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

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ABSTRACT

The $In_yGa_{1-y}As_{1-x}N_x$ 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 μm 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 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

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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 × 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 (TMAl), 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 growth parameters were changed: the growth temperature T_g=566 ÷ 585 °C, the hydrogen flow rate through the saturator with TBHy - $V_{H2/TBHy}$=1100 ÷ 3000 ml/ min, the ratio of the gallium to indium source concentration in the gas phase III_{Ga}/III_{In}=4.8 and 6.9. Stable parameters during all runs were: the arsine flow rate V_{AsH3}=50 ml/ min (for GaAsN and InGaAsN) and 300 ml/ min (for GaAs), the total flow of the hydrogen carrier gas V_{H2tot}=9.6 l/ min, the organic source temperatures: T_{TMGa}=-10 °C, T_{TMAl}=18 °C, T_{TMIn}=20 °C, T_{TBHy}=30 °C.

Two types of samples were investigated:

1. Undoped $GaAs_{1-x}N_x$/GaAs heterostructures consisted of 450 nm thick GaAs buffer and ~180 nm thick $GaAs_{1-x}N_x$ (samples: N41, N42, N44, N47, N48, N54).

2. Undoped MQW structure consisted of 450 nm thick GaAs buffer and 3 × $In_yGa_{1-y}As_{1-x}N_x$/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 AIIIBV-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 $GaAs_{1-x}N_x$/GaAs and MQW 3 × InGaAsN/GaAs heterostructures. *Fig. 1a* shows symmetric (004) scans of $GaAs_{1-x}N_x$ films with different nitrogen contents (x=0.55, 0.65, 1.5 %).

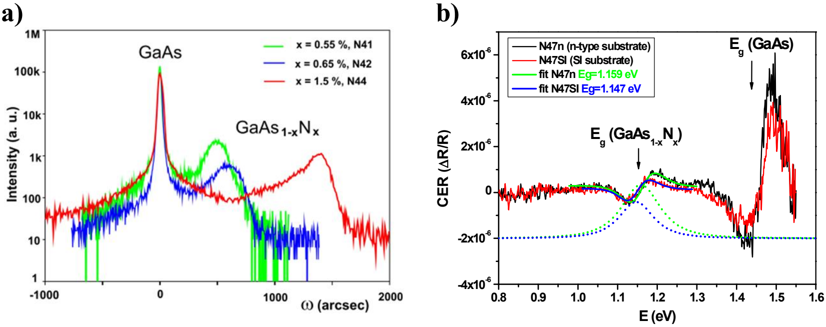

Fig. 1 – a) Rocking curve for the (004) reflection of $GaAs_{1-x}N_x$ with different nitrogen content; b) CER spectra of $GaAs_{1-x}N_x$ grown on n-type and SI GaAs substrate

For higher values of nitrogen the $GaAs_{1-x}N_x$ 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 $GaAs_{1-x}N_x$ (x=1.95 %) grown on n-type and SI GaAs substrates. Based on the transition related to $GaAs_{1-x}N_x$ 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 GaAs$_{1-x}$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 GaAs$_{1-x}$N$_x$ epilayers grown at T_g=566 °C as a function of the hydrogen flow rate through the saturator with TBHy - $V_{H2/TBHy}$. The growth temperature of 566 °C determined from our earlier results [5] guarantees the efficient nitrogen incorporation without degradation of the structural quality. The GaAs$_{1-x}$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 GaAs$_{1-x}$N$_x$ films. The most efficient nitrogen incorporation occurs in the range of $V_{H2/TBHy}$=1500 ÷ 2500 ml/ min, above 2500 ml/ min the saturation of the nitrogen content is observed. The lowest value of the GaAs$_{1-x}$N$_x$ band gap of 1.12 eV was determined from CER spectra for the sample N54 (x=2.26 %).

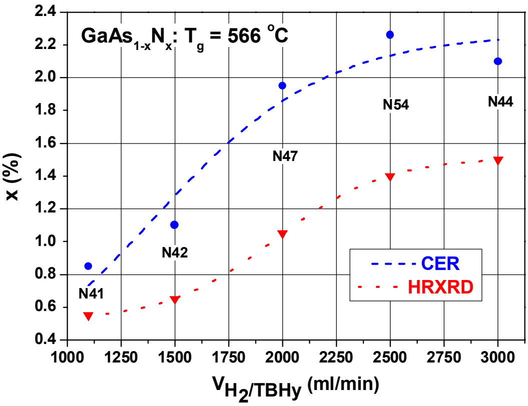

Fig. 2 – The nitrogen content in GaAs$_{1-x}$N$_x$ grown at T_g=566 °C versus the flow rate $V_{H2/TBHy}$ estimated from rocking curves (HRXRD) and CER spectra

In the case of MQW structures the main efforts were focused on optimization the growth parameters to get the In$_y$Ga$_{1-y}$As$_{1-x}$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, 585 °C; $V_{H2/TBHy}$=1500 ml/ min; III$_{Ga}$/III$_{In}$=4.8. The symmetric (004) HRXRD scans for the MQW structures grown at 566 °C (NI43) and 585 °C (NI46) are presented in figure 3a. It seems that the interface quality is better for the sample NI46 grown at 585 °C. The nitrogen and indium contents in In$_y$Ga$_{1-y}$As$_{1-x}$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 (~11 %) with increasing T_g.

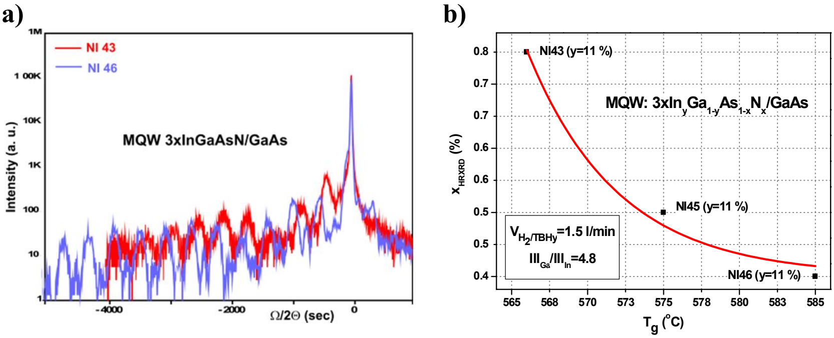

Fig. 3 – a) The symmetric (004) HRXRD scans for the MQW structures grown at 566 °C (sample NI43) and 585 °C (sample NI46); b) the nitrogen content in $In_yGa_{1-y}As_{1-x}N_x$ quantum wells as a function of the growth temperature T_g

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.

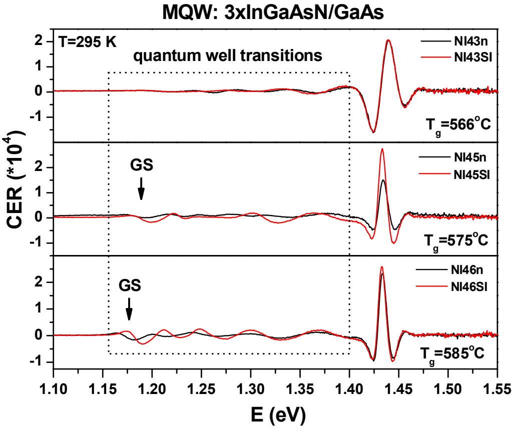

Fig. 4 – CER spectra of the MQW structures grown at 566 °C (sample NI43), 575 °C (sample NI43) and 585 °C (sample NI46). Black and red line corresponds to the n-type and undoped SI GaAs substrate, respectively

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 $In_yGa_{1-y}As_{1-x}N_x$ by increasing the III_{Ga}/III_{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 with increasing the indium content. Our first experimental results and HRXRD measurements showed that by increasing the III_{Ga}/III_{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 distri-bution inside the investigated structures. The SIMS profiles of $GaAs_{1-x}N_x$/GaAs (sample N54) and MQW (sample) heterostructures are presented in *fig. 5*.

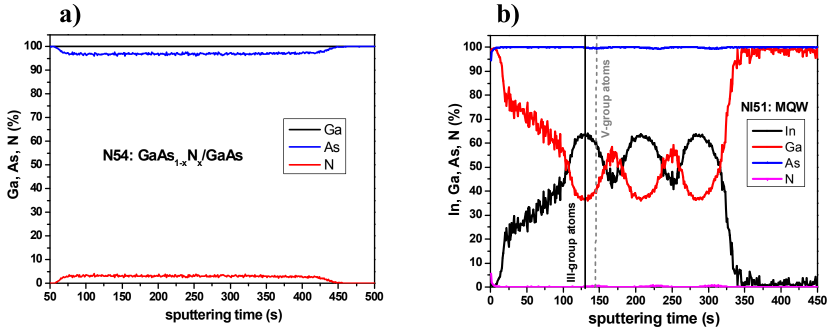

Fig. 5 – SIMS profiles of heterostructures: *a* – GaAsN/GaAs (sample N54); *b* – MQW (sample NI51).

The nitrogen concentration in $GaAs_{1-x}N_x$ (*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 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 InGaAsN/GaAs interface.

CONCLUSIONS

This work presents the optimization of the epitaxial growth of undoped GaAsN layers and multiple quantum well (MQW) - 3 × InGaAsN/GaAs - structures obtained by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE). The optimal growth parameters for GaAsN with the band gap near 1 eV are: T_g=566 °C, $V_{H2/TBHy}$=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

$In_yGa_{1-y}As_{1-x}N_x$ wells grown at higher temperatures the III_{Ga}/III_{In} ratio was increased. First experimental results confirmed this decision.

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