ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 13, No. 1. 2007

Effects of the Low Energy Ion Beam Nitridation on GaAs Surface Structure and Electrical Characteristics of Au-*n*GaAs and Co-*n*GaAs Schottky Contacts

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Received 06 October 2006; accepted 29 January 2007

Effects of the 65 eV – 320 eV energy nitrogen ion beam irradiation on surface structure and electrical properties of the Au -GaAs and Co-GaAs Schottky contacts were investigated. Formation of the thin GaN or $GaAs_xN_{1-x}$ type layer as a result of the GaAs surface 65 eV and 320 eV nitrogen ion beam treatment was observed. Thickness of this layer increased with increase of the ion energy and ion current density. Ion beam nitridation in all cases resulted in decreased effective barrier height of Au-*n*GaAs and Co-*n*GaAs Schottky contacts. Low frequency noise of the irradiated Schottky contacts measured at room and liquid nitrogen temperatures in all cases exceeded noise of the reference samples. Current-voltage (I-V) characteristics of Au-GaAs and Co-GaAs fabricated on nitrogen ion beam irradiated GaAs surface were very similar. It means, that I-V characteristics of these contacts depends on properties of the irradiation modified GaAs surface layer. There were revealed, that the influence of the nitrogen ion beam irradiation on electrical characteristics of the Schottky contacts increases with increase of the ion energy, ion current density and treatment time. GaAs Schottky contact low frequency noise level, non-ideality factor and effective barrier height increased as a result of the ion irradiation angle change from glancing (oblique) to the normal.

Keywords: GaAs, ion beam nitridation, Schottky contact, electrical properties, XPS.

1. INTRODUCTION

GaAs surface nitridation by plasma or low-energy ion beam received considerable interest. The first reason for such a interest is related to the difficulties to grow epitaxial GaN layers onto the technologically well-established substrates such as GaAs due to the lattice mismatch between the growing film and substrate. In such a case the buffer layer can be formed by GaAs nitridation to overcome lattice-mismatch [1, 2]. On the other hand, control of the electronic properties of GaAs surface as well as reduction of the high density of surface states are the key issues in the fabrication of the GaAs-based electronic and optoelectronic devices [3 – 5].

GaAs surface nitridation by low energy ion beam has some advantages over plasma nitridation process due to the increased possibilities to control parameters of the technological process such as ion beam energy and ion current density. In such a way ultrathin GaN layers can be formed even at room temperature [6 – 9]. However, many aspects of the GaAs ion beam nitridation effects remains unclear, while some reported data are contradictory. Different authors used ion beams of different energy for GaAs surface nitridation: 500 eV [6], 1.2 keV [7], 0.5 keV – 3 keV [8, 9]. Irradiation by ion beam of such energy results in creation of the defects at the GaAs surface. The influence of that defects can be observed by measuring the electrical properties of metal-GaAs contact: decrease of the effective barrier height for n-type semiconductor and increase for p-type semiconductor [10 – 12]. Effects of the hydrocarbon ion beam resulted in larger decrease of the ion beam treatment dependence upon ion incidence angle – GaAs surface glancing angle irradiation by 800 eV energy resulted in lower effective barrier height of the GaAs Schottky contact in comparison with the case of the irradiation at 45° angle [12]. However, glancing angle irradiation results in lower level of the low frequency noise as well [12]. While there were reported in [13], about the decreased thickness of the nitrided GaAs surface layer with increase of the ion incidence angle. It can be mentioned, that formation of the defects as a result of Ar ion beam irradiation of GaAs surface was not observed only when ion beam energy was <50 eV [14]. GaAs surface irradiation by Xe ion beam before evaporation of the metal resulted in improvement of the GaAs Schottky contact properties (increase of the effective barrier height and decrease of the nonideality factor) when ion beam energy was <80 eV [15]. Therefore, ion beam energy should be decreased to avoid formation of the radiation defects as a result of the GaAs ion nitridation. However, there are few studies regarding effects of the GaAs surface irradiation by <500 eV energy nitrogen (NH_3, N_2+H_2) ion beam. The influence of the ion incidence angle must considered as well.

In present study effects of the GaAs surface nitridation by 65 eV – 380 eV energy ion beam were investigated. The influence of the angle of the ion incidence were studied as well.

2. EXPERIMENTAL

Ion beam nitridation of GaAs surface has been performed using closed drift ion source. Parameters of the technological process are presented in Table 1.

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In this research, the samples (Schottky barrier diodes) for study of the electrical characteristics were fabricated on epitaxial *n*GaAs (100) wafers doped at 10^{17} cm^{-3}. Au-Ge-Ni ohmic contacts were deposited on n^+-substrate after degreasing in dimethylformamide and acetone. The sintering of the ohmic contacts was completed by the 15 min heating at 330 °C temperature in N_2 gas ambient. After the same chemical cleaning, (like in the case of ohmic contact) and surface etching in $NH_4OH : H_2O_2 : H_2O = 3 : 1 : 144$ solution the samples were immediately loaded into the vacuum equipped with a closed drift ion source. Parameters of the ion beam nitridation technological process are presented in Table 1. In most cases nitridation was performed using as a reagent N_2 gas. In several experiments $N_2 + H_2$ (97 : 3) gas mixture has been used. After the surface treatment by ion beam, samples were immediately reloaded into the another vacuum unit were Schottky contact metal was deposited on the ion beam irradiated GaAs surface. The Schottky contact metallization was 300 nm thickness Au or Co layer. Diameter of the circular Schottky contacts was 500 μm. Reference samples were fabricated without any ion beam treatment step.

Table 1. Technological parameters of the ion beam nitridation process

Temperature (K)	293
Energy (eV)	65 – 380
Ion beam current density ($\mu A/cm^2$)	6 – 200
Angle of incidence	0° (normal to surface), 70°
Gas used	N_2 $N_2 + H_2$ (97 : 3)
Work pressure (Pa)	$4 \cdot 10^{-2} – 10^0$

Samples for XPS analysis were formed without the any ohmic contacts. GaAs pieces after the ion beam nitridation were immediately loaded into the XPS analysis system.

Current-voltage characteristics of the Schottky contacts have been measured using the picoammeter/voltage source Keithley 6487. Capacitance – voltage characteristics of the samples were investigated using a capacitance meter E7-12 (at 1 MHz frequency).

One of the main parameters of a metal-semiconductor interface is height of the potential barrier between the metal and semiconductor (Schottky-barrier height). Schottky barrier height is a measure of the mismatch of the energy levels for majority carriers across the MS interface [16]. The Schottky barrier height controls the electronic transport across MS interfaces and is, therefore, of vital importance to the successful operation of any semiconductor device [16]. In the present study barrier heights φ^*_b of the Schottky contacts were calculated from forward I-V characteristics using thermionic emission model [17]. In such a case possible influence of other charge carrier flow mechanisms such as tunneling and generation-recombination has been neglected. As a result barrier height calculated in such a way can substantially differ from the real Schottky barrier height. Therefore, it is called effective barrier height. Schottky contact effective barrier height $\varphi^*_{C\text{-}V}$ has been calculated from capacitance-voltage characteristics measured in reverse bias region as well [17]. Comparison of the effective barrier heights calculated by different methods can provide additional information about the homogeneity of the Schottky contact of the samples [16].

The spectra of the voltage fluctuations in the Schottky contacts were measured within a frequency range from 30 kHz to 20 kHz at constant current mode at a temperature range from 77 K to 380 K using spectrum analyzer CK4-72.

The X-ray Photoelectron spectra were recorded with the KRATOS ANALYTICAL XSAM800 XPS analyzer. The Al K_α radiation ($h\nu = 1486.6$ eV) was used. The energy scale of the system was calibrated according to Au4f 7/2, Ag3d 5/2, Cu2p 3/2 peaks, the analyzer being in the constant transition mode. All spectra were determined at the 20 eV pass energy and 0.1 eV energy increment. The fitting procedure was performed with "XPSPEAK-4.1" software [18]. Atomic concentration was calculated using original KRATOS software.

3. EXPERIMENTAL RESULTS

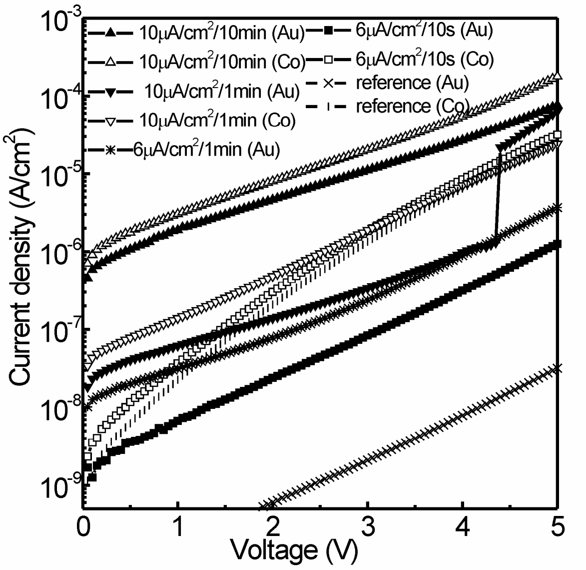
3.1. Electrical characteristics (I-V, C-V, low frequency noise)

It can be seen in Table 2, that glancing angle irradiation by nitrogen ion beam in all cases resulted in decrease of the effective barrier height calculated from I-V characteristic and increase of the reverse (leakage) current (Fig. 1, 2). It means, that even in the case of the lowest ion energies, formation of the radiation defects took place. It can be mentioned, that I-V characteristics of the reference Au-GaAs and Co-GaAs Schottky contacts were very different (Table 2, Fig. 1). However, there were relatively few differences between the Au-GaAs and Co-GaAs Schottky contacts fabricated on the GaAs surface treated under the same ion beam irradiation conditions. It means, the shape of the Schottky barrier and I-V characteristics of the Schottky contact depends on the properties of the irradiation modified GaAs surface layer. It should be associated with increase of the tunneling current strength as a result of the formation of the radiation defects which can act as donor impurities. Leakage current of the Co-GaAs Schottky contacts formed on the irradiated GaAs in all cases was larger than leakage current of the respective GaAs Schottky contacts (except the samples fabricated on the GaAs surface irradiated by 320 eV energy nitrogen ion beam) (Fig. 1). In the case of the samples fabricated on the GaAs surface irradiated by 65 eV energy ion beam, φ^*_b decreased and nonideality factor increased with increase of the ion beam current density (irradiation dose collection rate) and irradiation time (total irradiation dose). Increase of the leakage current was observed as well. In the case of the contacts fabricated after 10 s or 1 min GaAs surface ion nitridation, nonideality factor was relatively low (<1.1). However, increase of the irradiation time up to 10 min resulted in substantial increase of the nonideality factor. It must be mentioned that in our previous study increase of the 1 keV nitrogen ion beam glancing angle irradiation time up to 10 min and 30 min resulted in no additional changes of the nonideality factor [10]. While decrease of the effective barrier height was much more pronounced [10]. It can be explained by deeper penetration of the higher energy ions: in [10] irradiation by lighter inert gas ions (He) resulted in smaller decrease of the effective barrier height and larger increase of the nonideality factor in comparison with GaAs Schottky contacts fabricated on the GaAs irradiated by Ar ion beam.

φ^*_b of GaAs Schottky contacts fabricated on GaAs surface 1 min irradiated by 120 eV energy 60 μA/cm^2 ion current beam was lower than in the case of the samples formed on GaAs surface1 min irradiated by 65 eV energy 10 μA/cm^2 ion beam current density ion beam. It was higher than effective barrier height of the GaAs Schottky contact fabricated on GaAs surface 10 treated by 65 eV energy 10 μA/cm^2 ion current density nitrogen ion beam. Increase of the ion beam energy up to 310 eV resulted in further decrease of the effective barrier height. However, φ^*_b of the GaAs Schottky contact fabricated on GaAs surface 10 min irradiated by 65 eV energy 10 μA/cm^2 ion current density nitrogen ion beam was the lowest. It means, that the same ion beam irradiation effect on GaAs Schottky contact electrical characteristics can be obtained both by increase of the irradiation time and ion beam current density.

In the case of the GaAs surface ion beam nitridation at the incident angle normal to the surface in all cases resulted in larger nonideality factors in comparison with the respective samples fabricated on GaAs surface irradiated at glancing angle. In the case of 1 min irradiation by 65 eV energy 6 μA/cm^2 ion beam current density ion beam effective barrier height was the same and difference between the nonideality factors was only 0.02. However, in the case longer irradiation times or higher ion beam energies nonideality factor of the samples fabricated on GaAs surface irradiated at normal angle was substantially larger. While effective barrier height was higher in the case of the glancing angle ion irradiation. It can be explained by higher ion penetration depth in the case of the irradiation at normal angle: as a result radiation modified layer is thicker, but density of the radiation defects is lower (radiation defects are spread over the larger volume). Surprisingly, leakage current was very similar for samples formed on GaAs surface irradiated at glancing and normal angles (Fig. 2).

It can be seen in Table 2, that short GaAs surface irradiation by 65 eV energy ion beam resulted in decrease of the $\varphi^*_{C\text{-}V}$. It can be explained by etching of the GaAs surface and partial removal of the chemical compounds associated with higher barrier height areas. Removal of the oxides as well as As from the GaAs surface can be supposed. However, increase of the treatment time as well as ion energy resulted in increase of the $\varphi^*_{C\text{-}V}$. It can be explained by growth of the nitride layer. Effective barrier height calculated from the capacitance-voltage characteristics ($\varphi^*_{C\text{-}V}$) in all cases was higher than φ^*_b. In the case of the reference samples, $\varphi^*_{C\text{-}V}$ was larger for Co-GaAs Schottky contact. On the one hand, φ^*_b lower than $\varphi^*_{C\text{-}V}$ can be explained by two factors. Barrier lowering due to the image forces is neglected in the case of the $\varphi^*_{C\text{-}V}$. While presence of the tunneling (field emission and thermo-ionic field emission) currents results in lowering of



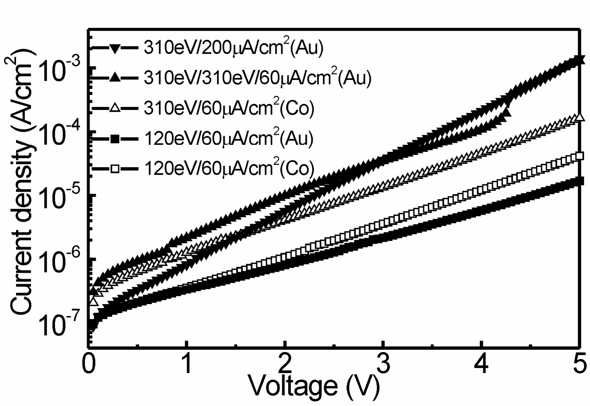


Fig. 1. Effects of the glancing angle irradiation by nitrogen ion beam on reverse current of the Au-GaAs and Co-GaAs Schottky contacts

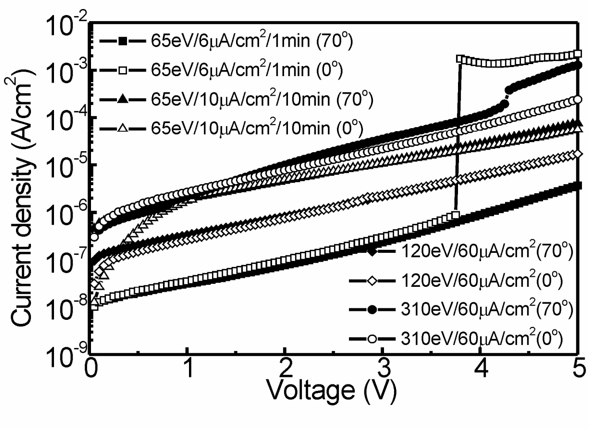


Fig. 2. Reverse I-V characteristics of Au-GaAs and Co-GaAs Schottky contacts fabricated on GaAs surface irradiated by nitrogen ion beam at different incidence angles (glancing – 70°, normal to surface – 0°)

the effective barrier height calculated from the I-V characteristics (φ^*_b). However difference between the φ^*_b and $\varphi^*_{C\text{-}V}$ is too large to be explained by factors mentioned above. Therefore, inhomegeneity of the Schottky contact (presence of the different barrier height areas) must be

Table 2. Effects of the ion beam nitridation on electrical properties of Au-GaAs and Co-GaAs Schottky contacts(φ^*_b – effective barrier height calculated from I-V characteristics, φ^*_{CV} – effective barrier height calculated from C-V characteristics, n – nonideality factor)

Ion beam energy (eV)	Ion current density (μA/cm²)	Irradiation time (min)	Ion beam incidence angle (to the surface normal)								
			70°						0°		
			Au-GaN-GaAs			Co-GaN-GaAs			Au-GaN-GaAs		
			φ^*_b (eV)	n	$\varphi^*_{C\text{-}V}$ (eV)	φ^*_b (eV)	n	$\varphi^*_{C\text{-}V}$ (eV)	φ^*_b (eV)	n	$\varphi^*_{C\text{-}V}$ (eV)
Reference sample (on chemically polished GaAs)			0.92	1.03	1.13	0.72	1.19	1.30	–	–	–
65	6	1/6 (10s)	0.69	1.05	0.86	0.67	1.11	1.29	–	–	–
65	6	1	0.64	1.05	1.20	–	–	–	0.64	1.07	2.60
65	10	1	0.62	1.09	0.96	0.61	1.07	1.02	–	–	–
65	10	10	0.52	2.96	1.50	0.54	1.37	1.09	0.66	2.78	8.00
120	60	1	0.58	1.11	0.92	0.58	1.15	1.01	0.63	1.83	–
310	60	1	0.55	1.32	1.25	0.56	1.39	1.40	0.55	3.49	2.50
310	200	1	0.59	1.27	3.60	–	–		–	–	–

considered. Current transport in inhomogeneous Schottky contact is dominated by low barrier height areas [16]. Therefore φ^*_b should be associated with that low barrier height patches. While measurement using capacitance-voltage characteristics yields average Schottky barrier height for a whole contact (diode) [16].

It was shown in [19, 20], that GaAs surface nitridation by $N_2:H_2$ (97 : 3) plasma results in formation of the substantially thicker nitride layer. It should be mentioned, that GaAs surface treatment by hydrogen plasma can result in increased effective barrier height and decreased leakage current of GaAs Schottky contact due to the hydrogen passivation of the impurities [21]. Therefore, in the present study effects of the GaAs surface treatment by $N_2:H_2$ (97 : 3) ion beam were compared with effects of the nitride ion beam treatment. It can be seen in Table 3, that effective barrier height φ^*_b of Au-GaAs Schottky contact fabricated on the GaAs surface treated by N_2+H_2 ion beam is higher in comparison with GaAs surface treated by N_2 ion beam under the same process conditions (ion energy, ion current density, time) by 0.14 eV – 0.15 eV. However, effective barrier height φ^*_b of the irradiated samples is still higher than effective barrier height of the reference sample. It seems, that hydrogen was passivated only part of the radiation induced defects. It can be seen in Fig. 3, that leakage current of the Au-GaAs Schottky contact fabricated on the GaAs surface treated by $N_2 + H_2$ ion beam is higher in comparison with GaAs surface treated by N_2 ion beam is larger (Fig. 3) as well as nonideality factor While $\varphi^*_{C\text{-}V}$ in the case of the samples treated by N_2+H_2 ion beam is larger by 0.3 eV. It seems, that $N_2 + H_2$ ion beam treatment resulted in increased inhomogeneity of the Au-GaAs Schottky contacts.

Low frequency noise of the selected samples can be seen in Fig. 4. At room temperature low frequency noise of the reference Au-GaAs sample as well as Au-GaAs and Co-GaAs Schottky contacts fabricated on GaAs surface 1 min irradiated by 65 eV energy ion beam was very low – at the level of the thermal noise. However, irradiation by 120 eV energy ion beam resulted in increase of the low frequency noise by several orders. While in the case of the sample irradiated by 310 eV energy nitrogen ion beam level of the noise was so high, that it was impossible to

Table 3. Comparison of the effects of $N_2 + H_2$ and N_2 ion beam nitridation on electrical properties of Au-GaAs Schottky contacts (ion beam energy 65 eV, treatment time 1 min)

Ion current density (μA/cm²)	Gas reagents used					
	N_2			N_2+H_2		
	φ^*_b (eV)	n	$\varphi^*_{C\text{-}V}$ (eV)	φ^*_b (eV)	n	$\varphi^*_{C\text{-}V}$ (eV)
Reference sample	0.92	1.03	1.13	0.92	1.03	1.13
6	0.64	1.05	1.20	0.79	1.11	1.5
10	0.62	1.09	0.96	0.76	1.15	2

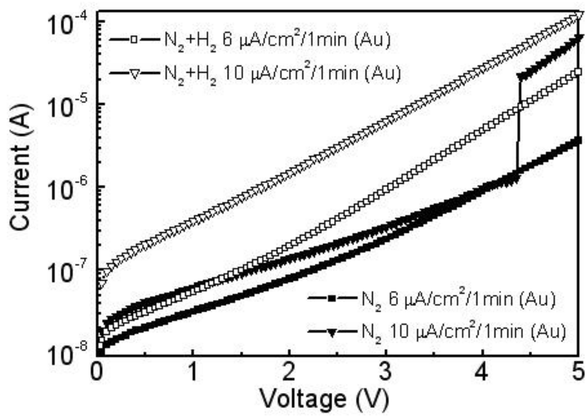


Fig. 3. Effects of $N_2 + H_2$ and N_2 ion beam nitridation on reverse I-V characteristics of Au-GaAs Schottky contacts (ion beam energy 65 eV, treatment time 1 min)

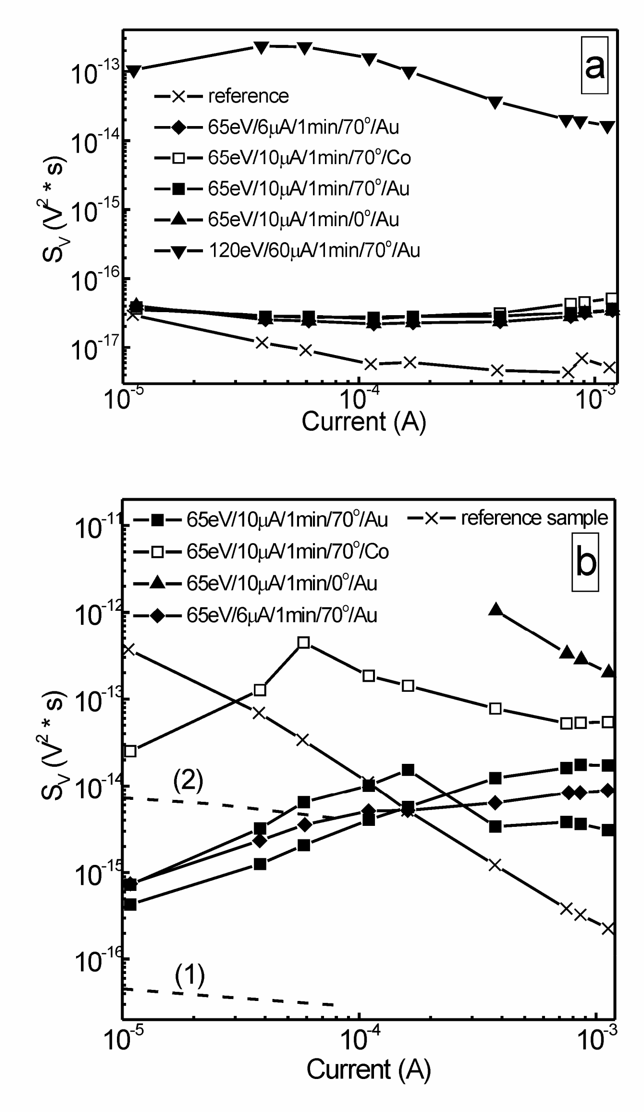


Fig. 4. Low frequency noise of the Au-GaAs and Co-GaAs Schottky contacts at room (a) and liquid nitrogen (b) temperature

measure it. At liquid nitrogen temperature low frequency noise of the Au-GaAs Schottky contacts fabricated on GaAs surface 1 min treated by 65 eV energy, 6 μA/cm^2 and 10 μA/cm^2 ion beam was nearly the same. While low frequency noise of Co-GaAs Schottky contact formed on the GaAs surface treated under the same conditions was higher. Low frequency noise level of the reference sample was higher at lower current and lower at higher current densities. However, low frequency noise of the Al-GaAs Schottky contact fabricated on GaAs surface after the 1 min ion beam glancing angle nitridation by 1 keV energy, 6 μA/cm^2 ion beam current density ion beam reported in [10] was substantially lower than low frequency noise of Au-GaAs Schottky contact fabricated on GaAs surface 1 min treated by 65 eV energy 6 μA/cm^2 current density ion beam.

3.2. XPS spectra

Effects of the ion beam nitridation by glancing angle nitrogen ion beam on GaAs surface chemical composition and structure were investigated using X-ray photoelectron spectroscopy. Shift of Ga3d peak by ~ 0.3 eV as a result of the treatment by 1 min nitridation by 65 eV energy 10 μA/cm^2 current density nitrogen ion beam can be seen in Fig. 5. New sub-peaks at 19.85 eV and 20.6 eV can be observed as well. The first shoulder can be described as a Ga-N bond. Similar difference between the binding energies of Ga-As and Ga-N XPS peaks (in our case 0.65 eV) was reported in [7, 22]. Second new component most possibly can be associated with presence of Ga oxides in newly formed nitrides layer (in [23] XPS peak of the similar energy is described Ga-O). Binding energy of As3d XPS peak increased by ~ 0.2 eV as a result of the ion beam nitridation. It can be associated with increase of As-As bonding (more elemental As at the GaAs surface). New component of the As3d XPS peak can be seen at 42.2 eV as well. Similar results were reported in [22, 23]. It was explained by formation of As-N bonds [22, 23]. It can be mentioned, that in our previous study As3d binding energy did not change after irradiation by 1 keV energy 6 μA/cm^2 current density nitrogen ion beam.

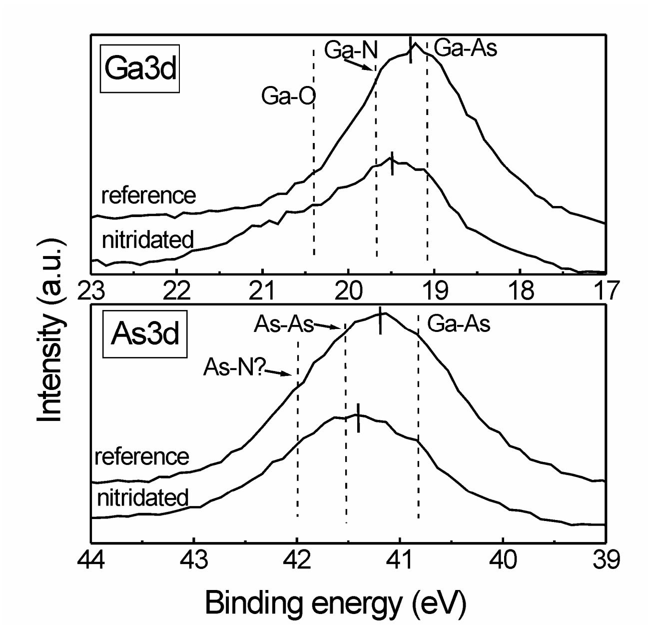


Fig. 5. Effects of GaAs surface nitridation on Ga3d and As3d XPS spectra (nitrogen ion beam energy 65 eV, ion beam current density 10 μA/cm^2, irradiation time 1 min)

Appearance of the new XPS peak near the Ga Auger peak as a result of the GaAs surface 1 min nitridation by 65 eV energy, 10 μA/cm^2 current density ion beam can be seen in Fig. 6. Binding energy of the new peak (~397 eV) is typical for N1s peak of nitrogen and its compounds. However, intensity of the N1s peak exceeded intensity of the Ga Auger peak only when measured at 50° angle to surface normal. While in the case of the GaAs surface 1 min irradiated by 320 eV energy and 200 μA/cm^2 current density ion beam intensity of N1s peak is higher than intensity of the Ga Auger peak even in the case of the measurement at normal angle. It means, that formation of the thicker GaN layer took place. It can be seen in Fig. 6, that in the case of 10 min ion beam nitridation by 1000 eV energy 6 μA/cm^2 current density ion beam similar results were obtained [10]. It can be mentioned, that after 3 min irradiation by 1000 eV, 6 μA/cm^2 current density ion beam no formation of the nitride layer was observed [10].

Binding energy of the Ga2p XPS peak increased by ~1 eV as a result of 1 min nitridation by 65 eV energy, 10 μA/ cm^2 current density ion beam. It can be explained by formation of the nitride layer as well.

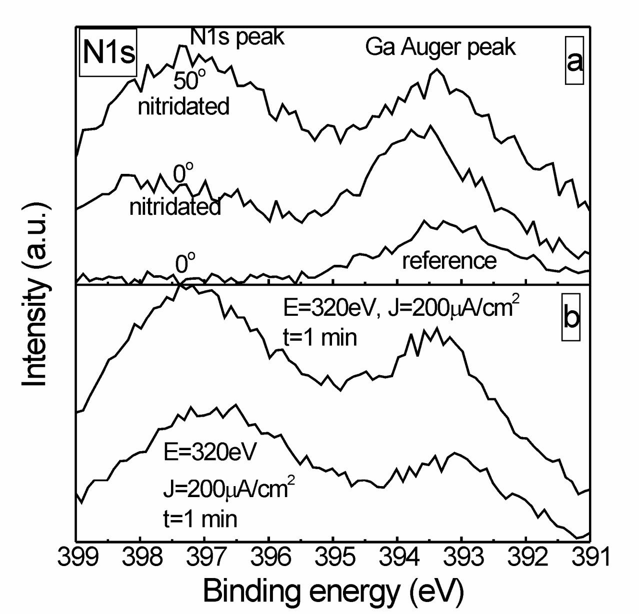


Fig. 6. Effects of GaAs surface nitridation on N1s XPS spectra: reference sample and sample treated by 1 min 65 eV energy, 10 μA/cm^2 current density ion beam (nitridated GaAs surface measured at normal angle (0°) and 50° angle to surface normal) (a); 1 nitridated min 320 eV energy, 200 μA/cm^2 current density ion beam and 10 min nitridated by 1000 eV energy, 6 μA/cm^2 current density ion beam [10] (measured at normal angle to surface) (a)

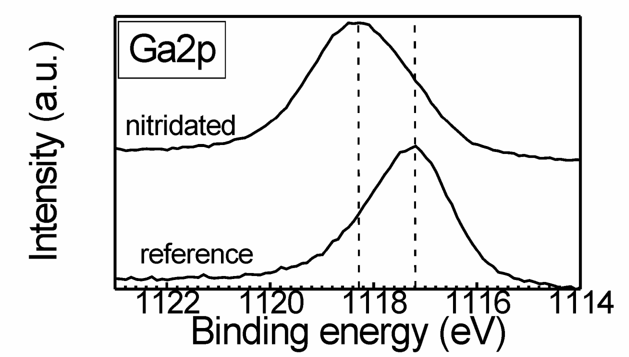


Fig. 7. Effects of the Effects of GaAs surface nitridation on Ga2p XPS spectra (nitrogen ion beam energy 65 eV, ion beam current density 10 μA/cm^2, irradiation time 1 min)

CONCLUSIONS

In conclusion formation of the thin GaN or $GaAs_xN_{1-x}$ type layer and layer of the radiation induced electrically active donor-like defects as a result of GaAs surface irradiation by 65 eV – 320 eV energy nitrogen ion beam has been observed. Thickness of the layer increased with increase of the ion energy and ion beam current density. The dependence of the electrical properties of GaAs Schottky contacts on nitrogen ion beam irradiation conditions (ion beam energy, ion beam current density, irradiation time, ion incidence angle) has been revealed. Homogeneity of the Schottky contacts fabricated on nitrogen ion treated GaAs surface was dependent on Schottky contact metal as well. GaAs surface irradiation in all cases resulted in decreased homogeneity of the Schottky contacts. GaAs surface glancing angle treatment by $N_2 : H_2$ (97 : 3) ion beam instead of "pure" nitrogen ion beam resulted in increased inhomogeneity of the Au-GaAs Schottky contacts.

Acknowledgments

Support of the Lithuanian Science and Studies Foundation should be acknowledged.

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