

# INVESTIGATION OF THE EPITAXIAL GROWTH OF AIIIBV-N HETEROSTRUCTURES FOR SOLAR CELL APPLICATIONS

Ściana Beata<sup>1\*</sup>, Damian Radziejewicz<sup>1</sup>, Damian Pucicki<sup>1</sup>, Jarosław Serafińczuk<sup>1</sup> and Marek Tlaczala<sup>1</sup>, Robert Kudrawiec<sup>2</sup>, Jaroslav Kováč<sup>3</sup>, Andrej Vincze<sup>3</sup>

- 1 Faculty of Microsystem Electronics and Photonics, Wrocław University of Technology, Janiszewskiego 11/17, 50-372, Wrocław, Poland
- 2 Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370, Wrocław, Poland
- 3 Department of Microelectronics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 812 19, Bratislava, Slovakia

## ABSTRACT

The  $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$  alloy semiconductor alloys, so called diluted nitrides (AIIIBV-N), have been extensively studied recently. Unusual properties of these materials such as a huge and negative band gap bowing coefficient and a large conduction band offset come mainly from a large size and electronegativity difference between N and As atoms. These features make AIIIBV-N alloys very promising for applications in 1.3 – 1.55  $\mu\text{m}$  lasers and very efficient multijunction solar cells. On the other hand the small amount of nitrogen strongly deteriorates the material quality of diluted nitrides. So, a lot of research efforts are focused on understanding the reasons of the generated defects and optimisation the growth methods (mainly MBE and MOVPE technologies). This work presents the influence of the growth parameters on the properties of undoped GaAsN/GaAs and multiple quantum well (MQW) InGaAsN/GaAs heterostructures obtained by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE). The structural and optical properties of the mentioned structures were examined using high resolution X-Ray diffraction HRXRD, contactless electroreflectance spectroscopy CER ( $T = 300\text{ K}$ ), secondary ion mass spectrometry (SIMS). The influence of the growth temperature and the nitrogen source concentration in a gas phase on the composition and material quality of both GaAsN epilayers and InGaAsN quantum wells is presented and discussed.

**Key words:** diluted nitrides, APMOVPE epitaxy, MQW InGaAsN/GaAs, HRXRD, CER, SIMS

## INTRODUCTION

The InGaAsN/GaAs heterostructures proposed in 1996 by Kondow et al. [1] have been successfully used in telecom laser constructions on GaAs substrate. Additionally, the InGaAsN with a bandgap of 1 eV are lattice

---

\* e-mail: beata.sciana@pwr.wroc.pl, tel: (+48)0713559866 ext.53

matched to both GaAs and Ge for the nitrogen and indium contents of around 3 % and 9 %, respectively. These features make this semiconductor an ideal candidate for high-efficiency multijunction solar cells (MJSCs) based on the Ge/InGaAsN/GaAs/InGaP structure [2]. The growth technology of the GaAsN alloy-based diluted nitrides is very difficult because of the large miscibility gap between GaAs and GaN. The incorporation of more than 3 % of nitrogen into GaAs crystalline structure drastically deteriorates the optical quality of GaAsN epilayers [3]. They contain a lot of the point defects (vacancies, antisites, interstitials) and impurities (oxygen, carbon, hydrogen). The main efforts of the investigators have been made to understand physics of these alloys, to optimize the growth conditions and improve their structural and optical quality in order to application in high-performance optoelectronic devices.

This work presents the epitaxial growth of undoped GaAsN layers and multiple quantum well (MQW) -  $3 \times$  InGaAsN/GaAs - structures obtained by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE). The main growth parameters such as the growth temperature, the hydrogen flow rate through the bubbler with the organic nitrogen source and the molar ratio of the gallium to indium in the gas phase were changed to achieve the high material quality and alloy composition suitable for application in MJSCs. The properties of the obtained structures were examined using HRXRD, CER and SIMS methods while the most of the growth characteristics were estimated based on HRXRD measurements.

### **EXPERIMENTAL AND MEASUREMENT DETAILS**

The investigated heterostructures were grown by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE) with AIX200 R&D AIXTRON horizontal reactor on (100)-oriented semi-insulating SI GaAs and Si-doped n-type GaAs substrates. Trimethylgallium (TMGa), trimethylaluminium (TMAI), tertiarybutylhydrazine (TBHy) and arsine ( $\text{AsH}_3$ ; 10 % mixture in  $\text{H}_2$ ) were used as the growth precursors. High purity hydrogen was employed as a carrier gas. The following growth parameters were changed: the growth temperature  $T_g=566 \div 585$  °C, the hydrogen flow rate through the saturator with TBHy -  $V_{\text{H}_2/\text{TBHy}}=1100 \div 3000$  ml/ min, the ratio of the gallium to indium source concentration in the gas phase  $\text{III}_{\text{Ga}}/\text{III}_{\text{In}}=4.8$  and 6.9. Stable parameters during all runs were: the arsine flow rate  $V_{\text{AsH}_3}=50$  ml/ min (for GaAsN and InGaAsN) and 300 ml/ min (for GaAs), the total flow of the hydrogen carrier gas  $V_{\text{H}_2\text{tot}}=9.6$  l/ min, the organic source temperatures:  $T_{\text{TMGa}}=-10$  °C,  $T_{\text{TMAI}}=18$  °C,  $T_{\text{TMIn}}=20$  °C,  $T_{\text{TBHy}}=30$  °C.

Two types of samples were investigated:

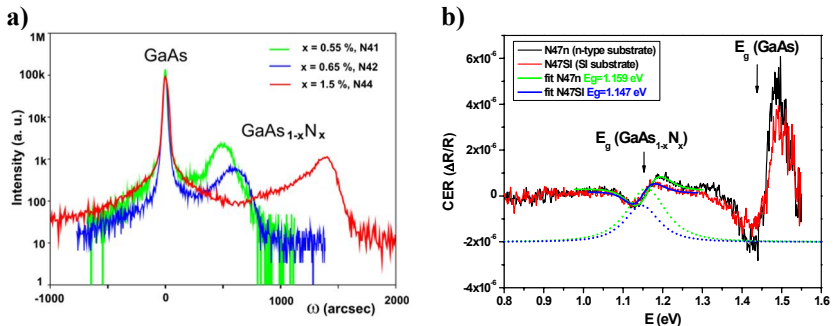
1. Undoped  $\text{GaAs}_{1-x}\text{N}_x/\text{GaAs}$  heterostructures consisted of 450 nm thick GaAs buffer and  $\sim 180$  nm thick  $\text{GaAs}_{1-x}\text{N}_x$  (samples: N41, N42, N44, N47, N48, N54).

2. Undoped MQW structure consisted of 450 nm thick GaAs buffer and  $3 \times \text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x/\text{GaAs}$  MQW region capped by 40 ÷ 50 nm thick GaAs (samples: NI43, NI45, NI46, NI49, NI51, NI53).

Structural properties of the obtained heterostructures were studied by high resolution X-Ray diffraction (HRXRD). The modification and improvement of the simulation programme of the HRXRD Philips equipment was performed for determination of the structural quality of diluted nitrides. The rocking curves allow the evaluation of the thickness and composition of the AlIIBV-N epilayers. The reciprocal space maps give additional information about the presence of the structural defects and the relaxation state. Optical properties were analysed using contactless electroreflectance (CER) modulation spectroscopy. The reflectivity from the investigated sample is modulated by external electric field. This is a very useful, nondestructive method, very sensitive at room temperature described in [4]. SIMS measurements performed using a Cameca Magnetic Sector instrument and sputtering with Cs Gun allowed to obtain the composition depth profiles of investigated structures.

## RESULTS AND DISCUSSION

The investigations were concentrated on determination of the influence of the technological parameters on efficiency of nitrogen incorporation into GaAs and InGaAs alloys and properties of the obtained  $\text{GaAs}_{1-x}\text{N}_x/\text{GaAs}$  and MQW  $3 \times \text{InGaAsN}/\text{GaAs}$  heterostructures. Fig. 1a shows symmetric (004) scans of  $\text{GaAs}_{1-x}\text{N}_x$  films with different nitrogen contents ( $x=0.55, 0.65, 1.5\%$ ).



**Fig. 1** – a) Rocking curve for the (004) reflection of  $\text{GaAs}_{1-x}\text{N}_x$  with different nitrogen content; b) CER spectra of  $\text{GaAs}_{1-x}\text{N}_x$  grown on n-type and SI GaAs substrate

For higher values of nitrogen the  $\text{GaAs}_{1-x}\text{N}_x$  reflex shifts to the higher diffraction angles indicating that the lattice constant normal to the surface decreases. Additionally, some deterioration of the structural quality is visible by lowering of the reflex intensity and its broadening. Fig. 1b presents two CER spectra (performed at 300 K) of  $\text{GaAs}_{1-x}\text{N}_x$  ( $x=1.95\%$ ) grown on n-type and SI GaAs substrates. Based on the transition related to  $\text{GaAs}_{1-x}\text{N}_x$  epilayer the band

gap energy of this material can be determined what allows the evaluation of the nitrogen content using band-anticrossing BAC model. Some difference between the  $\text{GaAs}_{1-x}\text{N}_x$  composition grown on Si-doped and undoped SI substrates were observed for both CER and HRXRD measurements.

Fig. 2 presents the nitrogen content ( $x$  parameter) in  $\text{GaAs}_{1-x}\text{N}_x$  epilayers grown at  $T_g=566^\circ\text{C}$  as a function of the hydrogen flow rate through the saturator with TBHy -  $V_{\text{H}_2/\text{TBHy}}$ . The growth temperature of  $566^\circ\text{C}$  determined from our earlier results [5] guarantees the efficient nitrogen incorporation without degradation of the structural quality. The  $\text{GaAs}_{1-x}\text{N}_x$  composition was estimated from the rocking curves and CER spectra (BAC model). The divergence of the nitrogen composition estimated using CER and HRXRD methods are probably connected with the presence of interstitials defects and strains in  $\text{GaAs}_{1-x}\text{N}_x$  films. The most efficient nitrogen incorporation occurs in the range of  $V_{\text{H}_2/\text{TBHy}}=1500 \div 2500$  ml/min, above 2500 ml/min the saturation of the nitrogen content is observed. The lowest value of the  $\text{GaAs}_{1-x}\text{N}_x$  band gap of 1.12 eV was determined from CER spectra for the sample N54 ( $x=2.26\%$ ).

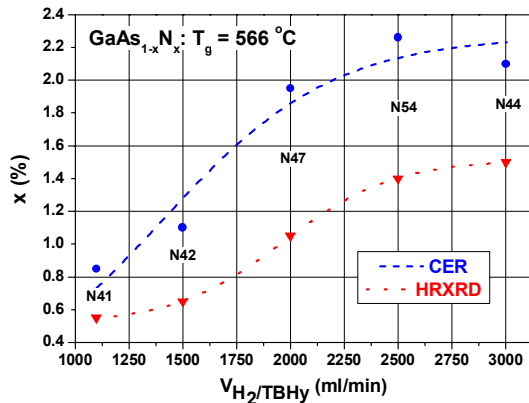
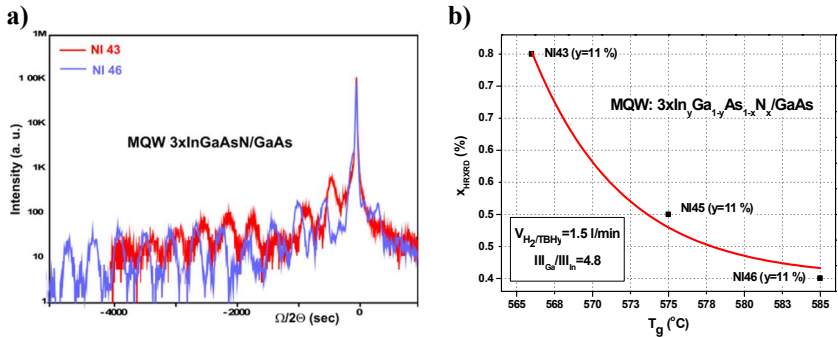


Fig. 2 – The nitrogen content in  $\text{GaAs}_{1-x}\text{N}_x$  grown at  $T_g=566^\circ\text{C}$  versus the flow rate  $V_{\text{H}_2/\text{TBHy}}$  estimated from rocking curves (HRXRD) and CER spectra

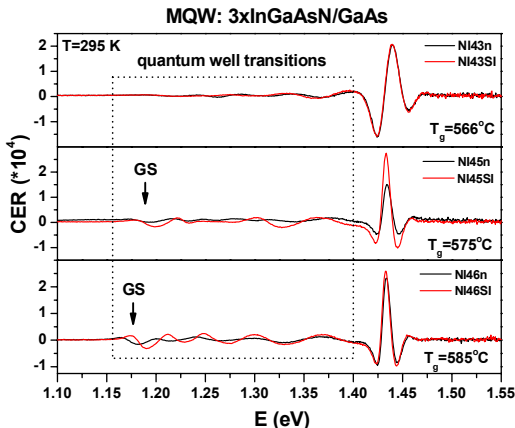
$585^\circ\text{C}$ ;  $V_{\text{H}_2/\text{TBHy}}=1500$  ml/min;  $\text{III}_{\text{Ga}}/\text{III}_{\text{In}}=4.8$ . The symmetric (004) HRXRD scans for the MQW structures grown at  $566^\circ\text{C}$  (NI43) and  $585^\circ\text{C}$  (NI46) are presented in figure 3a. It seems that the interface quality is better for the sample NI46 grown at  $585^\circ\text{C}$ . The nitrogen and indium contents in  $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$  quantum wells were determined by comparison of the measurement and simulations curves. The results shown in fig. 3b indicate that the nitrogen content decreases from 0.75 % to 0.4 % - enhanced N desorption from the surface [6] - while the indium content is constant ( $\sim 11\%$ ) with increasing  $T_g$ .

In the case of MQW structures the main efforts were focused on optimization of the growth parameters to get the  $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$  alloy with the band gap near 1 eV and lattice matched to GaAs. At first step we investigated the influence of the growth temperature  $T_g$  on the quantum well composition and the structural and optical quality of the MQW region. The growth parameters were as follows:  $T_g=566, 575,$



**Fig. 3** – a) The symmetric (004) HRXRD scans for the MQW structures grown at 566 °C (sample NI43) and 585 °C (sample NI46); b) the nitrogen content in  $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$  quantum wells as a function of the growth temperature  $T_g$

The CER spectra of the investigated MQW structures grown on n-type (black line) and undoped (red line) GaAs substrates are presented in *fig. 4*. The quantum well (QW) transitions appear below the band gap of GaAs (1.43 eV). In the case of the structure grown at 566 °C (sample NI43) the QW transitions are nearly invisible what indicates the poor optical quality. This is connected with decreasing the rate of the surface reactions (the migration length of the atoms also decreases), the insufficient arsine decomposition and more efficient incorporation of impurities at low growth temperatures.

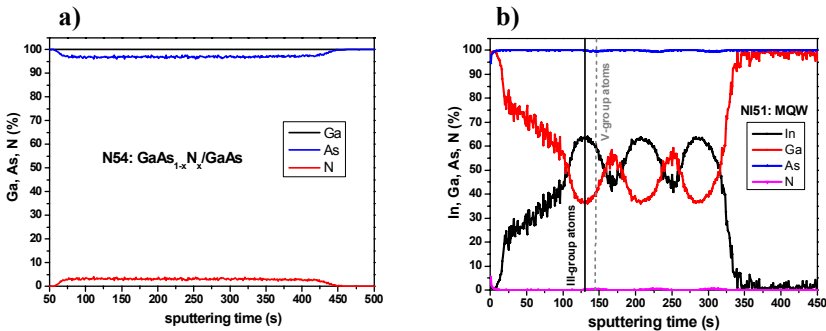


**Fig. 4** – CER spectra of the MQW structures grown at 566 °C (sample NI43), 575 °C (sample NI43) and 585 °C (sample NI46). Black and red line corresponds to the n-type and undoped SI GaAs substrate, respectively

MQW structures grown at higher temperatures (samples NI45, NI46) exhibit the strong and distinct QW transitions and the energy of ground state (GS) can be determined. Based on the obtained results we decided to increase the nitrogen content in  $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$  by increasing the  $\text{III}_{\text{Ga}}/\text{III}_{\text{In}}$  ratio. Due to the weaker In-N bond strength (7.70 eV/atom) in comparison with the Ga-N (9.12 eV/atom) bond [7] the nitrogen incorporation in InGaAs alloys decreases

es with increasing the indium content. Our first experimental results and HRXRD measurements showed that by increasing the  $\text{III}_{\text{Ga}}/\text{III}_{\text{In}}$  ratio from 4.8 to 6.9 we increased the nitrogen content from 0.5 % to 1.3 % for the MQW structure grown at 575 °C.

SIMS measurements were carried out to get information about the atom distribution inside the investigated structures. The SIMS profiles of  $\text{GaAs}_{1-x}\text{N}_x/\text{GaAs}$  (sample N54) and MQW (sample) heterostructures are presented in *fig. 5*.



**Fig. 5** – SIMS profiles of heterostructures: *a* –  $\text{GaAs}_{1-x}\text{N}_x/\text{GaAs}$  (sample N54); *b* – MQW (sample NI51).

The nitrogen concentration in  $\text{GaAs}_{1-x}\text{N}_x$  (*Fig. 5a*) is about 3 % what is higher than the  $x$  value determined from HRXRD ( $x=1.4$  %) and CER spectra ( $x=2.26$  %). SIMS measurements give information about the total N concentration inside the sputtered material while the HRXRD corresponds to the substitutional N concentration hence such a large discrepancy between the nitrogen contents estimated from these two methods. In the case of the MQW structure the composition of the  $\text{InGaAsN}$  quantum wells is more difficult to evaluate. The SIMS profile of the sample NI51 grown at 575 °C (*Fig. 5b*) shows some difference between the III-group and V-group atoms position what can be connected with the interdiffusion process at the  $\text{InGaAsN}/\text{GaAs}$  interface.

## CONCLUSIONS

This work presents the optimization of the epitaxial growth of undoped  $\text{GaAsN}$  layers and multiple quantum well (MQW) -  $3 \times \text{InGaAsN}/\text{GaAs}$  - structures obtained by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE). The optimal growth parameters for  $\text{GaAsN}$  with the band gap near 1 eV are:  $T_g=566$  °C,  $V_{\text{H}_2/\text{TBHY}}=2500$  ml/min. In the case of MQW structures the low growth temperature drastically deteriorates their optical quality, so the higher values of  $T_g$  are required. In order to increase the nitrogen content in

$\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$  wells grown at higher temperatures the  $\text{III}_{\text{Ga}}/\text{III}_{\text{In}}$  ratio was increased. First experimental results confirmed this decision.

#### *Acknowledgements*

This work was co-financed by Polish Ministry of Science and Higher Education under the grant no. N N515 607539, by the European Union within European Regional Development Fund, through grant Innovative Economy (POIG.01.01.02-00-008/08), by Wroclaw University of Technology statutory grant and Slovak-Polish International Cooperation Program no. SK-PL-0017-09.

#### **REFERENCES**

- [1] M. Kondow, K. Uomi, A Niwa, T. Kitatani, S Watahiki, Y. Yazawa, Jap. J. Appl. Phys., 1996, Vol. 35, P. 1273-1275.
- [2] S.R. Kurtz, D. Meyers, J.M. Olson, In: Proceedings of the 26<sup>th</sup> IEEE Photovoltaic Specialists Conference, Anaheim, USA, IEEE, New York, 1997, P. 875-878.
- [3] S.R. Kurtz, A.A. Allerman, C.H. Seager, R.M. Sieg, E.D. Jones, Appl. Phys. Lett., 2000, Vol. 77, P. 400-402.
- [4] M. Motyka, R. Kudrawiec, and J. Misiewicz, Phys. Status Solidi A, 2007, Vol. 204, P. 354-363.
- [5] B. Ściana, D. Pucicki, D. Radziejewicz, J. Serafińczuk, B. Paszkiewicz, A. Szyszka, M. Tłaczała, P. Poloczek, G. Sęk, J. Misiewicz, R. Srnanek, J. Kovac, In: Proceedings of 12th European Workshop on Metalorganic Vapour Phase Epitaxy, Bratislava, June 3-6, 2007, P. 109-112.
- [6] Growth and properties of GaAsN structures, J. Toivonen, Helsinki University of Technology, 2003.
- [7] Y. Fawang, N. Yoshiki, T. Masashi, Y. Takayuki, S. Shiro, J. of Cryst. Growth, 2005, Vol. 282, P. 29-35.