussion

The analysis of the role of nitrogen in optical properties of GaAs-based QWs heterostructures was based on three types of the structures which differ in composition of the QWs. To achieve the best contrast in properties of the samples, the structures with GaInAs, GaInNAs and GaNAs QWs have been chosen for investigation. From the PL measurements it is clearly seen that the samples #A, #B and #C differ in both PL intensities and the rate of decay of the signal with the temperature. These properties of the samples were confronted with the calculated theoretical energy band diagrams of the considered QWs. The structural parameters of the investigated MQW samples, determined from HRXRD analysis, were used to calculate the energy band diagrams. The calculated energy band diagrams of the samples #A, #B and #C are presented in

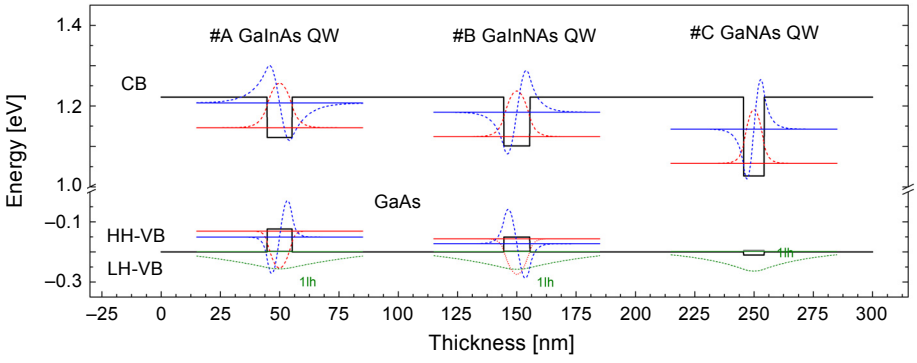

Fig. 2. Comparison of the energy band diagrams of the samples #A, #B and #C.

T a b l e 2. Complementary data describing band structures of the investigated structures. Only data referring to the main transitions are presented.

	Structure				
	#A	#B	#C	#D	#E
CBO [eV]	**0.100**	**0.121**	**0.195**	0.165	0.068
HH-VBO [eV]	**0.077**	**0.050**	–	0.027	0.052
LH-VBO [eV]	–	–	**0.005**	–	–
$\nu_{1,\,e}$ [eV]	**0.076**	**0.098**	**0.164**	0.153	0.027
$\nu_{1,\,hh}$ [eV]	**0.077**	**0.044**	**-**	0.025	0.035
$\nu_{1,\,lh}$ [eV]	–	–	**<0.001**	–	–
m_e^* [m_0]	**0.0612**	**0.0709**	**0.0965**	0.0817	0.0631
m_{hh}^* [m_0]	**0.3206**	**0.3251**	**0.3350**	0.3293	0.3237
m_{lh}^* [m_0]	**0.0816**	**0.0845**	**0.0913**	0.0870	0.0843
E_{1e1h} [eV]	**1.276**	**1.276**	**1.257**	1.244	1.361
Overlap integral [%]	**97.958**	**99.586**	**64.971**	**99.887**	**92.983**

Fig. 2. There are illustrated the CBO and heavy holes and light holes VBOs together with main energy states and wave function of electrons and holes. The complementary data describing the band structure of the samples are collected in Table 2. From the optical efficiency point of view, it is really important to analyse the values of band offsets, confinement potentials of the ground states of electron $\nu_{1,\,e}$, heavy holes $\nu_{1,\,hh}$ and light holes $\nu_{1,\,lh}$ together with the energetic differences between the following electronic states in the QWs.

On the basis of the chosen samples and in agreement with the band anticrossing model, the role of nitrogen on the confinement potential engineering is clearly seen. While the addition of indium to GaAs introduces the band offsets in valence and conduction bands, leads to the regular type I band alignment on the GaInAs/GaAs interface, the addition of nitrogen results in an extremely different band alignment. In accordance with the BAC calculations and the experiment [13], nitrogen has an impact only on the conduction band and of course on the lattice mismatch correlated strains. The VBO created at the interface of the GaNAs/GaAs heterostructure is a result of the shear and hydrostatic stresses induced by the mutual lattice mismatch of those materials. For the GaNAs/GaAs QW tensile stresses lead to formation of type II band alignment for heavy holes (HH) and type I for light holes (LH) band. Lack of confinement of heavy holes in the GaNAs QW, small LH-VBO and small effective mass of light holes result in lack of location of any energy states of the holes within the GaNAs thin QWs, as presented in Fig. 2 for the sample #C. In that sample, higher amount of nitrogen, compared to the other two structures #A and #B, results in much bigger CBO. Those changes in electronic structure finally lead to weak wave functions overlap and according to Fermi's golden rule should lead to weaker PL intensity. However, in the case of the sample #C, it is observed that not only the strongest PL signal but also the

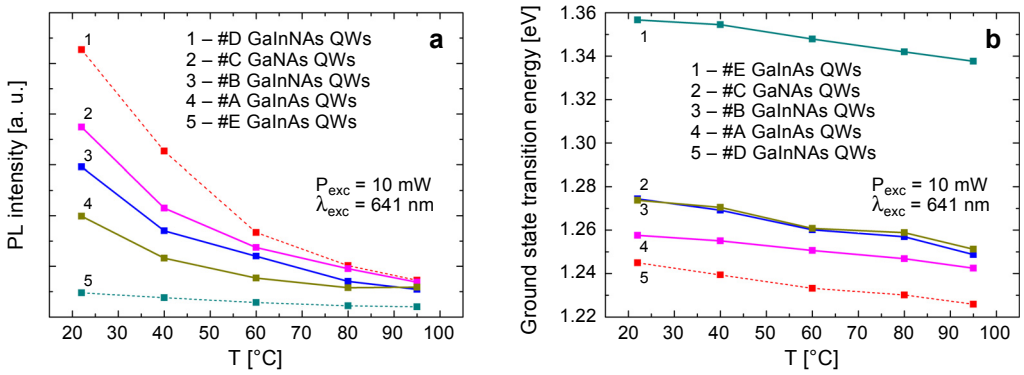

Fig. 3. Changes in the PL intensities (**a**) and ground state transition energies (**b**) of the investigated Ga(In)(N)As/GaAs MQW structures as a function of temperature.

temperature of PL quenching is the highest for that sample (Fig. 3**a**). During the thermal analysis of the PL intensity, the changes in the emitted wavelength were monitored as well (Fig. 3**b**).

Comparing the QWs of the structure #A and #B, it is understood that reduction of indium content and adding nitrogen increase the electron effective masses (Table 2), tune the QW band offsets and carriers confinement potentials leading to better overlap of the ground states wave functions in the case of structure #B. Despite the fact that those changes have a significant impact on the confinement potential of heavy holes, reducing it almost two times from $\nu_{1,\,\mathrm{hh}} = 0.077$ eV for GaInAs QW to $\nu_{1,\,\mathrm{hh}} = 0.044$ eV for GaInNAs QW, the ground state wave functions overlap integrals change slightly (from 97.958% for sample #A to 99.586% for sample # B) due to big effective mass of heavy holes m^*_{hh}. Further reduction of heavy holes confinement potential to $\nu_{1,\,\mathrm{hh}} = 0.025$ eV, how it is presented in the case of the sample #D with GaInNAs QWs, does not increase the percentage of the overlap integral significantly (99.887% for the sample #D). The strongest PL signal of that structure can be linked with thicker QWs (16.5 nm) and better confinement of the electrons at the ground state. The lowest PL signal was observed for the structure #E with thinner GaInAs/GaAs QWs. The lowest value of electron confinement potential $\nu_{1,\,\mathrm{e}} = 0.027$ eV in the case of those QWs is a result of lower indium content and thinner QWs. It is worth to point out that the confinement potential of heavy holes in the sample #E QWs is higher than for the sample #D. From that analysis it is deduced that the confinement of the holes has a minor impact on investigated optical properties.

The unique properties were found out in the case of the sample #C with GaNAs/GaAs QWs. As it was already mentioned, in that case there is only a very weak confinement of light holes $\nu_{1,\,\mathrm{lh}} < 0.001$. That is the reason why the ground state wave functions overlap integrals are significantly smaller (64.971%) in comparison to other investigated structures. However, this structure is characterized by a higher value of $\nu_{1,\,\mathrm{e}} = 0.164$ eV, the strongest PL intensity from the series of the structures with com-

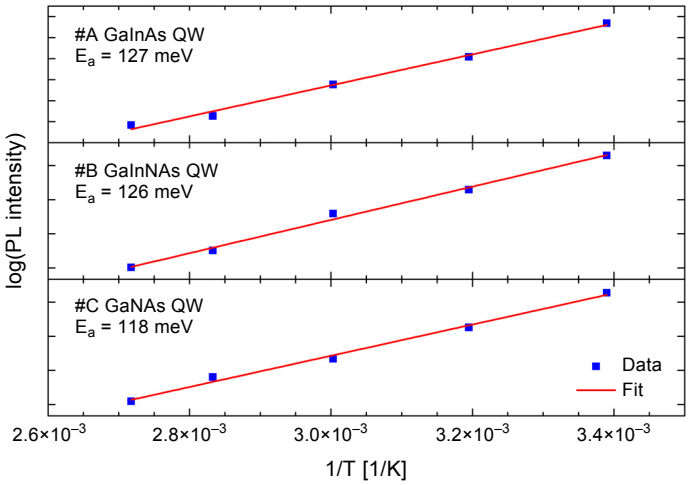

Fig. 4. The Arrhenius plots presenting the changes in PL intensities in temperature for the samples #A, #B and #C.

parable QWs thickness and higher temperature of PL quenching. Therefore it could be concluded that tuning the electron confinement potential by adding nitrogen has a major impact on the optical properties of the GaInNAs QWs with a negligible effect of valence band modification. However, in accordance with Fermi's golden rule, the week localization of holes in the QWs of the structures #C, which leads to a significantly lower wave functions overlap, should be a main factor quenching the PL intensity of such structure. Thus, more detailed analysis was conducted in order to study the origin of a strong PL signal of the structure with GaNAs/GaAs QWs. The Arrhenius plots presenting the changes in PL intensities of the considered structures in temperature are presented in Fig. 4. The corresponding activation energy E_a for the samples #A, #B and #C estimated from the fits to the Arrhenius plots are equal to 127, 126 and 118 meV, respectively. The achieved values of E_a are comparable with the confinement energies of electrons in the QWs or the difference between the following electron energy states like it is for the sample #C with GaNAs QWs. Those big values of E_a show that the main mechanism responsible for quenching the PL signal is connected rather with the thermal activation of electrons and their escape from the QWs. However, the sample #C with GaNAs QWs is characterized by the lower value of E_a what is in agreement with its rate of PL quenching (see Fig. 3**a**). Nevertheless, the sample #C emits the strongest signal in room temperature what is contrary to the weak confinement of the holes in the QWs of that structure. It must be pointed out that the theoretical predictions and calculations neglect two factors which can affect the PL signal strength. First are the alloy inhomogeneities in growth direction and lateral phase segregation. Such structural inhomogeneities are commonly observed in the dilute nitrides alloys, also by the authors [14], and can be a source of localized states which confine holes in the QWs, leading to an increase in wave functions overlap and finally to a sig-

nificant increase in PL intensity. The second factor is electrons-holes Coulomb interaction, which in the case of the sample #C seems to be the strongest due to the biggest value of electron confinement potential.

4. Summary

Optical properties of GaInNAs/GaAs MQW structures tailored at 1.0 μm have been investigated by PL spectroscopy. The properties of the samples were confronted with energy band diagrams of their QWs. Analysis of the energy band structure was based on structural data determined from HRXRD. It was shown that the simple theoretical analysis of electronic structure of diluted nitride QWs suffers from low accuracy of the description of the real properties of the QW structures. From the investigation, it is concluded that the electrons confinement potential has the greatest impact on the PL intensity and photoluminescence quenching temperature and that is the reason that the structure #C with GaNAs/GaAs QWs shows the best thermal and optical properties (from the series #A, #B and #C). It is also stated that the theoretical predictions do not take into account strong alloy inhomogeneities which are present in the case of dilute nitrides alloys and electrons-holes Coulomb interaction, what can lead to hole confinement in the QWs layers. Finally, it is proved that nitrogen plays a key role in the tuning the properties of the Ga(In)(N)As QWs.

Acknowledgements – This work was co-financed by Wrocław University of Science and Technology statutory grant and by the European Union within European Regional Development Fund, through grant Innovative Economy POIG.01.01.02-00-008/08.

References

[1] JASCHKE G., AVERBECK R., GEELHAAR L., RIECHERT H., *Low threshold InGaAsN/GaAs lasers beyond 1500 nm*, Journal of Crystal Growth **278**(1–4), 2005, pp. 224–228.

[2] ISHIKAWA F., TRAMPERT A., PLOOG K.H., *Low substrate temperature and low As-pressure growth concept for the molecular beam epitaxial growth of 1.55 μm (Ga,In)(N,As) multiple quantum wells*, Journal of Crystal Growth **301–302**, 2007, pp. 529–533.

[3] BANK S.R., BAE H., GODDARD L.L., YUEN H.B., WISTEY M.A., KUDRAWIEC R., HARRIS J.S., *Recent progress on 1.55-μm dilute-nitride lasers*, IEEE Journal of Quantum Electronics **43**(9), 2007, pp. 773–785.

[4] GUPTA J.A., SPROULE G.I., WU X., WASILEWSKI Z.R., *Molecular beam epitaxy growth of 1.55 μm GaInNAs(Sb) double quantum wells with bright and narrow photoluminescence*, Journal of Crystal Growth **291**(1), 2006, pp. 86–93.

[5] NIU Z.C., ZHANG S.Y., NI H.Q., WU D.H., ZHAO H., PENG H.L., XU Y.Q., LI S.Y., HE Z.H., REN Z.W., HAN Q., YANG X.H., DU Y., WU R.H., *GaAs-based room-temperature continuous-wave 1.59 μm GaInNAsSb single-quantum-well laser diode grown by molecular-beam epitaxy*, Applied Physics Letters **87**(23), 2005, article 231121.

[6] BISPING D., PUCICKI D., FISCHER M., KOETH J., ZIMMERMANN C., WEINMANN P., HOEFLING S., KAMP M., FORCHEL A., *GaInNAs-based high-power and tapered laser diodes for pumping applications*, IEEE Journal of Selected Topics in Quantum Electronics **15**(3), 2009, pp. 968–972.

[7] Ryczko K., Sęk G., Misiewicz J., Langer F., Höfling S., Kamp M., *On the oscillator strength in dilute nitride quantum wells on GaAs*, Journal of Applied Physics **111**(12), 2012, article 123503.

[8] Dirac P.A.M., *The quantum theory of the emission and absorption of radiation*, Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character **114**(767), 1927, pp. 243–265.

[9] Albo A., Bahir G., Fekete D., *Improved hole confinement in GaInAsN-GaAsSbN thin double-layer quantum-well structure for telecom-wavelength lasers*, Journal of Applied Physics **108**(9), 2010, article 093116.

[10] Tansu N., Yeh J.-Y., Mawst L.J., *Experimental evidence of carrier leakage in InGaAsN quantum-well lasers*, Applied Physics Letters **83**(11), 2003, pp. 2112–2114.

[11] Pucicki D., Bielak K., Kudrawiec R., Radziewicz D., Ściana B., *Determination of indium and nitrogen contents of InGaAsN quantum wells by HRXRD study supported by BAC calculation of the measured energy gap*, Materials Science – Poland **31**(4), 2013, pp. 489–494.

[12] Bisping D., Hoefling S., Pucicki D., Fischer M., Forchel A., *Room-temperature singlemode continuous-wave operation of distributed feedback GaInNAs laser diode at 1.5 μm*, Electronics Letters **44**(12), 2008, pp. 737–738.

[13] Kudrawiec R., Motyka M., Andrzejewski J., Misiewicz J., Gollub D., Forchel A., *Photoreflectance and photoluminescence study of step-like GaInNAs/GaInNAs/GaAs quantum wells*, IEE Proceedings – Optoelectronics **151**(5), 2004, pp. 313–316.

[14] Pucicki D., Bielak K., Ściana B., Radziewicz D., Latkowska-Baranowska M., Kováč J., Vincze A., Tłaczała M., *Determination of composition of nonhomogeneous GaInNAs layers*, Journal of Crystal Growth **433**, 2016, pp. 105–113.

Received November 2015
in revised form January 3, 2016