

Electro-optical properties of diluted GaAsN on GaAs grown by APMOVPE*

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In this paper we report on the optical and electrical studies of single $GaAs_{1-x}N_x$ epitaxial layers grown on GaAs substrates by means of atmospheric pressure metal organic vapour phase epitaxy (APMOVPE). Three kinds of samples with 1.2 %, 1.6 % and 2.7 % nitrogen content were studied. Optical properties of the layers were investigated with the use of room temperature transmittance and reflectance measurements. Subsequently Schottky Au–GaAs_{1-x}N_x contacts were processed and characterized by current-voltage (*I-V*) and capacitance-voltage (*C-V*) measurements within 80 – 480 K temperature range. From the *I-V* and *C-V* characteristics the ideality factor, series resistance and built-in potential were determined. Obtained diodes can be used for further studies on defects with the use of DLTS method.

Keywords: GaAs_{1-x}N_x; I-V; C-V; transmittance and reflectance spectra.

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1. Introduction

Dilute nitride semiconductors, such as $GaAs_{1-x}N_x$ and $In_yGa_{1-y}As_{1-x}N_x$ alloys, have attracted considerable attention due to their unique physical properties and wide range of their possible application in optoelectronics, especially in infrared laser diodes for 1.3 and 1.55 μ m [1, 2] and high efficiency multi-junction solar cells (MJSC) [3, 4]. The introduction of small amounts of nitrogen into GaAs drastically decreases the band gap energy of $GaAs_{1-x}N_x$ structure down to about 1 eV and simultaneously reduces the lattice parameters of the crystal. This phenomenon provides great possibilities of growing $GaAs_{1-x}N_x$ layers lattice matched to GaAs substrates. In present paper single undoped $GaAs_{1-x}N_x$ epitaxial layers grown on GaAs by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE) were investigated. APMOVPE is relatively cheap in comparison with molecular beam epitaxy (MBE) and low pressure metal organic vapour phase epitaxy (LPMOVPE) methods. Additionally, the growth dynamics is easy to control and the suitable optimization of APMOVPE technological parameters allows one to obtain the epitaxial heterostructures with material quality comparable with two mentioned techniques. The growth parameters determined for APMOVPE can be easily adapted to LPMOVPE, however, MOVPE growth in atmospheric pressure conditions decreases the amount of structural defects connected with dangling bonds which are saturated by the overflow of hydrogen. The main growth parameters (growth temperature and the hydrogen flow rate through the bubbler with the organic nitrogen source) were changed to achieve the material quality and alloy composition suitable for application in MJSCs. The optical properties of the investigated structures were examined using room

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temperature (RT) transmittance (T) and reflectance (R) measurements. Based on these measurements the N content -x of the layers was estimated and compared with those obtained from high resolution X-Ray diffraction (HRXRD), contactless electroreflectance (CER) and photocurrent (PC) analysis. The aim of present studies was to achieve Schottky diodes with rectifying properties enabling application of the space charge techniques to study defects in the structures. Therefore, the layers were used to define Schottky contacts and the contacts were characterized by electrical methods: current - voltage (I-V) and capacitance - voltage (C-V)measurements. Obtained contacts can be used to perform DLTS studies on defects present in the layers.

2. Samples

The investigated structures were grown by APMOVPE in AIX200 R&D AIXTRON horizontal reactor on (100)-oriented Si-doped n-type GaAs substrates. Trimethylgallium (TMGa), tertiarybutylhydrazine (TBHy) and arsine (AsH₃) were used as the growth precursors. High purity hydrogen was employed as a carrier gas. During runs the hydrogen flow rate was changed through the saturator with TBHy $- V_{H2/TBHy} = 1500 -$ 3000 ml/min. The other parameters were as follows: growth temperature Tg = 566 °C, arsine flow rate V_{AsH3} = 50 ml/min (for GaAsN) and 300 ml/min (for GaAs), total flow of the hydrogen carrier gas V_{H2tot} = 9.6 l/min, organic source temperatures: T_{TMGa} = -10 °C, T_{TBHy} = 30 °C.

In this paper three kinds of samples with different nitrogen contents x, labeled by us as N42N, N48N and N44N were investigated. Nitrogen content was determined by *HRXRD* measurements to be equal to 1.2 %, 1.6 % and 2.7 %, respectively [5]. The GaAs_{1-x}N_x/GaAs heterostructures consisted of 450 nm thick GaAs buffer and 200 – 300 nm thick GaAs_{1-x}N_x layer (Fig. 1). To measure electrical properties of the junctions gold Schottky contacts of 0.5 mm² area were prepared by electrolitography technique on the front side of the GaAs_{1-x}N_x layer. An AuGe served as the ohmic contact to the n-type GaAs substrates.



Fig. 1. A diagram of $GaAs_{1-x}N_x/GaAs$ heterostructures.

3. Experimental

The transmittance and reflectance measurements were carried out at room temperature (RT), while *I-V* and *C-V* measurements were performed within the temperature range of 80 K to 480 K. The transmitted and reflected light was dispersed by triple grating Czerny-Turner monochromator and detected by Ge and Si detectors with a lock-in amplifier. The current-voltage (*I-V*) and capacitancevoltage (*C-V*) characteristics were measured with the use of the system developed at Warsaw Institute of Physics Polish Academy of Sciences and by the Microelectronics and Nanostructure Group at School of Electrical and Electronic Engineering at the University of Manchester.

In order to estimate the value of energy gap, absorption and reflectance spectra were measured at room temperature. The first derivative of the absorption coefficient has a maximum in the vicinity of the band gap [6, 7] whereas the reflectance spectrum exhibits a "dip" at the same wavelength.

According to the thermionic emission model, the I-V characteristics of a metal-semiconductor junction can be analyzed by the following equation [8]:

$$I = SA^*T^2 \exp(-\frac{q\Phi_B}{kT}) \left[\exp\left(\frac{q(V - IR_s)}{nkT}\right) - 1 \right]$$
(1)

where S is the Schottky contact area, A^* – the effective Richardson constant, T – temperature, q – the elementary charge, Φ_B – Schottky barrier height, k – Boltzmann constant, R_s – series resistance and n – ideality factor. Built-in voltage (a barrier height as it is seen from the semiconductor side), V_{bi} , and Φ_B are interrelated [8]:

$$q\Phi_B = qV_{bi} + E_{F_n} \tag{2}$$

where E_{Fn} is Fermi level distance from the conduction band edge.

The ideality factor *n* is given by equation:

$$n = \frac{q}{kT \cdot \frac{d(\ln I)}{dV}} \tag{3}$$

and it can be determined from the linear part of the *I-V* characteristics represented in a semilogarithmic $\ln I-V$ plot. Schottky barrier height can be also determined with the use of the $\ln I-V$ plot from the extrapolated value of current density at zero voltage. Next, the value of built-in voltage V_{bi} can be determined with the help of equation 2 once E_{Fn} is known.

For a metal-n-type semiconductor Schottky diode, *C-V* measurements yield the donor net concentration N_{C-V} and the value of built-in voltage V_{bi} . The relation between capacitance and voltage is given by [9]:

$$\frac{S^2}{C^2} = \frac{2(V_{bi} + V)}{\varepsilon_s \varepsilon_0 q N_{C-V}} \tag{4}$$

where ε_s is the semiconductor permittivity and ε_0 – the vacuum permittivity. The slope of the $\frac{S^2}{C^2}$ against V plot reveals N_{C-V} whereas V_{bi} can be obtained from the intersection of the $\frac{S^2}{C^2}$ line with the voltage axis. Based on the N_{C-V} Fermi level position E_{Fn} can be calculated using formula [8]:

$$E_{F_n} = \frac{kT}{q} \ln \frac{N_c}{N_{C-V}} \tag{5}$$

where N_C is the density of states at the bottom of conduction band. Subsequently, Schottky barrier height may be obtained using Eq. 2.

4. Results and discussion

Optical properties of the studied heterostructures were verified by the transmittance and reflectance measurements. Fig. 2. shows a room temperature transmittance spectra of $GaAs_{1-x}N_x/GaAs$ samples. Using the transmittance and reflectance spectra the energy corresponding to the band gap of $GaAs_{1-x}N_x$ and GaAs can be determined. Comparisons of the reflectance with the derivative of transmittance spectra for N42N, N48 and N44 are given in Figs. 3, 4, 5, respectively. The arrows indicate the excitonic band gap transition of $GaAs_{1-x}N_x$ and the dotted lines – GaAs band gap.



Fig. 2. Transmittance spectra of $GaAs_{1-x}N_x/GaAs$ samples. The inset shows derivatives of the transmittance.



Fig. 3. Reflectance spectrum and derivative of the transmittance spectrum for N42N.

Using the transmittance and reflectance measurements (more accurately a maximum of transmittance derivative and reflectance "dip") the energy, which corresponds to excitonic band gaps of the GaAs_{1-x}N_x for samples N42N, N48N and N44N (Table 1) have been determined.



Fig. 4. Reflectance spectrum and derivative of the transmittance spectrum for N48N. The arrows point to the excitonic band gaps of the $GaAs_{1-x}N_x$ layers, and the dotted lines indicate GaAs band gap.



Fig. 5. Reflectance and derivative of the transmittance spectra for N44N.

Once the energy of the excitonic band gap is determined, the $GaAs_{1-x}N_x$ nitrogen content x can be extracted from the equation:

$$\Delta E_g = 3.91 x^{2/3} \tag{6}$$

where $\Delta E_g = E_g (GaAs) - E_g (GaAs_{1-x}N_x)$ [6, 10] (at RT $E_g (GaAs) = 1.42$ eV). The strength of this model is in its excellent agreement with the experimentally determined band gap of GaAs_{1-x}N_x with $10^{-3} < x < 10^{-2}$ [6, 10]. Table 1 presents a comparison of nitrogen contents x for the studied samples (N42N, N48N and N48N) obtained by different methods: transmittance, reflectance, *CER* [5], *XRD* [5] and *PC* [5] measurements.

It can be noticed that nitrogen content for sample N42N estimated with the help of various methods is similar, regardless of the used method. In the case of sample N48N its nitrogen content determined from the measurement of transmittance is close to the value calculated using the HRXRD method, but differs from the value obtained with the CER method. For N44N, comparable results were obtained by means of transmittance, CER and PC. The HRXRD result is higher. The above conclusions are true taking into account that the experimental error for nitrogen content x obtained from the T and R measurements has been estimated as 0.02 %. In the paper [5] there was no information on the experimental error for nitrogen content x which was obtained from CER, XRD and PC measurements.

Table 1. Comparison of nitrogen contents x for the studied samples (N42N, N48N and N48N) obtained by different methods.

Sample	Energy	x (%)	x (%)	x(%)	x(%)
	(eV)	T and R	CER	HRXRD	PC
N42	1.229	1.08	1.10	1.2	1.06
N48	1.137	1.96	1.04	1.6	_
N44	1.126	2.06	2.10	2.7	2.21

Rectifying properties of the studied Schottky Au–GaAsN diodes were verified by the *I-V* and *C-V* measurements within the temperature range 80 K to 480 K. Fig. 6a shows the *I-V* curves for all samples measured at 400 K. The built-in voltage V_{bi} , series resistance R_s and ideality factor were calculated using the *I-V* characteristics with the use of equations 1, 2, 3, 5 and N_{C-V} was obtained from *C-V* measurements. The results are given in Table 2. The room temperature $\frac{S^2}{C^2}$ (V) characteristics are shown in Fig. 7. A good linearity of the characteristics up to -1 V allowed us to apply Eq. 4 to determine built-in voltage V_{bi} and carrier concentration N_{C-V} (Tab. 2).

Exemplary results collected in Fig. 6, 7 and in Table 2 let us conclude that the rectifying proper-

Sample	T(K)	<i>I-V</i> characteristics			C-V characteristics		
		$V_{\rm bi}(V)$	$Rs(\Omega)$	n	$V_{\rm bi}$ (V)	$N_{\text{C-V}} (cm^{-3})$	
N42	400	0.54	26.75	1.63	0.74	8.0×10^{15}	
	200	1.72	11.43	4.21	2.25	1.7×10^{16}	
N48	400	0.66	43.10	1.82	0.78	9.0×10^{15}	
	200	2.03	26.65	8.04	2.49	1.5×10^{16}	
N44	400	0.63	46.97	1.64	0.77	8.8×10^{15}	
	200	1.93	28.89	4.17	2.49	1.5×10^{16}	

Table 2. Parameters obtained from the *I-V* and *C-V* characteristics.



Fig. 6. *I-V* characteristics: (a) The ln*I(V)* curve measured at T = 400 K for different samples. The inset shows *I-V* characteristics in a linear scale, (b) The ln*I(V)* curves at different temperatures for the sample N44N.

ties of the diodes deteriorate at lower temperatures for both, the ideality factor and built-in voltage increase. In Table 2 the values of built-in voltage determined from I-V characteristics are lower than those calculated from the C-V measurements. This result is in accordance with the fact that in reality Schottky contacts (metal layers) are deposited so that they were either polycrystalline or amorphous. Therefore the result is not surprising because the current always chooses the channels with lower barrier heights. Series resistances are low enough to perform DLTS studies on the diodes within a wide range of temperatures.

5. Conclusions

In summary, we present in this study the results of optical characterization of $GaAs_{1-x}N_x$ heterostuctures grown by atmospheric pressure metal organic vapour phase epitaxy (APMOVPE) on GaAs substrates. Using transmittance and reflectance measurements energy gap E_g was determined and the nitrogen content was calculated for the three samples (N42N, N48N and N44N). The value of nitrogen contents were compared with the values obtained by other methods. Schottky Au-GaAs_{1-x}N_x/GaAs diodes were processed and characterized by I-V and C-V measurements. The ideality factor, series resistance and built-in potential were determined. The obtained Schottky Au- $GaAs_{1-x}N_x/GaAs$ diodes can be used for further studies on defects with the use of DLTS method.



Fig. 7. (a) The *C*-*V* characteristics at T = 400 K for the studied samples. The inset shows the $S^2/C^2(V)$ curve, (b) The *C*-*V* curves at various temperatures for the sample N44N.

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