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Determination of indium and nitrogen contents of InGaAsN quantum wells by HRXRD study supported by BAC calculation of the measured energy gap*

D. PUCICKI[1†], K. BIELAK[1], R. KUDRAWIEC[2], D. RADZIEWICZ[1], B. ŚCIANA[1]

[1]Faculty of Microsystem Electronics and Photonics, Wrocław University of Technology, Z. Janiszewskiego 11/17, 50-372, Wrocław

[2]Inst. of Physics, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370, Wrocław

Determination of indium and nitrogen content in InGaAsN quantum wells (QWs) is often based on the analysis of high-resolution X-ray diffraction (HRXRD) measurements. The comparison of diffraction curves of two similar samples, with and without nitrogen, together with an assumption of constant indium incorporation efficiency during the growth of layers with and without nitrogen, may lead to a large deviation in the determined In and N content. The HRXRD curve simulations supported by bandgap determination and calculations seem to be a solution of this problem. Comparison of the results achieved from simulated HRXRD curves with the calculations of all QWs transitions measured by contactless electro-reflectance (CER) can lead to reduction of deviations in composition determination of InGaAsN quantum wells. The proposed algorithm was applied for investigation of InGaAsN QWs grown by atmospheric pressure metalorganic vapor phase epitaxy (APMOVPE).

Keywords: *dilute nitrides; composition determination; quantum well; BAC band-anticrossing model; HRXRD high resolution X-ray diffraction*

1. Introduction

InGaAsN alloys have attracted considerable attention in recent years not only because of the possibility of extending the wavelength range of GaAs-based photonic devices beyond 1 μm but also because of the opportunity of fundamental study on determination of uncommon physical properties [1–3]. Due to the large lattice mismatch between GaAs and zinc-blende-type GaN, small amount of substitutionally incorporated N causes a rise of substantial tensile strain in pseudomorphic GaNAs layers on GaAs. The most promising range of N concentration in the InGaAsN alloy seems to be below 2 %, where the band-gap reduction is sharp and the material quality quite good. Nowadays the nitrogen containing quaternary, GaAs based alloys are widely used in many optoelectronic devices like photovoltaic cells, photodetectors, lasers or optical amplifiers. Therefore, for elaboration of technology of such devices and determination of many material parameters of InGaAsN alloys, the compositions of these materials must be precisely determined.

There are few facts which create numerous problems with determination of indium and nitrogen content in InGaAsN layers. First of all, by adding nitrogen into InGaAs alloy the residual compressive strains corresponding to the presence of In are compensated by nitrogen related tensile strain. In agreement with Vegard's law, which expresses the InGaAsN lattice parameter as follows: $a_0^{In_yGa_{1-y}As_{1-x}N_x}(x,y) = x\cdot y\cdot a_0^{InN} + x\cdot(1-y)\cdot a_0^{GaN} + y\cdot(1-x)\cdot a_0^{InAs} + (1-x)\cdot(1-y)\cdot a_0^{GaAs}$, this situation leads to many different compositions of InGaAsN alloys with the same mismatch to GaAs lattice [4], which is illustrated in Fig. 1.

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†E-mail: Damian.Pucicki@pwr.wroc.pl

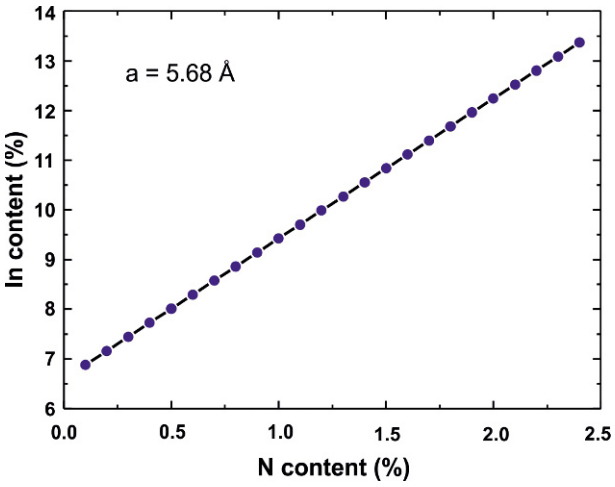


Fig. 1. Different combinations of indium and nitrogen contents for the InGaAsN lattice constant of 5.68 Å.

Secondly, there are many ways of nitrogen incorporation into InGaAsN layers leading to overestimation of nitrogen content. As discussed by Li *et al*. there are adverse conditions for interstitial incorporation of isolated nitrogen atoms due to their high formation energy in the lattice. Energetically favored are complexes such as split interstitial N–As complexes that induce a compressive strain in the crystal and N–N complexes, which causes less tensile strain than the substitutional N_{As} atoms. The presence of those complexes causes a considerable deviation from Vegard's law (up to 30 % for N content higher than 1.5 %) and the variation of the lattice constant with N content [5]. By the way, the above mentioned defects are responsible for forming the additional energy trap levels within the bandgap, which is the main reason of non-radiative recombinations. The third factor providing deviation, which is mostly observed in QWs, is a gradient profile of indium and nitrogen content along the layer. The inhomogeneous asymmetric distribution of nitrogen atoms along the growth direction seems to be induced due to the dominance of surface kinetics, nonlinear dependence of N incorporation on In content and the strain gradient effect on the effective diffusion of N [6]. All of the above mentioned factors have a significant influence on the shape of measured HRXRD curves of InGaAsN layers containing epistructures. Thus, it is impossible to determine simultaneously both the indium and nitrogen fractions in InGaAsN by applying the only one characterization technique such as high-resolution X-ray diffraction.

For precise determination of In and N content in InGaAsN alloys many techniques are often combined. In the literature, one can find several techniques proposed to be used simultaneously, like secondary ion mass spectroscopy (SIMS), HRXRD, transmission electron microscopy (TEM), Raman spectroscopy, ellipsometry or even optical absorption measurements [7–11]. In spite of many assumptions, the most common way to determine indium and nitrogen concentration in InGaAsN layers is a combination of HRXRD curves simulations with bandgap determination from photoluminescence (PL) spectroscopy [4].

For proper determination of In and N content of the InGaAsN alloys we proposed to support the diffraction curves simulations by contactless electro-reflectance measurements and indium and nitrogen contents calculations based on the band anticrossing (BAC) theory [12, 13]. By correlation of the QW transitions determined from CER measurements, the calculations of all QW subbands energies and HRXRD simulations allow us to obtain more precisely defined In and N content in investigated InGaAsN layers.

2. Experimental details

The investigated heterostructures were grown by atmospheric pressure metalorganic vapour phase epitaxy (APMOVPE) in AIX200 R&D AIXTRON horizontal reactor on (100)-oriented semi-insulating (SI) GaAs or Si-doped n-type GaAs substrates. Trimethylgallium (TMGa), trimethylindium (TMIn), tertiarybutylhydrazine (TBHy) and arsine (AsH_3:10 % mixture in H_2) were used as the growth precursors. High purity hydrogen was employed as a carrier gas. The following parameters were changed during the runs: the growth temperature Tg = 566 – 585 °C, the hydrogen flow rate through the saturator with TBHy $V_{H2/TBHy}$ = 1100 – 3000 ml/min.

Investigated undoped multi quantum well (MQW) structures consisted of 450 nm thick GaAs buffer and 3 × $In_yGa_{1-y}As_{1-x}N_x$/GaAs quantum wells region capped by 40 – 50 nm thick GaAs.

The optical and energetic properties of the grown heterostructures were investigated by PL and CER. In contrast to commonly used emission-type experiments such as PL, which usually probes only the ground state, the absorption-like measurement CER is one of the powerful tools, which allows one to investigate a large number of sharp spectral features including those related to excited state transitions in low-dimensional structures. CER spectroscopy is particularly useful because it is performed in contactless mode which is nondestructive for the samples. In addition, these technique is very sensitive at room temperature. Thus, in this paper we present the more detailed CER spectra of the discussed structures.

X-ray diffractometry was applied to study the structural properties of the grown epistructures. The HRXRD measurements were performed with MRD Philips diffractometer, exploiting a four-crystal Bartels monochromator and CuKα1 radiation. The X-ray diffractograms of the (004) symmetrical reflection were analyzed using dynamical diffraction analysis. X'Pert Epitaxy v.4.1 of PANalytical B.V. software was used for diffractograms simulations.

3. Results

As it was mentioned above, two nondestructive techniques: HRXRD and PL are combined and proposed as the most common solution to determine indium and nitrogen concentration in InGaAsN. Due to ambiguity of fundamental transition determination from PL peak positions, discussed also by Lu *et al.* [4], in our study we applied CER measurements to determine effective E_g of the investigated quantum wells. In Fig. 2 one can see the difference of the PL maxima positions for the examined samples #NI43n and their fundamental transitions energy taken from the CER measurement.

Then the following algorithm was proposed in order to determine In and N content. The thicknesses and the compositions of InGaAsN QWs were preliminary determined from the periods and positions of the satellite peaks of the measured XRD curves and the growth rates. These values were used to calculate the effective E_g of the QWs by using BAC theory. Then the bandgap energy, calculated from the preliminary obtained In and N content, was compared with the energies of the first resonance on the CER spectra which are attributed to transitions between heavy-hole and electron subbands (Fig. 3). If there are the differences between the bandgap energies obtained from the calculations and from CER measurements, the HRXRD analysis must be improved. The simulations of the X-ray diffractograms were carried on until fitting between the simulated and measured curves was reached and the obtained In and N content applied in BAC calculations gave the energy gap E_g converged with the CER measurements. In that way the grown InGaAsN/GaAs MQW containing structures were characterized before application of the new algotithm, described below.

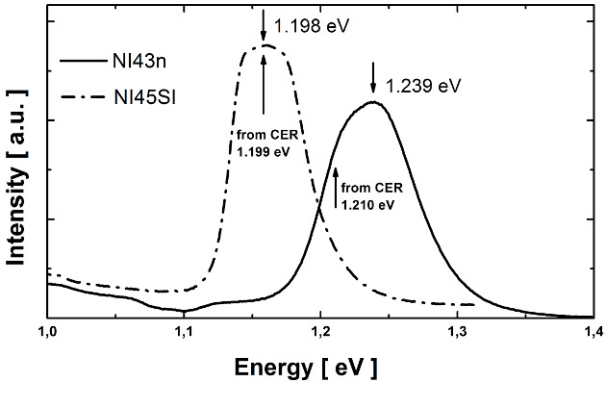


Fig. 2. PL spectra of the #NI43n and #NI45SI samples containing 3 × InGaAsN/GaAs QWs with marked first CER resonance energy.

Unfortunately, we demonstrated that in case of investigated structures, there were several different compositions of InGaAsN alloys which provided convergence of the HRXRD simulation and bandgap calculations with the measurements, which is illustrated in Fig. 4.

To increase the accuracy of the In and N content determination we proposed to take into consideration all of the QWs transitions measured by

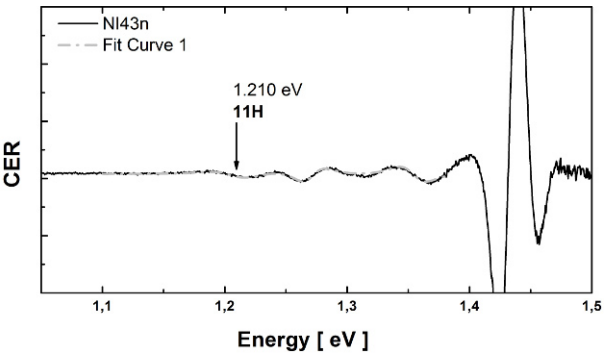
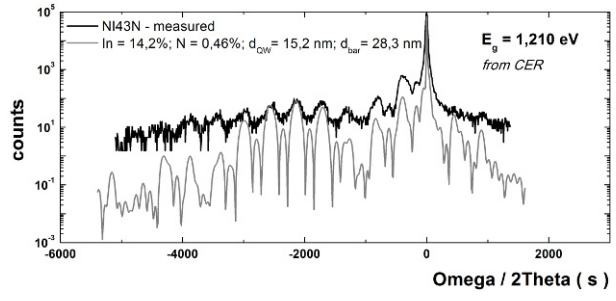
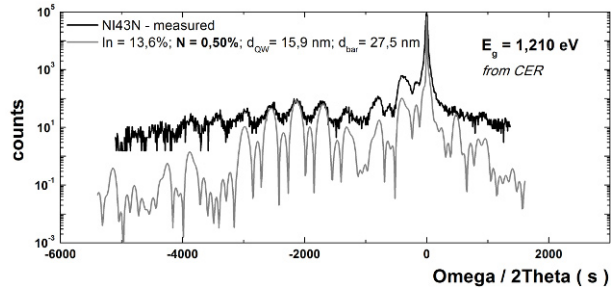


Fig. 3. CER spectrum of the #NI43n samples containing 3 × InGaAsN/GaAs QWs grown on the n-type (100) GaAs substrate with marked first QWs resonance.



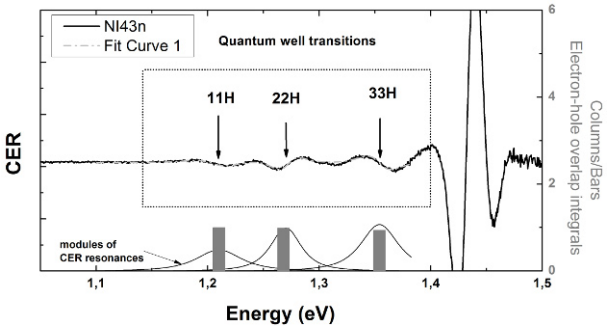
(a)



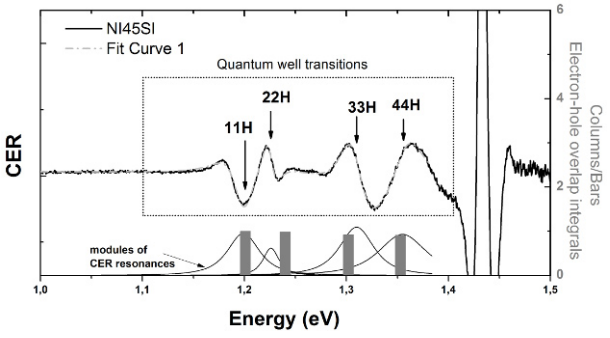
(b)

Fig. 4. The (004) $\omega/2\theta$ diffraction rocking curve of the InGaAsN/GaAs MQW structure #NI43N with obtained two different simulations (a) and (b) (gray curves) resulting from different In and N contents.

CER (Fig. 5) and to calculate higher energy levels of the quantum wells too. In the algorithm, besides a comparison with the calculations of the first QW transition, we proposed the comparison with all of them. The In and N content determination procedure by correlation of HRXRD simulations with the QWs transitions calculations can be finished when the convergence of simulated and measured X-ray diffractograms with QWs calculations and CER spectrums is achieved.



(a)



(b)

Fig. 5. CER spectra of the samples containing 3 × InGaAsN/GaAs QWs with marked QWs transitions: (a) sample #NI43n and (b) sample #NI45SI.

The calculations of QWs transitions were performed within the framework of the usual envelope function approximation [14]. The excitonic effect was neglected. The band anticrossing model with parameters E_N and C_{NM} dependent on the indium content [13] was applied in order to find the band gap energy for InGaAsN layers. According to the BAC model we have assumed that the influence of nitrogen localized states on the valence band structure is neglected and the effective mass of light and heavy hole does not change after adding nitrogen atoms. The electron effective mass was assumed to be 50 % larger than in N-free host that is in accordance with BAC model predictions and experimental studies of electron effective mass in this materials system [15]. The conduction band offset for

unstrained InGaAsN/GaAs interface has been assumed to be 80 %. The biaxial strain was calculated based on the Pikus-Bir Hamiltonian. The energy shifts due to hydrostatic d_{EH} and shear d_{ES} strain components, strain tensor in the plane of the interfaces, C_{11} and C_{12} elastic stiffness constants and the hydrostatic and shear deformation potentials were taken into account as it was described in [15].

It is well known that the composition of the InGaAsN influences the energy of the QWs transitions. On the other hand, the width of the QWs influences the energies of transitions and energy differences between them. Thus, the complete simulation of all QWs transitions correlated with HRXRD curves simulations can lead to confirmation of the determined compositions and thicknesses of the InGaAsN QWs.

The structure was characterized according to the above mentioned algorithm and the compositions and thicknesses of the grown InGaAsN QWs were determined. For the structures #NI43n, whose parameters are presented in the Fig. 4, the nitrogen content, indium content and QWs thickness were now defined as 15.5 %, 0.41 % and 13.7 nm, respectively. The (004) $\omega/2\theta$ diffraction curve of the #NI43n InGaAsN/GaAs triple QWs structure is illustrated in Fig. 6. The same algorithm was applied for investigation of the #NI45SI InGaAsN/GaAs triple quantum well structure. The CER spectrum with marked energies of QWs transitions is shown in Fig. 5b. The (004) $\omega/2\theta$ diffraction curve of this sample is presented in Fig. 7. For that sample the nitrogen content, indium content and QWs thickness were determined as 14.6 %, 0.54 % and 9.1 nm, respectively.

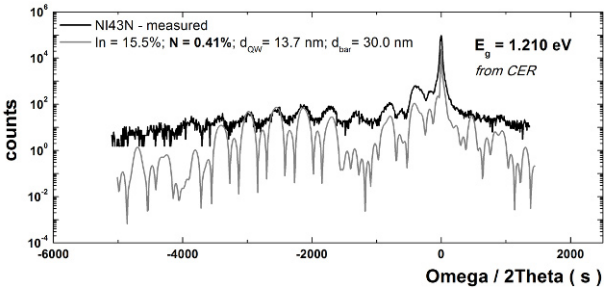


Fig. 6. (004) $\omega/2\theta$ diffraction rocking curve of the #NI43n 3 × InGaAsN/GaAs MQW structure.

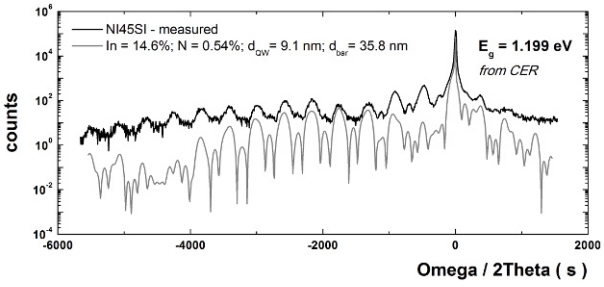


Fig. 7. (004) $\omega/2\theta$ diffraction rocking curve of #NI45SI 3 × InGaAsN/GaAs MQW structure.

The values of the transitions energies of the discussed MQW structures both the calculated and obtained from CER measurements are collected in the Table 1.

4. Conclusions

In this work we present the new algorithm for determination of indium and nitrogen content in InGaAsN quantum wells. The HRXRD curves simulations in combination with CER measurements and all QWs transitions calculations were proposed to increase the accuracy of InGaAsN compositions determination. In the case of considered structures, the energies of QWs transitions were compared with theoretical calculations which allowed us not only to determine the In and N contents but also to prove the thicknesses of the grown QWs.

By using only HRXRD or CER measurements for InGaAsN composition determination a lot of ambiguity leading to over- or underestimation of In and N content may occur. By applying the suggested algorithm to investigate the InGaAsN/GaAs MQW structures, the ambiguity of subjective convergence of simulated and measured XRD curves was eliminated. In addition, the thicknesses of the QWs and barrier layer were confirmed by separation of the energy states in QWs. In the case of mentioned structures #NI43n and #NI45SI, the described methods of structural characterization led finally to better convergence of the HRXRD simulations which provided more accurate In and N contents in investigated QWs. For sample #NI43n the indium content, nitrogen content and the QWs thicknesses were determined to be 15.5 %, 0.41 % and 13.7 nm, respectively.

Table 1. Comparison of the calculated energies of the QW transitions and the energies obtained from the CER measurements.

#NI43n			#NI45SI		
Transitions	Energies from CER	Calculated energies	Transitions	Energies from CER	Calculated energies
11H	1.210	1.210	11H	1.199	1.201
22H	1.270	1.268	22H	1.226	1.240
33H	1.354	1.354	33H	1.310	1.302
			44H	1.355	1.353

The sample #NI45SI contained three 9.1 nm thick $In_{0.146}Ga_{0.854}As_{0.9946}N_{0.0054}$ QWs.

Due to mutual compensation of strain induced by In and N in the InGaAsN alloy and different ways of nitrogen incorporation it is impossible to get information about structural properties of InGaAsN layer using only one method of characterization. The proposed algorithm allows one not only to confirm the QWs thickness but also get more precise information about the contribution of indium and nitrogen in the band structure formation, which is the result of the bigger change of the electron effective mass as a function of nitrogen content in InGaAsN compared to the influence of indium.

Moreover, the proposed method of structural characterization can be also used for investigation of the inhomogeneous QWs with a gradient of In or N content or even step like QWs. The HRXRD curves of that type QWs can be also simulated using X'Pert Epitaxy software and the inhomogenity of the QWs can be observed in the separation of CER resonances.

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