Semiconductor Physics, Quantum Electronics & Optoelectronics, 2008. V. 11, N 3. P. 209-216.

PACS 73.23.+y, 73.40.Sx, 73.40.Gk

Heat-resistant barrier and ohmic contacts based on TiB_x and ZrB_x interstitial phases to microwave diode structures

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Abstract. We investigated thermal stability of Au–TiB_x (ZrB_x) barrier contacts, as well as ohmic contacts with a TiB_x diffusion barrier to *n*-Si (GaAs, InP, GaP, GaN, SiC). The electrophysical measurements of Schottky barrier diodes and ohmic contacts were performed both before and after rapid thermal annealing (RTA) up to 600 °C for the structures on Si, GaAs, InP and GaP, as well as up to higher temperatures for GaN (~900 °C) and SiC (~1000 °C). The concentration depth profiles of contact components were taken using Auger electron spectrometry, while phase composition and surface morphology of the metallization layers on test structures were determined using x-ray diffraction and atomic force microscopy. It was shown that the silicon, indium phosphide, gallium phosphide and gallium arsenide contact structures retained their properties and layer structure after RTA up to 600 °C. Contact degradation occurred at a temperature of 800 °C. The structures based on SiC (GaN) remained stable at temperatures up to 1000 °C (900 °C).

Keywords: Schottky barrier, ohmic contact, diffusion barrier, wide-gap semiconductors.

Manuscript received 09.06.08; accepted for publication 20.06.08; published online 15.09.08.

1. Introduction

To make highly reliable solid-state microelectronic devices that would be tolerant to active actions, such contact metallization systems have to be used that could restrict the effect of factors stemming from migration and corrosion processes. Based on both the results of our previous complex investigations of physico-chemical mechanisms of formation and degradation of contact structures characteristics [1-4] and literature data [5-10], the following factors are to be mentioned:

- appearance at boundaries between phases (in the course of metal–semiconductor contact formation) of a thermodynamically non-equilibrium interlayer of complex composition whose characteristics vary under operation of contact structures and active actions on them;
- generation of structural defects near semiconductor surface due to reactions between contacting layers of different physical nature;
- formation of local nonuniformities in the junction region of metal–semiconductor contact due to distinctions of solid-phase interactions between metal and semiconductor in different interfacial areas;
- presence of oxide layers at the boundary between phases of metal–semiconductor contact;
- appearance of intrinsic stresses due to distinctions in crystal structures and thermodynamic parameters of contact-forming materials.

Thus, the problem of developing reliable contacts is determination of interrelation between the above factors, design-technological approaches used when making metal–semiconductor contacts, and active actions on the contacts that make it possible to minimize their negative effect.

The attempts to stabilize the contact electronic characteristics (with concurrent reduction of contact area and depth) by applying the traditional thermodynamic and kinetic approaches failed. The way based on introduction of stabilizing layers – diffusion barriers (DBs) (that do not are products of interactions between phases in contacting layers) – in the contact structure [11] turned out to be more promising. Such an approach enables one to make essentially novel versions of smaller contact structures for solid-state semiconductor devices that are tolerant to various extreme actions.

The requirements imposed on contact metallization are as follows. The materials for DBs must have high

conductivity (as well as thermal and chemical stability) and small coefficient of thermal expansion. Besides, formation of layers of these materials having various structure and morphology should not lead to considerable technological problems. It was found [12-15] that nitrides and borides of IV, V and VI group metals meet the above requirements. They demonstrate such properties of materials with predominant covalent bonding as high thermal stability, rigidity and melting temperature and are chemically inactive. At the same time, their electrical, thermal and optical properties are close to those of materials with metallic bonding. They belong to the close-packed structures whose composition and crystalline state can be varied over wide limits.

Following are the results of our investigations of various contact systems (involving layers of titanium and zirconium diborides) for microwave diode structures based on Si, GaAs, InP, GaP and SiC 4H epitaxial n-n^+ structures, as well as GaN–i-Al_2O_3 heterostructures and SiC 6H and SiC 15R bulk wafers. Most attention is paid to the features of the physico-chemical processes occurring at contact formation, as well as the factors that restrict thermal stability of the contacts.

2. Formation of contact systems

The TiB_x, ZrB_x and Au films (each ~0.1 μm thick) for barrier contacts were obtained using magnetron sputtering in an argon atmosphere (~0.7 Pa pressure in the chamber). TiB_x and ZrB_x were sputtered from powder targets of stoichiometric composition [16-19].

The ohmic contacts for n^+-Si were prepared using magnetron sputtering of Ti followed by its burning-in at a temperature T = 450 °C and deposition of TiB_x and Au buffer layer. The ohmic contacts to GaAs, GaP and InP were made with gold–germanium eutectic Au:Ge (88:12) or Au:Ge (97:3) alloy; those to n-SiC were formed with silicide phase of nickel Ni_2Si, while the ohmic contacts to n-GaN were formed with titanium metallization. The DBs were made using sputtering of TiB_x (in the case of ohmic contacts to Si, GaP, InP and SiC) or TiB_x and Mo (TiB_x and Al) for GaAs (GaN).

The substrates were as follows: the Si, GaAs, InP and GaP epitaxial n-n^+ structures (~3÷5 μm layers, donor concentration in the n-layers of ~10^{16} cm^{-3}), ~1 μm n-GaN layer (donor concentration of ~10^{17} cm^{-3}) grown on Al_2O_3, wafers of bulk n-SiC 6H and n-SiC 15R (dopant concentration of ~10^{18} cm^{-3}) and n-n^+-SiC 4H epitaxial structures (thickness of ~1.5 μm, impurity concentration in the n-layer of ~10^{17} cm^{-3}).

We studied, both before and after rapid thermal annealing (RTA) at T = 400, 600, 800 and 1000 °C for 60 s, the samples of two types: test structures and Schottky barrier diode (SBD) structures (diameter of ~100 μm). For the test structures with continuous metallization, we investigated concentration depth profiles in the contact structures (with Auger electron spectrometry), as well as phase composition and surface morphology of metallization layers using x-ray diffraction (XRD) technique and atomic force microscopy. For the test TLM (transmission line method) structures with different metallization layers, we studied contact resistivity ρ_c (in the 77–400 K temperature range), both before and after RTA at T = 400, 500, 600, 800, 900 и 1000 °C. For the SBD structures, we took I–V curves from which the Schottky barrier (SB) height φ_B and ideality factor n were determined (see Table 1).

The electronographic studies showed that the sputtered TiB_x and ZrB_x layers were nanostructured; the size of ordered areas was below 3 nm [20]. RTA did not lead to changes in TiB_x film structure. This result was typical of all the structures studied. The nanostructured state of the TiB_x and ZrB_x films was retained after RTA at T = 900 °C (for gallium nitride samples) and 1000 °C (for silicon carbide samples) [21, 22]. The feature of such nanostructured TiB_x and ZrB_x layers was considerable slowing-down of grain boundary diffusion in the metal–semiconductor contact region. This factor leads to essential distinction of the properties of barrier contacts based on amorphous TiB_x and ZrB_x phases from those of contacts formed by polycrystalline metal or alloy films using the traditional technique.

Table 1. Effect of RTA on SB height φ_B and ideality factor n of Au–TiB_x (ZrB_x)–n-Si (GaAs, InP, GaP, GaN, SiC) SBDs.

SBD structures	φ_B, V					n				
	initial	400 °C	600 °C	800 °C	1000 °C	initial	400 °C	600 °C	800 °C	1000 °C
Au–TiB_x–n-n^+-Si	0.55	0.6	0.56	0.58		1.2	1.2	1.28	1.77	
Au–ZrB_x–n-n^+-Si	0.54	0.55	0.55	0.55		1.08	1.08	1.1	1.2	
Au–TiB_x–n-n^+-GaAs	0.8	0.79	0.78			1.18	1.2	1.23		
Au–TiB_x–n-n^+-InP	0.5	0.5	0.53			1.1	1.2	1.5		
Au–TiB_x–n-n^+-GaP	0.89	0.9	0.9	0.9		1.16	1.18	1.18	1.2	
Au–TiB_x–n-GaN	0.9			0.9		1.3			1.3	
Au–ZrB_x–n-GaN	0.89			0.89		1.28			1.28	
Au–TiB_x–n-SiC 6H	0.82			0.82	0.82	1.2			1.2	1.2
Au–ZrB_x–n-SiC 6H	0.79			0.8	0.8	1.2			1.2	1.2
Au–ZrB_x–n-n^+-SiC 4H	0.83			0.83	0.83	1.2			1.2	1.2
Au–ZrB_x–n-SiC 15R	0.78			0.78	0.78	1.5			1.5	1.5

3. Structure and physico-chemical properties of TiB_x and ZrB_x films on semiconductor substrates before and after RTA

Au–TiB$_x$ (ZrB$_x$)–n-n$^+$-Si. The concentration depth profiles for components of the Au–TiB_x–*n*-n^+-Si and Au–ZrB_x–*n*-n^+-Si contact metallization were obtained with Auger electron spectroscopy before and after RTA at T = 400, 600 and 800 °C. An analysis of these profiles and metallization surface morphology showed that, at annealing temperatures ≤600 °C, the layer structure of metallization is retained for both types of contact metallization, and no considerable redistribution of structure components occurs [23]. Increase of RTA temperature to 800 °C leads to damage of contact layer structure, and topographic nonuniformity of the contact surface does not obey the Gaussian distribution. The above facts indicate an essential role of activation processes at the interfaces between phases. The interfacial microrelief formed under such conditions is determined by chemical reactions between the components of metal and semiconductor.

Presence of different phases and interfacial roughness related to it favor some impairment of electrophysical characteristics, in particular, considerable increase of the ideality factor n (see Table 1).

Thus, the thermal degradation threshold of the Au–TiB_x–*n*-n^+-Si and Au–ZrB_x–*n*-n^+-Si contact structures is determined by tolerance of the TiB_x and ZrB_x layers for heat actions.

Au–TiB$_x$–n-n$^+$-InP. The results of layer-by-layer Auger analysis of the Au–TiB_x–*n*-n^+-InP contacts before and after RTA at T = 400 and 600 °C also indicate absence of considerable intermixing at the interfaces between phases, both in the initial sample and those after RTA at temperatures up to 600 °C. They are also confirmed by the XRD patterns for the same samples [24]. An analysis of those patterns taken before and after RTA up to 600 °C showed presence of a quasi-amorphous TiB_x film. The processes occurring in the contact structure exposed to RTA at >600 °C indicate intensification of chemical reactions between the components of the contact-forming pair. In this case, there exists no mechanism of restriction of interactions between phases related to ingress of atoms to the reaction area and alloy formation. Mass transfer intensification after RTA at T = 800 °C is due to relaxation of intrinsic stresses in the contacts accompanied with cracking of the contact system. The measurements of SB parameters support the above conclusion (see Table 1).

The ***Au–TiB$_x$–n-n$^+$-GaAs (GaP)*** contact systems demonstrated similar structural, physico-chemical and electrophysical properties both before and after RTA. In this case, the common physical process leading to variation of electrophysical parameters of the TiB_x–InP (GaAs, GaP) barrier contacts was RTA-induced relaxation of intrinsic stresses in the contact systems [19]. Given in Table 2 are our experimental data on the effect of RTA on strain ε in the TiB_x–InP (GaAs, GaP) contact systems. One can see that relaxation processes are most pronounced after RTA at T = 600 °C; whatever the distinction in thermal expansion coefficients of TiB_x and III–V semiconductor compounds, the ε values decrease as RTA temperature is increased. Relaxation of intrinsic stresses induces atomic interdiffusion from TiB_x film to the substrate and from semiconductor to the film that increases after cracking of the contact system. A typical morphology of the TiB_x–GaAs contact after RTA at T = 800 °C is shown in Fig. 1. Such mechanism of intrinsic stress relaxation is supported by the data on layer-by-layer Auger analysis performed for the TiB_x–InP (GaAs, GaP) contact systems [19].

Table 2. Strains ε in TiB_x-*n*-GaAs (InP, GaP) contacts.

RTA modes	ε (TiB_x–GaAs)	ε (TiB_x–InP)	ε (TiB_x–GaP)
initial	4×10^{-5}	2×10^{-5}	8×10^{-4}
400 °C, 60 s	3.8×10^{-5}	1.5×10^{-5}	7×10^{-4}
600 °C, 60 s	0.6×10^{-5}	0.7×10^{-5}	5×10^{-4}
800 °C, 60 s	0.8×10^{-5}	0.2×10^{-5}	

The electrophysical parameters of the diode structures under investigation demonstrated high resistance to RTA up to temperatures of ~600 °C (see Table 1).

The ***Au–TiB$_x$ (ZrB$_x$)–n-SiC 6H*** contact systems (contrary to the TiB_x–InP (GaAs, GaP) contacts) did not demonstrate changes in component distributions at the interfaces between phases after RTA up to T = 1000 °C (Figs. 2 and 3). The thickness (~20 nm) of junction layer at the Au–TiB_x (ZrB_x)–*n*-SiC 6H interface, as well as its composition, remained practically the same after RTA. This supported the conclusion about thermal stability of contact barrier properties (see Table 1) and indicated absence of intense interaction between the contact components and SiC. The latter statement is supported also by the results of XRD analysis showing retention of quasi-amorphous state of the TiB_x and ZrB_x films after RTA at 1000 °C (otherwise intense grain boundary diffusion would be observed). In this case, the electrophysical parameters of SBs practically did not change after RTA at 1000 °C (see Table 1).

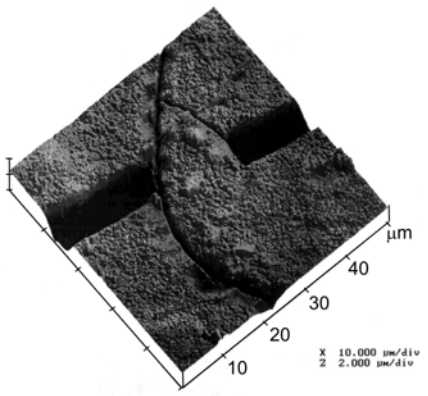

Fig. 1. Typical morphology of Au–TiB_x–GaAs contact after RTA at T = 800 °C.

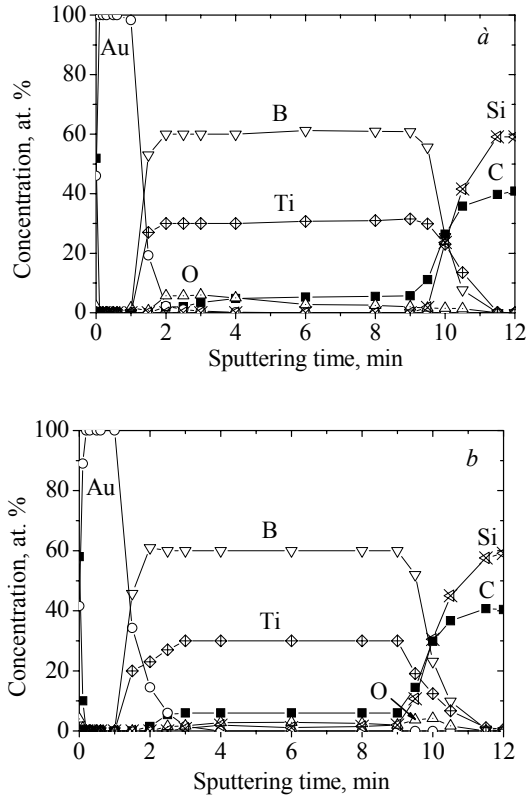

Fig. 2. Concentration depth profiles for Au–TiB_x–*n* SiC 6H contacts before (a) and after (b) RTA at T = 1000 °C for 90 s.

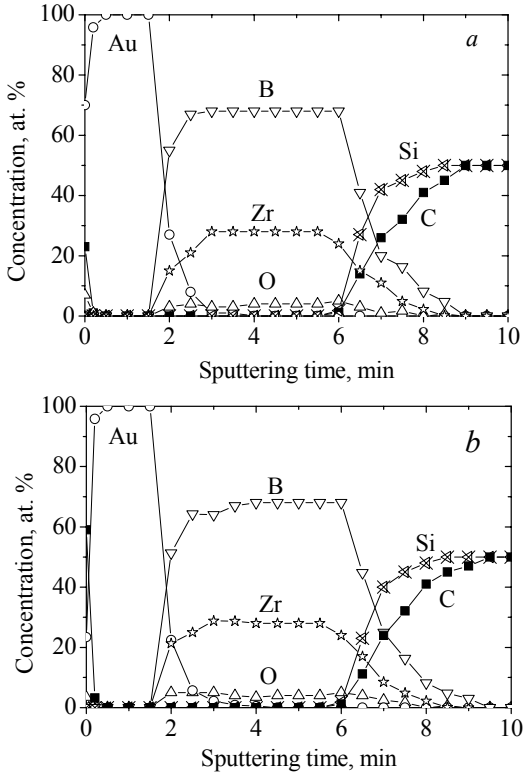

Fig. 3. As in Fig. 2 but for Au–ZrB_x–*n*-SiC 6H contacts.

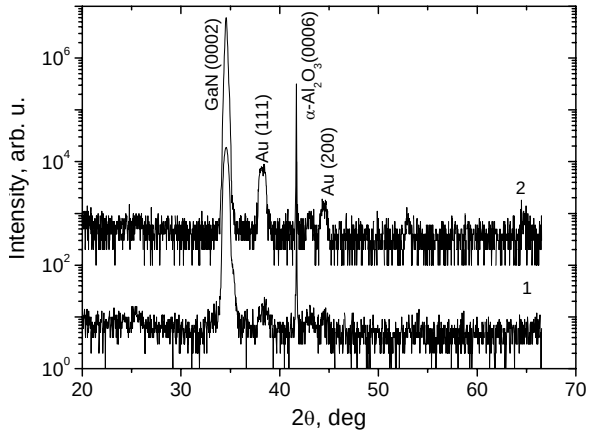

Fig. 4. .XRD patterns for Au–TiB_x–*n*-GaN samples: 1 – initial, 2 – after RTA at T = 900 °C for 30 s.

One can see from the above results that the threshold of thermal degradation of contact systems based on TiB_x and ZrB_x on SiC 6H may be related to tolerance of TiB_x and ZrB_x films for heat actions, as well as in the case of similar systems on Si.

The ***Au–TiB$_x$ (ZrB$_x$)–n-GaN*** contact systems were studied with XRD technique, both before and after RTA at T = 900 °C. The XRD patterns for the initial Au–TiB_x–*n*-GaN sample, as well as that after RTA at T = 900 °C for 30 s, were obtained by us earlier [25]; they are presented in Fig. 4. In both cases, the TiB_x film was x-ray-amorphous. No formation of other phases due to metallurgical processes in the metallization layers was detected. This indicated their thermal stability. An increase of the Au (111) peak intensity after RTA indicates presence of texture [111] related to thermally activated growth of Au grains. The essential distinction of those contact systems from the above-mentioned is structural nonuniformity of the GaN film grown on sapphire. This resulted from considerable lattice mismatch between GaN and Al_2O_3. Therefore, determination of the thermal threshold of degradation of such contact structure needs further structural and physico-chemical investigations of those objects. The results on parameters of the Au–TiB_x–*n*-GaN SBs, both initial and after RTA at temperatures up to 900 °C, show their thermal stability, thus indicating thermal stability of the TiB_x–*n*-GaN interface (see Table 1).

Our Auger analysis of the Au–TiB_x (ZrB_x)–*n*-GaN contact systems confirmed presence of layered structure in both initial and exposed to RTA up to 900 °C samples.

4. Electrophysical properties of contacts before and after RTA

Barrier contacts. The electrophysical parameters of SBs of all barrier contacts under investigation were determined from the measurements of forward branches of *I–V* curves; they are presented in Table 1. The feature of these *I–V* curves was that they could be described in

Table 3. Parameters of ohmic contacts with DBs before and after RTA.

Contacts	N_B, cm^{-3}	ρ_c, Ω·cm^2							φ_B, V	Ref.
		initial.	400 °C	500 °C	600 °C	800 °C	900 °C	1000 °C		
Si–Ti_2Si–TiB_x–Au	2×10^{19}	2.1×10^{-6}	2.1×10^{-6}		1.3×10^{-6}	8×10^{-6}			0.04–0.05	[21]
GaAs–AuGe–TiB_x–Au	$(5\div9)\times10^{19}$		5.2×10^{-5}	1.9×10^{-5}	2.5×10^{-5}	3.6×10^{-4}			0.1–0.14	[32]
InP–AuGe–TiB_x–Mo–Au	10^{18}	1.03×10^{-4}	2.2×10^{-5}		2.59×10^{-5}	2.25×10^{-4}			0.1÷0.15	[34]
SiC–Ni_2Si–TiB_x–Au	1.2×10^{18}	rectifying						10^{-4}	0.3	[35]
GaN–Ti–Al–TiB_x–Au	10^{17}	rectifying					10^{-4}		0.33*	[36]
GaP–Au–Ge–TiB_x–Au	10^{17}	1.4×10^{-3}	1.4×10^{-3}	1.2×10^{-4}	1.1×10^{-4}				φ_{B1} = 0.038 φ_{B2} = 0.078	[37]

the terms of the theory of thermionic emission because the ideality factors of all diode structures (the initial ones and those after RTA) lied within 1.08÷1.2.

As to the mechanism of current flow on the forward-biased SBDs based on *n*-SiC 6H and *n*-GaN, their over-barrier current dominates at high temperatures only. In the 77–400 K temperature range, tunneling according to the dislocation mechanism prevails [38]. The SB height dependence on the semiconductor ionicity also agreed with that predicted by the theory of thermionic emission. One can conclude from the results given in Table 1 that, whatever the results of structural and physico-chemical analysis, the interfaces of the contact systems under investigation remained thermally stable after RTA at temperatures up to 600 °C (for Si, GaAs, InP and GaP SBs) and even higher temperatures, ~900 °C (for GaN SBs) and ~1000 °C (for SiC SBs) This result also indicates high heat-resistance of the TiB_x and ZrB_x barrier-forming films. Some authors proposed to apply those films when making ohmic contacts with DBs (e.g., from ZrB_2 and W_2B layers to GaAs) [26], for improvement of thermal stability of light-emitting diodes based on the InGaN/GaN heterojunctions with TiB_2 DBs [27], ohmic contacts to *p*-GaN with W_2B_2 [28], ohmic and barrier contacts to *n*-GaN with ZrB_2 and CrB_2 to *n*-GaN [29-32].

Ohmic contacts. The contact resistivity ρ_c was determined for all contact systems studied with the TLM technique, while the barrier height φ_B for ohmic contacts was determined from the results of measurements of temperature dependence of contact resistance. The ρ_c and φ_B values measured for both the initial samples and those after RTA are given in Table 3. One can see that the parameters of ohmic contacts with TiB_x DBs on Si, InP, GaP and GaAs do not change considerably after RTA at 400, 500 and 600 °C. This is due to absence of interaction with neighboring metallization layers. This effect is retained also after RTA at T = 800 °C; however, relaxation of intrinsic stresses at cracking intensifies mass transfer between the metallization and metal layers and semiconductor and thus results in increase of ρ_c, while φ_B does not change considerably.

As to the parameters of Au–TiB_x–AuGe–*n*-GaP ohmic contacts, an analysis of the contact resistivity ρ_c vs temperature curve shows that it has two sections with different slopes ($\varphi_{B1} \approx 0.038$ V and $\varphi_{B2} \approx 0.078$ V). This indicates contact nonuniformity. RTA up to T = 600 °C does not change substantially the contact parameters. This shows that ohmic contact formation is proceeding in the course of component sputtering at T = 450 °C. Some incompleteness of reactions between phases at the contact-forming film–GaP interface is removed during RTA at T = 500 (600) °C for 1 min. This was supported by the results of XRD analysis.

The XRD patterns for both initial Au–TiB_x–AuGe–*n*-GaP sample and those after RTA at T = 500–600 °C for 60 s are shown in Fig. 5. For all samples studied, the TiB_x film was x-ray-amorphous. Along with the gold peaks, those of germanium, GeP_3 and (weak) $AuGaO_2$ are observed in the XRD for the initial sample. No other phases resulting from metallurgical processes in the metallization layers were found. The portions of $AuGaO_2$ and GeP_3 phases increased after RTA at T = 500 °C. A new phase ($Au_{0.72}Ge_{0.28}$) appeared after RTA at T = 600 °C. Its appearance is accompanied with a drastic drop of both the GeP_3 phase portion and pure gold peaks. A decrease of the intensity of Au(111) and Au(200) peaks after RTA at 600 °C indicates redistribution of gold in the layers due to its diffusion and formation of new phases. These results correlate well with those obtained from the Auger spectra.

It turned out also that the mechanism of current flow in ohmic contacts to heavily doped semiconductors ($N_B \geq 10^{18}$ cm^{-3} for Si and InP) is determined, over a wide temperature range, by tunneling of charge carriers. The thermal threshold in the ohmic metallization with TiB_x DBs to those materials is determined by TiB_x tolerance for heat actions, as in the case of barrier contacts to Si, GaAs, GaP and InP formed with interstitial phases.

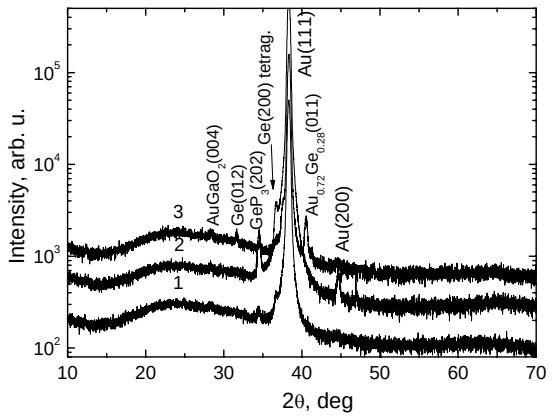

Fig. 5. XRD patterns for Au–TiB_x–AuGe–*n*-GaP samples: 1-initial, 2 (3) – after RTA at T = 500 °C (600 °C) for 60 s.

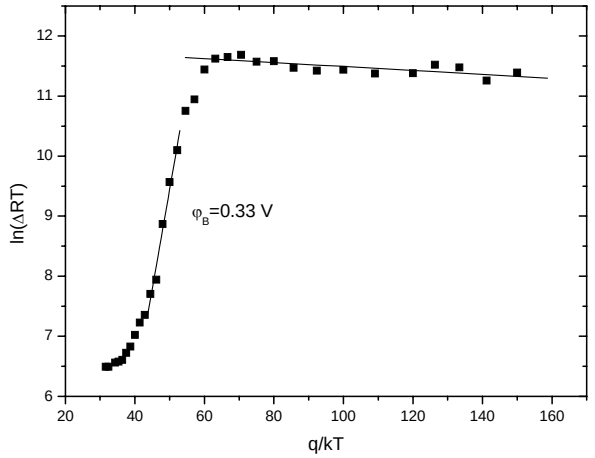

Fig. 6. Contact resistance as function of inverse temperature for Au–TiB_x–Al–Ti–*n*-GaN contacts.

The ohmic contacts to GaN and *n*-SiC were exposed to RTA at 900 and 1000 °C. In this case, ρ_c value for SiC did not exceed 10^{-4} Ω·cm^2, while for GaN it was 10^{-6} Ω·cm^2 (the best samples). The mechanism of current flow in the ohmic contact to GaN was determined by tunneling in the wide temperature range 77–200 K and by thermionic emission in the 220–280 K temperature range (Fig. 6). Thermal stability of ohmic contacts with DBs to wide-gap semiconductors SiC and GaN, as well as that of the TiB_x (ZrB_x)–*n*-SiC and TiB_x (ZrB_x)–*n*-GaN barrier contacts, is determined by tolerance of TiB_x films for high-temperature actions.

8. Conclusion

An analysis of the Refs. [26-32], as well as our above results, shows that an interest in borides of refractory metals (in particular concerning their application in contact systems to wide-gap semiconductors) stems, first of all, from thermal and chemical inactivity of those contact components. These features, as well as high conductivity, are retained after high-temperature treatments that simulate both short-term overloads and long-term extreme operation modes [39].

One should note, however, that practical application of these contact materials with unique properties in the manufacturing technology for semiconductor devices is still at its start, and there are many questions to be answered. Among such items are (i) radiation resistance of contact systems involving borides of refractory metals serving as DBs or barrier-forming layers, (ii) the role of presence of many phases in such systems, and (iii) the effect of the above factor on structural and electrophysical properties of the contacts (or, ultima analysi, on the heat- and radiation-resistance and reliability of the corresponding devices and systems).

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