ISSN 1063-7826, Semiconductors, 2009, Vol. 43, No. 8, pp. 1086–1091. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.E. Belyaev, N.S. Boltovets, V.N. Ivanov, R.V. Konakova, V.P. Kladko, Ya.Ya. Kudryk, A.A. Lebedev, V.V. Milenin, V.N. Sheremet, 2009, published in Fizika i Tekhnika Poluprovodnikov, 2009, Vol. 43, No. 8, pp. 1125–1130.

FABRICATION, TREATMENT, AND TESTING OF MATERIALS AND STRUCTURES

Properties of GaN(SiC)–(Ti, Zr)B_x Contacts Subjected to Rapid Thermal Annealing

A. E. Belyaev[a], N. S. Boltovets[b], V. N. Ivanov[b], R. V. Konakova[a]^, V. P. Kladko[a], Ya. Ya. Kudryk[a], A. A. Lebedev[c], V. V. Milenin[a], and V. N. Sheremet[a]

[a] *V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kiev, 03028 Ukraine*
^e-mail: konakova@isp.kiev.ua
[b] *State Enterprise Research Institute "Orion", Kiev, 03057 Ukraine*
[c] *Ioffe Physicotechnical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia*

Submitted January 13, 2009; accepted for publication January 14, 2009

Abstract—The effect of rapid thermal annealing on the structural and physical properties of Au–(Ti, Zr)B_x–GaN(SiC) contacts and diode structures on their basis is investigated. The X-ray-diffraction investigations and the layer-by-layer Auger analysis showed that the phase composition and structure of the GaN and SiC contacts are retained to the temperatures as high as 900 and 1000°C, respectively. The stability of interphase boundaries is confirmed by almost constant physical properties of contacts before and after the rapid thermal treatments. The Schottky-barrier height φ_b amounts to 0.89–0.9 eV for the contacts with GaN and 0.79–0.83 eV for SiC; the ideality factor n of the I–V characteristic amounts to $n = 1.2$ for the Au–TiB_x(ZrB_x)–n-GaN(SiC) contacts and $n \approx 1.12$ for the Au–ZrB_x–n-n^+-4HSiC contacts. The structural investigations indicate that there are glass-forming boron and metal oxides at an interphase boundary, which form a thin amorphous vitreous layer resistant against rapid thermal annealing and represent the diffusion barrier for the interphase transport.

PACS numbers: 73.40.Ns, 73.30+y, 85.30Kk, 81.05.Hd, 81.40.Ef, 81.40.Rs, 81.05.Rm

DOI: 10.1134/S1063782609080223

1. INTRODUCTION

The chemical reactions and diffusion processes at the interphase boundaries (IPBs) of metal–semiconductor (MS) contacts in solid-state electron devices stimulated by active factors (heating, irradiation, etc.) lead to their parametric instability and degradation. In an ideal case, a solitary relatively inert layer is necessary for semiconductor devices; this layer should provide the desired barrier height and prevent both the diffusion of atoms of technological metal layers deep into the semiconductor and the outward diffusion of its components.

As follows from [1–4], when forming the contacts to GaN and SiC wide-gap materials, the metals from IV–VI Groups of the Periodic system of elements providing qualitative electric and operational characteristics of contacts can be used. However, certain factors restricting their resistance to high temperatures and thermocycling processes were revealed.

1. Structural conversion of the phase composition of transition layers of contacts at moderate annealing. For example, the Ni–n-SiC contact retains its barrier characteristics to the annealing temperatures of 600°C and transforms into ohmic contact at 900°C, when nickel silicide proves to be the dominant product of interphase reactions at the interface [5]. The similar mechanism is implemented also in Me–GaN (here Me is a metal) contacts.

In [6], the annealing-stimulated chemical reactions between Ti and GaN were observed resulting in the formation a titanium-nitride film on the IPB. The departure of nitrogen atoms from the GaN lattice leads to the formation of a highly doped ($n \approx 10^{20}$ cm^{-3}) near-contact semiconductor layer providing the transformation of characteristics of a contact barrier into ohmic ones.

2. Oxidation of metal layers with a low activation energy of this process (Ta, Ti, Ga, etc.) during moderate thermal treatments. This factor causes the dependence of the chemical composition of IPB on the nature of metals under use. The inhomogeneous transition layer formed in this case can contain oxides of both metals and semiconductors in its composition [7, 8].

3. Occurrence and relaxation of internal stresses in contacts, which can appreciably affect the spreading of interfaces between contacting layers [9].

One of the most promising ways of eliminating the above negative factors is the use of interstitial phases, the microstructure of which can be presented as a metal matrix with nonmetal atoms (H, C, N, O, P, etc.) implanted into its interstices, as a metal layer to wide-gap semiconductors. These phases have highly pro-

nounced properties of metals in the combination with a high hardness and thermal and chemical stability [10].

Borides of refractory metals occupy the special place among interstitial phases, which is caused by specific properties of boron atoms caused by their size and electron structure. In borides, in contrast to the "classical" interstitial phases, the direct chemical bonds can be formed between the implanted nonmetal atoms. These bonds play no essential role in the structures with a low boron content (B atoms do not interact with each other). With increasing the B content in compounds with refractory metals, the chemical bonds between B atoms start to play a more and more essential role in the physical and chemical properties of these materials determining their structural features, crystallochemical, thermodynamic, thermal, electrophysical, thermoemission, optical, and mechanical parameters. Thus, varying the B content, it is possible to control the physical properties of these materials in a wide range with retaining highly pronounced metal properties [10–12].

We especially note one more important property of borides associated with their high corrosion stability. An appreciable interaction of borides with oxygen in air is observed only at the temperature of 600–700°C, the borides of the MeB_2 type being most resistant with respect to oxidation [10].

In this study, we analyze the thermal stability of the GaN and SiC contacts using quasi-amorphous films of refractory-metal borides, which are insufficiently investigated until now, as metallized layers. We also consider the effect of the two-layer metallization consisting of the boride and gold films (deposited in one technological cycle) on the thermal stability of the contact.

2. SAMPLES AND METHODS OF INVESTIGATION

The TiB_x, ZrB_x, and Au layers of 0.1 μm thick each were deposited by the method of the magnetron sputtering of powder targets with stoichiometric composition in argon at a pressure of $\sim 5 \times 10^{-3}$ Torr in the chamber [13, 14].

For forming the contacts, we used epitaxial n-GaN layers with the donor-impurity concentration of $\sim 10^{17}$ cm^{-3} and ~1 μm thick grown on Al_2O_3, the wafers of bulk n-6HSiC with the donor-impurity concentration of $\sim 10^{18}$ cm^{-3}, and also the epitaxial n-n^+-4HSiC structures with the dopant concentration of $\sim 10^{17}$ cm^{-3} in the n-type layer with the thickness of ~1.5 μm.

Before and after the rapid thermal annealing (RTA) at $T = 800$, 900, and 1000°C for 30 and 60 s, we investigated two types of samples: the test ones of 0.5×0.8 cm^2 in area and the diode structures with the Schottky barrier (SB) of ~100 μm in diameter.

With the test structures, we investigated the component-distribution profiles in the contacts by the Auger electron spectrometry in combination with ion etching. The phase composition of metallization layers is analyzed by the methods of the X-ray diffraction and photoelectron spectroscopy.

At the diode structures, we measured the I–V characteristics from which we determined the Schottky-barrier height φ_b and the ideality factor n of the I–V characteristic.

The use of quasi-amorphous borides layers enabled us to avoid uncertainties associated with the effect of structural–phase reconstructions in deposited metal layers on the physical properties of contacts as it was noted in [15, 16]. It is necessary to note that no such feature was observed in [17] when investigating the real contacts formed on monoatomic semiconductors.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The X-ray-diffraction investigations showed that the structure of the deposited TiB_x and ZrB_x layers is quasi-amorphous with the sizes of ordered areas of ≤3 nm. The quasi-amorphous state of TiB_x and ZrB_x films is retained after the RTA at $T = 900$°C for the structures on the basis of GaN and after the RTA at 1000°C for SiC contacts (Figs. 1 and 2).

In Figs. 3 and 4, we show the results of the layer-by-layer Auger analysis before and after the RTA of the Au—TiB_x(ZrB_x)–n-6HSiC contact systems. The boride–SiC interfaces remain sharp, and their extent (~20 nm) and atomic composition almost do not change even at high-temperature annealing (T = 1000°C, $t = 90$ s). The data of the layer-by-layer Auger analysis of the Au—TiB_x(ZrB_x)–GaN structures is also indicative of their high thermal stability and of no appreciable changes in the stoichiomerty of the near-surface GaN area even at annealing at ~900°C (Fig. 5).

On the basis of the presented X-ray-diffraction investigations and the layer-by-layer Auger analysis, we can conclude that the structure and phase composition of film coatings based on borides are retained up to the highest annealing temperatures and, consequently, the physical properties of interphase boundaries formed by borides with semiconductors do not change also.

This is confirmed by the data of electrical studies of the contacts listed in the table. Extreme annealing (900–1000°C) lead to no changes in electrical characteristics of the Schottky barriers.

The results of investigations given in the table somewhat differ from the data obtained in [18]. In [18], it was reported on the transformation of electrical properties of contact structures at thermal treatments. The SB value φ_b decreased with increasing the annealing temperature from 0.8 (initial samples) to

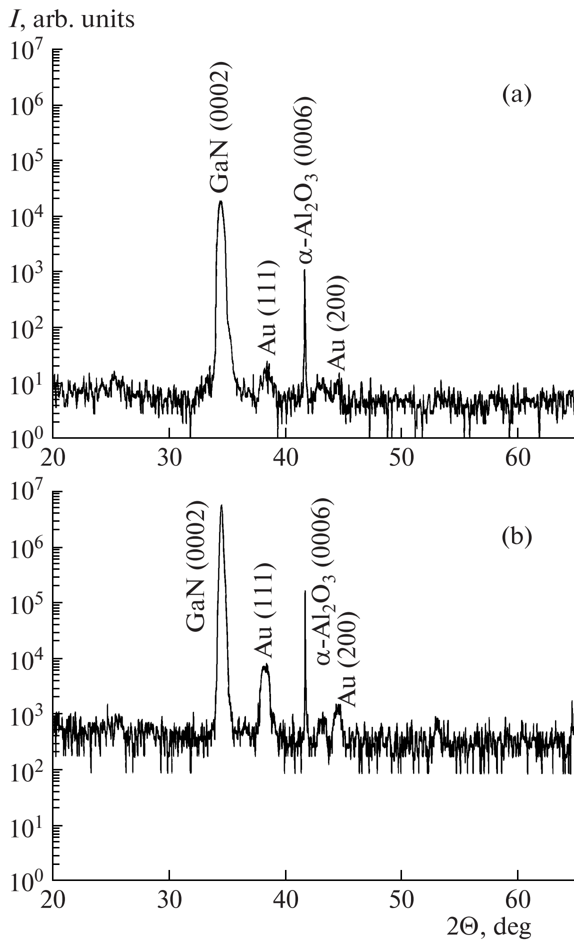

Fig. 1. X-ray diffraction patterns of the Au–TiBi$_x$–n-GaN structures: (a) initial, (b) after the rapid annealing at $T = 900°C$ for 30 s.

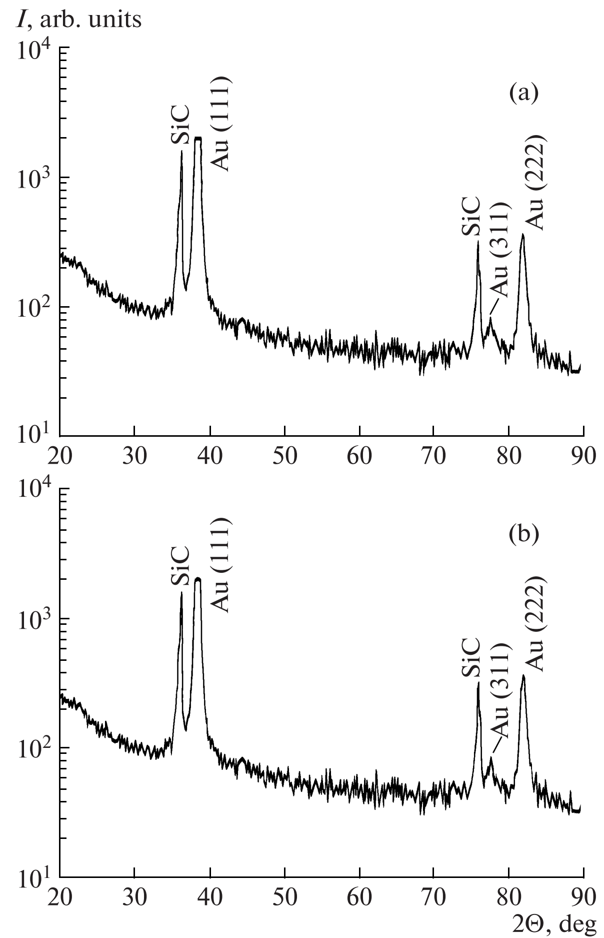

Fig. 2. X-ray diffraction patterns of the Au–TiBi$_x$–n-6HSiC structures: (a) initial, (b) after the rapid annealing at $T = 1000°C$ for 60 s.

0.6 eV at the temperature of 400°C, t = 20 min, in nitrogen atmosphere and, further, insignificantly increased at the annealing temperature of 600°C. In this case, the ideality factor of the I–V characteristic increased from 2.2 up to 3–4. The authors of [18] associated such changes in parameters of the contacts with the effect of annealing on the electric inhomogeneity at the interphase boundary of MS and, first of all, on the vacancy concentration in the surface layer of the semiconductor.

The degree of structural–chemical nonuniformity of the IPB depends on technological conditions of

Effect of the rapid annealing on the Schottky-barrier height φ_b and the ideality factor n of the I–V characteristics of the diode structures Au–(Ti, Zr)B$_x$–n-GaN(SiC) with Schottky barrier

Type of diode structures with Schottky barrier and the annealing time (RTA)	φ_b, eV				n			
	Initial samples	RTA temperature			Initial samples	RTA temperature		
		800°C	900°C	1000°C		800°C	900°C	1000°C
Au–TiB$_x$–n-GaN, RTA 30 s	0.9	0.9	0.89	–	1.2	1.2	1.2	–
Au–ZrB$_x$–n-GaN, RTA 30 s	0.89	0.89	0.89	–	1.2	1.2	1.2	–
Au–TiB$_x$–n-6HSiC, RTA 60 s	0.82	0.82	–	0.82	1.2	1.2	–	1.2
Au–ZrB$_x$–n-6HSiC, RTA 60 s	0.79	0.8	–	0.8	1.2	1.2	–	1.2
Au–ZrB$_x$–n–n^+-4HSiC, RTA 60 s	0.83	0.83	–	0.83	1.12	1.12	–	1.12

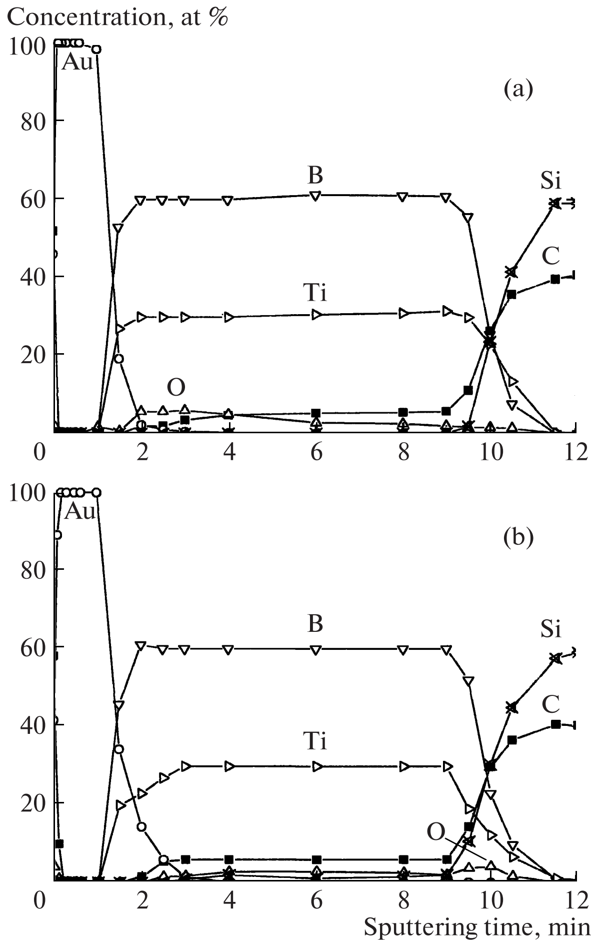

Fig. 3. Distribution of components in the Au–TiB_x–n-6HSiC contact as obtained by the Auger spectroscopy (a) before and (b) after the rapid annealing at $T = 1000°C$ for 90 s.

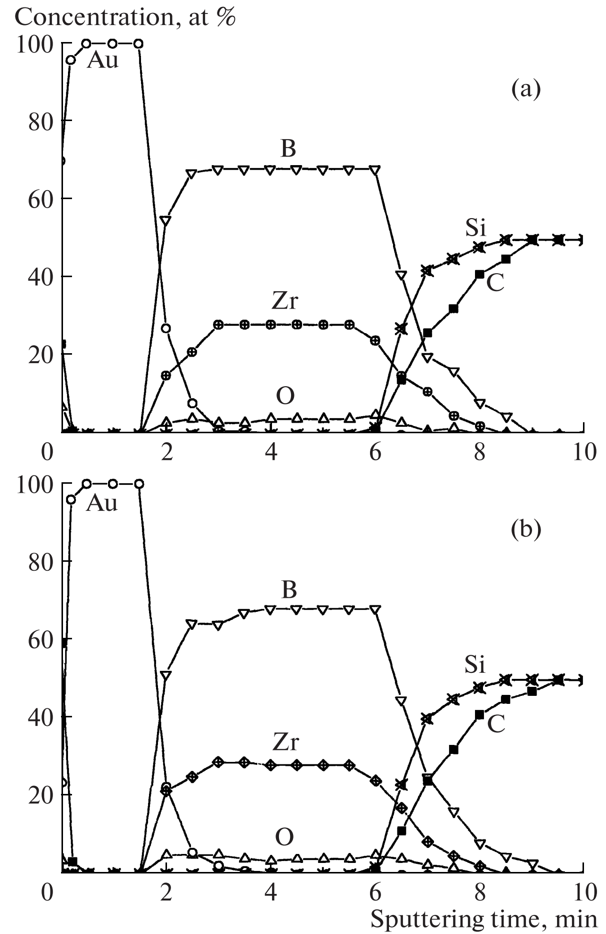

Fig. 4. Distribution of components in the Au–ZrB_x–n-6HSiC contact as obtained by the Auger spectroscopy (a) before and (b) after the rapid annealing at $T = 1000°C$ for 90 s.

boride-layer deposition influencing their nucleation and features of interaction with the semiconductor.

It was confirmed by the investigations fulfilled in [19], where the changes in the SB-height magnitude and the nonideality factor of the I–V characteristic for the ZrB_2–4H-SiC structures fabricated on semiconductor substrates at different temperatures were observed. An increase in the SB height to 1.07 eV was observed when depositing ZrB_2 on a substrate heated to 600°C from the original values of $\varphi_b = 0.87$ eV on the samples fabricated at almost room temperature. At the same time, the ideality factor n decreased from 2.71 at the room temperatures to ~1.06 at 600°C. The last fact indicates the IPB homogenization. It is confirmed also by the results on the effect of annealing at 200–500°C on the structures fabricated when depositing ZrB_2 on "hot" (800°C) and "cold" (20°C) substrates. In the first case, the annealing at 500°C resulted in a small (~0.08 eV) decrease in φ_b and in an increase in n (~0.1); in the second case, it led to an increase in φ_b (~0.07 eV) and a decrease in n from 3.1 to 2.0.

The changes in the SB parameters are even less considerable at the annealing in the contacts with quasi-amorphous layers (see table).

If we assume that the thermal treatment of contacts amounts only to decreasing the potential barrier, which is necessary to overcome the interphase mixing of its atomic components, and, hence, provides the energy advantage of the final state, the causes of electric nonuniformities of contacts are the processes of interphase transport including the chemical diffusion.

The presence of a single unpaired 2p electron at the outer orbital induces the high probability of formation of more stable configurations sp^2 and sp^3 by boron atoms, which provide the occurrence of strong covalent bonds both between the boron atoms and in its compounds with the atoms forming the SiC and GaN materials. Several covalent compounds of boron with carbon and silicon are known [10]. In the B–N system, one boron-nitride compound existing in three

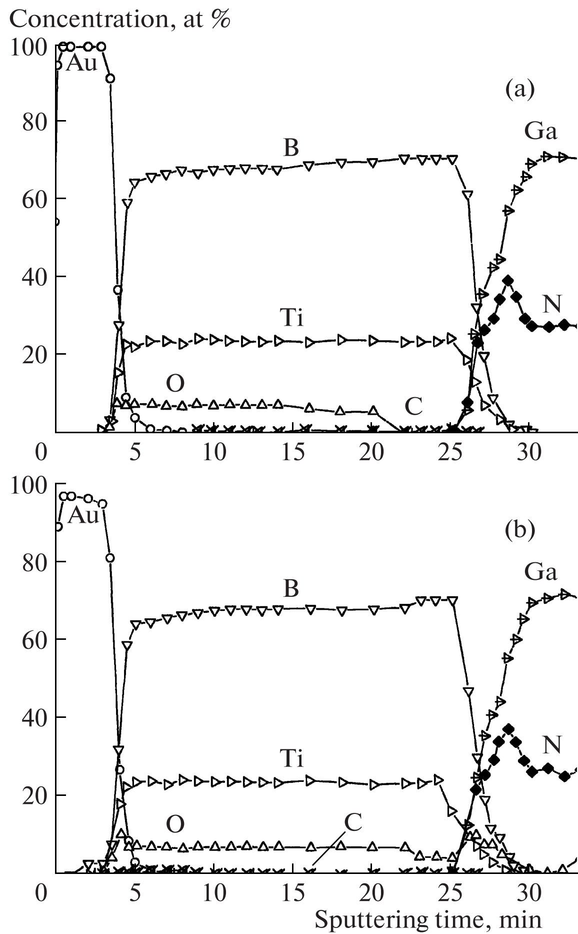

Fig. 5. Distribution of components in the Au–TiB$_x$–n-GaN contact as obtained by the Auger spectroscopy (a) before and (b) after the rapid annealing at $T = 900°C$ for 30 s.

modifications is found. No binary compounds were found in the Ga–B system. However, the data of the X-ray-diffraction analysis and the Auger electron spectroscopy, as well as the results of investigations carried out in [18, 19], do not confirm the occurrence of boron binary phases even at the highest temperatures of heat treatment of the contacts; i.e., the chemical bonds of boron with atoms of transition metals are more favorable in contrast to the mechanism of the solid-phase interactions in the transition layers of contacts based on titanium borides and nitrides to gallium arsenide; this mechanism was suggested in [20, 21].

Thus, the considered chemical interactions cannot be the cause of formation of the stable IPB with a small extent of the mixing area. The question arises, what is the cause of the observed features of the IPB formation and its high stability.

The complete identity of the effect of annealing irrespective of their temperature on the IPB characteristics of the contacts formed on semiconductors of different nature indicates that there is a unified mechanism determining the formation and the subsequent evolution of the boride–semiconductor boundaries.

The results of the layer-by-layer Auger analysis of contacts and the data of the X-ray photoelectron (XPE) spectroscopy and the Rutherford backscattering [19] indicate that there is a considerable content of oxygen both in boride films and in the transition areas of contacts. It is known that the oxidation of borides by oxygen in air begins at 600°C; at the same time, boron and metal oxides can arise even at lower temperatures at the initial stages of formation of the coating. Indeed, the XPE spectra measured in the binding-energy range (E_b) of core electrons O-1s, Zr-3d, and B-1s confirm the above assumption. It was found that a broad band, which is indicative of the presence of chemically nonequivalent Zr states in the layer at the interface, is observed in the spectra in the binding-energy region of 3d electrons of Zr. The lines in the spectra with the binding energies of the $3d_{5/2}$ electrons within 179.3–179.5 eV can be referred to as the chemical compounds of zirconium with boron, and the lines with E_b occurring in the range of 180.1–193.8 eV can be related to as the zirconium oxide phases [22].

The XPE spectra measured in the binding-energy region of the boron 1s electrons indicate that there are two states of boron atoms. First, with $E_b \approx 179.3$ eV, can be referred to as zirconium boride and, second, with $E_b \approx 190$ eV, can be assigned to boron oxide B_2O_3. The XPE spectra of the 1s electrons of oxygen, in which a shift of E_b is observed for the oxygen atoms characteristic of the formation of oxide phases [22] is also indicative of the presence of the Zr and B oxide phases in films. Since oxides of boron and metal components are glass-forming [23], we may assume that a thin amorphous vitreous layer resistant against rapid thermal annealing and representing the diffusion barrier for the interphase transport arises at the IPB.

The data of electrical measurements also support the presence of an amorphous layer located at the IPB and resistant against the investigated annealing modes. The annealing affected only slightly the ideality factor n and the SB height φ_b; i.e., the parameters of this layer did not vary at the annealing, and its presence provided the Fermi-level pinning in the semiconductor band gap.

Finally, certain differences in the characteristics of mixing areas in the Au–TiB$_x$–6H-SiC and Au–ZrB$_x$–6H-SiC structures can be a consequence of different porosity of the TiB$_x$ and ZrB$_x$ layers. The profiles of Au-atom distribution are also indicative of this fact. The penetration depth of Au in ZrB$_x$ is larger than in TiB$_x$; i.e., the zirconium boride has a higher concentration of pores which can act as sinks for the semiconductor atoms.

4. CONCLUSIONS

Thus, the described investigations confirm that it is promising to use borides of refractory metals in con-

tact systems to wide-gap semiconductors for improving their resistance to high-temperature overloads.

However, it should be noted that the use of these materials with unique properties in the technology of semiconductor devices is only beginning, and many problems associated with the operation of the contact structures in extreme operation modes are still not studied in full measure.

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Translated by V. Bukhanov