Semiconductor Physics, Quantum Electronics & Optoelectronics. 2002. V. 5, N 4. P. 457-464.

PACS: 73.40.Ns, 73.30.+y

Evolution of structural and electrophysical parameters of Ni/SiC contacts at rapid thermal annealing

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Abstract. Using X-ray phase analysis, Auger electron spectroscopy and atomic force microscopy, we investigated structural-phase transformations in the Ni/*n*-21R-SiC system induced by rapid thermal annealing in a vacuum (pressure of 10^{-2} Pa) in the 450–1100 °C temperature range. It was found that modification of contact *I-V* curves from barrier-type to ohmic is due to appearance of local contact areas with different barrier heights (among them areas with ohmic conduction). Generation of the above nonuniformities results from intense heterodiffusion of the system components, as well as formation and recrystallization of various nickel silicide phases (differing in stoichiometry) and degradation of planar uniformity of both interface and Ni film.

Keywords: Ni/SiC contact, Schottky barrier, nickel silicides, rapid thermal annealing (RTA), X-ray phase analysis, Auger analysis, atomic force microscopy.

Paper received 15.11.02; accepted for publication 17.12.02.

1. Introduction

Silicon carbide is a promising material for application in high-power electronic devices. It is characterized by high gap (from 2.3 up to 3.3 eV for different polytypes), as well as high value of critical electric field (3–4 MV/cm) and good thermal conductivity (4.9 W/cm·K). That is why SiC seems to be a potential candidate for development and production of various electronic facilities with new performance capabilities [1-3].

Various metal contacts (such as Al, Co, Pd, Ti, TiC, TiN, etc.) to silicon carbide have been intensively studied in recent years [4]. Many authors consider nickel as the most appropriate material for formation of ohmic and rectifying contacts to SiC [5, 6]. To control contact electric properties, one has to know the degree of structural-phase uniformity of contacts, as well as interface heterogeneity and stability, both at different stages of manufacturing technology and at extreme temperature modes of operation.

A well-known feature of thin-film systems (about 100 nm thick) is that new phases of film components and substrate are formed at interface at lower temperatures than in bulk materials. Besides, even slight variations of manufacturing technology, as well as presence of various structural defects, orientation and type of single-crystalline substrates and other factors, may lead to essential changes in proceeding of relaxation and phase ordering processes.

We performed a complex of structural and electrophysical studies of Ni/*n*-21R-SiC system exposed to rapid thermal annealing (RTA). Our objective was to investigate the features of structural changes at the interface and their relation to the electrophysical parameters of contacts.

2. Experimental procedure

Ni/*n*-21R-SiC contact structures were formed at the (0001) Si faces of single-crystalline SiC (polytype 21R) substrates. The 21R-SiC single crystals were Lely-grown and doped with nitrogen (concentration of $(1\div2)\cdot10^{18}\,cm^{-3}$).

Ohmic contacts to SiC were formed by resistive sputtering Ni film of 100 nm thickness onto chemically cleaned (0001) faces of the samples to be studied. The substrate temperature was 300 °C. After this the samples were exposed to RTA in a vacuum (pressure of 10^{-2} Pa) for 10 s at temperatures up to 1100 °C.

The barrier contacts were formed by thermal evaporation of Ni films (of the same thickness as in the case of

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ohmic contacts) onto chemically cleaned sample surfaces. The substrate temperature was 300 °C. Then the samples were exposed to RTA in a vacuum for 10 s in the temperature range from 450 up to 1100 °C. The heating rate was 100 K/s. RTA were performed using incoherent IR radiation (plant ITO-18MB) [7].

Comprehensive structural studies of the Ni/SiC system were performed using the following techniques: X-ray phase analysis, Auger electron spectroscopy and atomic force microscopy. The surface resistance of Ni films was measured using the four-probe technique. The contact barrier characteristics were studied with the stationary *I-V* curve technique.

3. Experimental results and discussion

The results of X-ray phase analysis have shown (Fig. 1) that even in the initial (before RTA) samples, along with polycrystalline nickel (of hexagonal modification) some other phase were present. These were $NiSi_2$ and δ-Ni_2Si phases, as well as a big amount of NiSi phase with preferred crystallite orientation along the <011> direction.

Increase of RTA temperature T up to 600 °C leads to decrease of texturing degree for the NiSi phase: height of the reflection peak (002) near 66° drops, while its width grows. Further increase of RTA temperature completely breaks preferred crystallite orientation and decreases amount of the above phase.

In addition, the amount of δ-Ni_2Si phase drastically increases after RTA at 600 °C and continues to grow with further RTA temperature. After RTA at 1100 °C the diffraction peaks related to X-ray reflection from that phase become considerably higher than those related to other phases. This indicates at predominance of the δ-Ni_2Si phase in the Ni/SiC system. The fact that half-width of these peaks steadily decreases as RTA temperature is increased indicates at a gradual rise of crystallite sizes and structural perfection of the δ-Ni_2Si phase. Despite this fact, there is no preferred orientation of the above phase crystallites (any orientation is equiprobable).

The behavior of $NiSi_2$ phase after RTA is quite different. When RTA temperature is increased, the amount of this phase rises slightly; but even RTA at 450 °C leads to intensity redistribution between the (111) and (511) relations (28.5° and 95.3°). After RTA at 1100 °C the peak of (511) relation practically disappears; at the same time a high narrow peak of (111) relation is clearly observed. Such change with temperature of the diffraction pattern formed by the $NiSi_2$ phase evidences that recrystallization of this phase occurs. As a result of this process, the crystallite sizes, as well as degree of their structural perfection, grow, and the crystallites are reoriented along the <111> direction.

The above character of phase ordering in the structure studied may be explained by assuming that there are two regions in the diffusion zone separated by a barrier that prevents them from diffusive homogenization. One of these regions may be a transition layer between SiC and Ni. This layer was formed at the stage of structure fabrication; it is enriched with silicon. When RTA temperature is increased, then recrystallization occurs in the above region, with intense formation of the $NiSi_2$ phase; in this case the SiC substrate assigns orientation (similarly to the case of epitaxial overgrowth).

The above picture is confirmed by the character of the Ni/SiC interface nano-relief revealed after Ni film removal by ion sputtering (Fig. 2). The interface relief of Ni/SiC structures that were exposed to RTA at temperatures not over 750 °C is characteristic of that for single-crystalline SiC surface. One can see a considerable number of linear defects of different depths, with clearly pronounced boundaries. After RTA at 900 °C the boundary surface becomes grainy, the lateral (vertical) grain sizes being 30–60 (1.5–3.0) nm. Further increase of RTA temperature up to 1100 °C considerably increases sizes of grain-like objects at the heteroboundary: their sizes (measured after Ni film removal) are 200–800 nm (lateral) and 70 nm (vertical). As mentioned above, just at such RTA temperatures a peak belonging to the textured $NiSi_2$ phase appears on the diffraction patterns. It seems plausible that these grains are just those of the recrystallized $NiSi_2$ phase.

Another evidence of a considerable interface modification after RTA is given by the Auger concentration depth profiles taken for the Ni/SiC contact components (see Fig. 3). One can see that even at 450 °C intense heterodiffusion processes are proceeding in the Ni film. They result in nonuniform distribution of Ni, Si and C atoms, but (as is evidenced by the results of X-ray phase analysis) practically do not change the phase composition at the interface. The degree of nonuniformity of the system components distribution in the contact somewhat increases with RTA temperature; however, the values of nonuniformity degree after RTA at 600, 750 и 900 °C remain close to each other. A considerable growth of the δ-Ni_2Si phase amount occurs just in this temperature range. The observed character of Si and C atoms distribution (see Fig. 3) is the subject of our further studies. It seems that it is just nonuniform carbon distribution in the contact that resulted in structure “layering”. A nonuniform character of carbon distribution (with appearance of a periodic band-like structure in the diffusion zone) was mentioned in a number of papers [8-10]; however, the mechanisms for its formation have not been considered.

One should note a considerable amount of carbon in the Ni film near-surface region even in the initial samples. This seems to be due to the Ni film crystal structure that favors intense grain-boundary diffusion of carbon: preferred crystallite orientation along the <111> direction and presence of nano-voids (they appear on the surface as an array of pits 2–6 nm in depth (Fig. 4). One can see from Fig. 4 that after RTA at 450 °C the film surface is covered with nano-islands (diameter of about 30 nm, height from 5 to 10 nm). Based on the results of Auger analysis, one can assume that these islands involve predominantly carbon (in the 450–900 °C temperature range

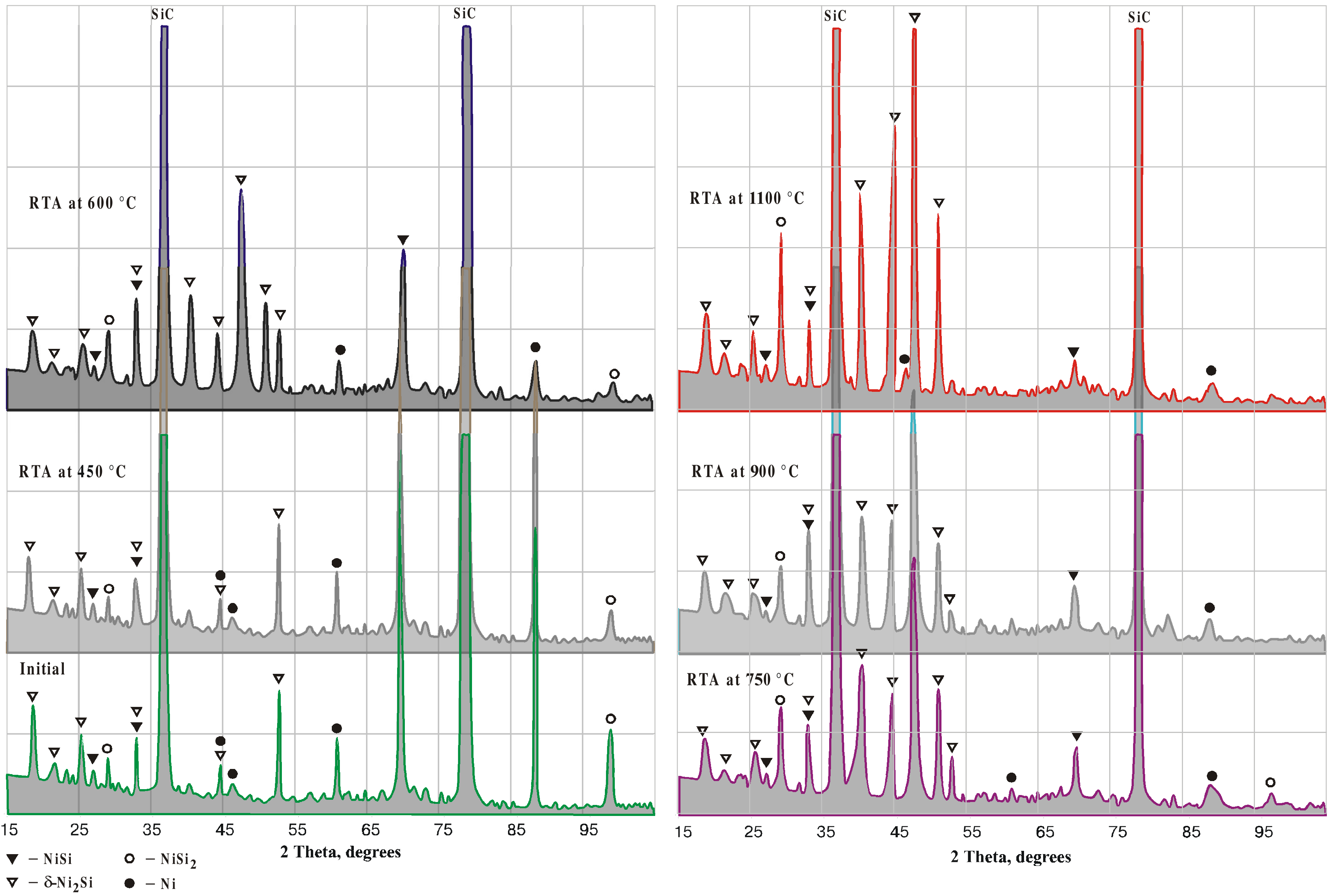

Fig. 1. X-ray diffraction patterns of Ni/SiC samples (Si side) after RTA at different temperatures.

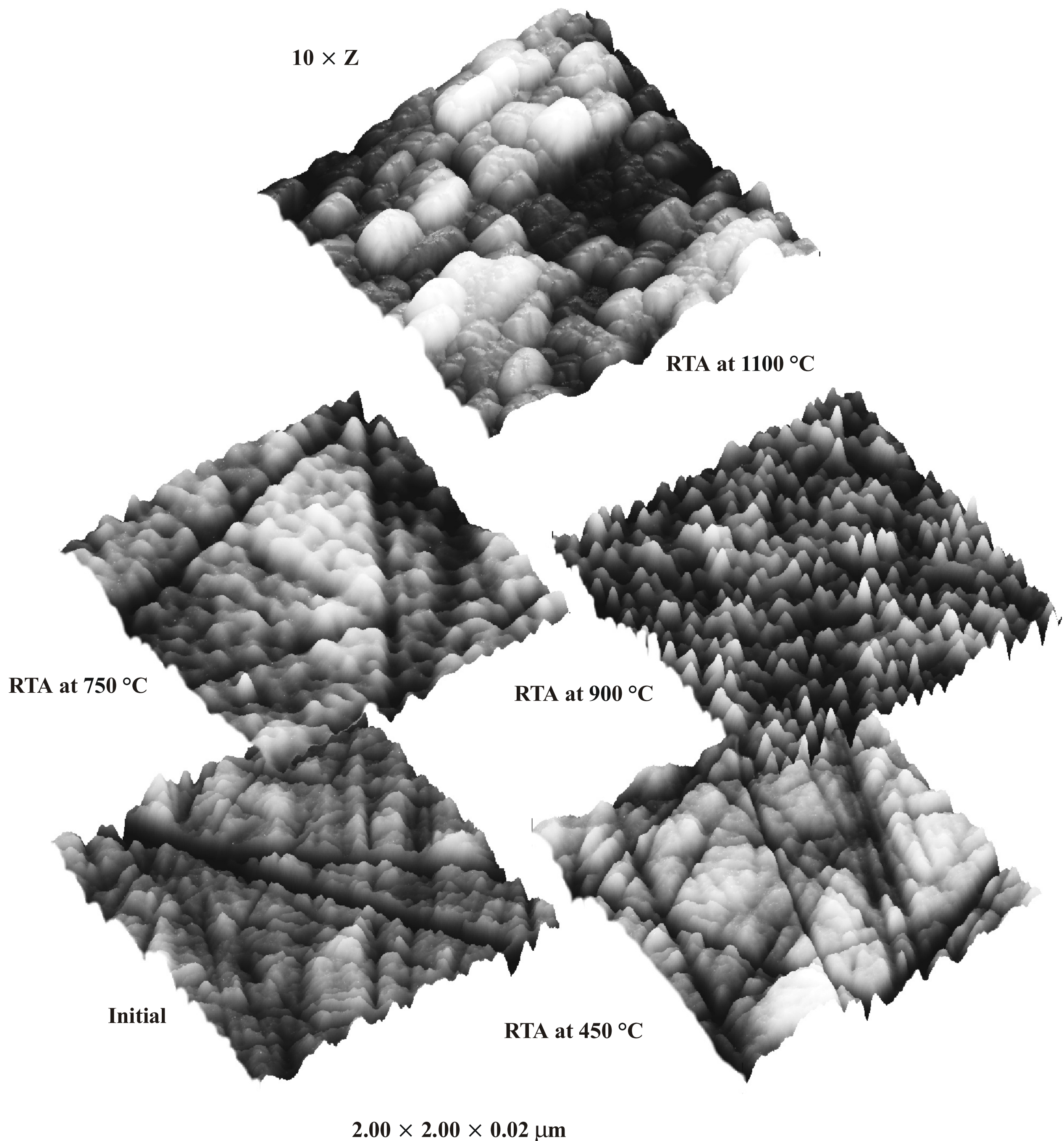

Fig. 2. Nano-relief (revealed after ion sputtering) of the Ni-SiC interface (Si side) after RTA at different temperatures.

the thickness of the near-surface carbon layer in the Auger concentration depth profile is the biggest at the mentioned RTA temperature). Increase of RTA temperature in the above range results in some thickness decrease for the carbon near-surface layer. This fact seems most likely to be due to processes of Ni film disruption and carbon segregation in the micro-voids that are free of Ni (Fig. 4). Appearance of such voids in the Ni film bulk after thermal annealing was observed in [11, 12] using transmission electron microscopy.

A considerable growth of δ-Ni_2Si phase amount and disappearance of peaks in the Si and C concentration depth profiles after RTA at 1100 °C are related to practically complete disruption of the Ni layer. This conclusion is supported by the results of atomic force microscopy studies. The structure surface was found to have many hollows whose lateral sizes were from 200 up to 1000 nm. The histograms of Ni film surface points (Fig. 5) are transformed from Gaussian to multimodal ones. This fact also may indicate at some contact "layering" into two main

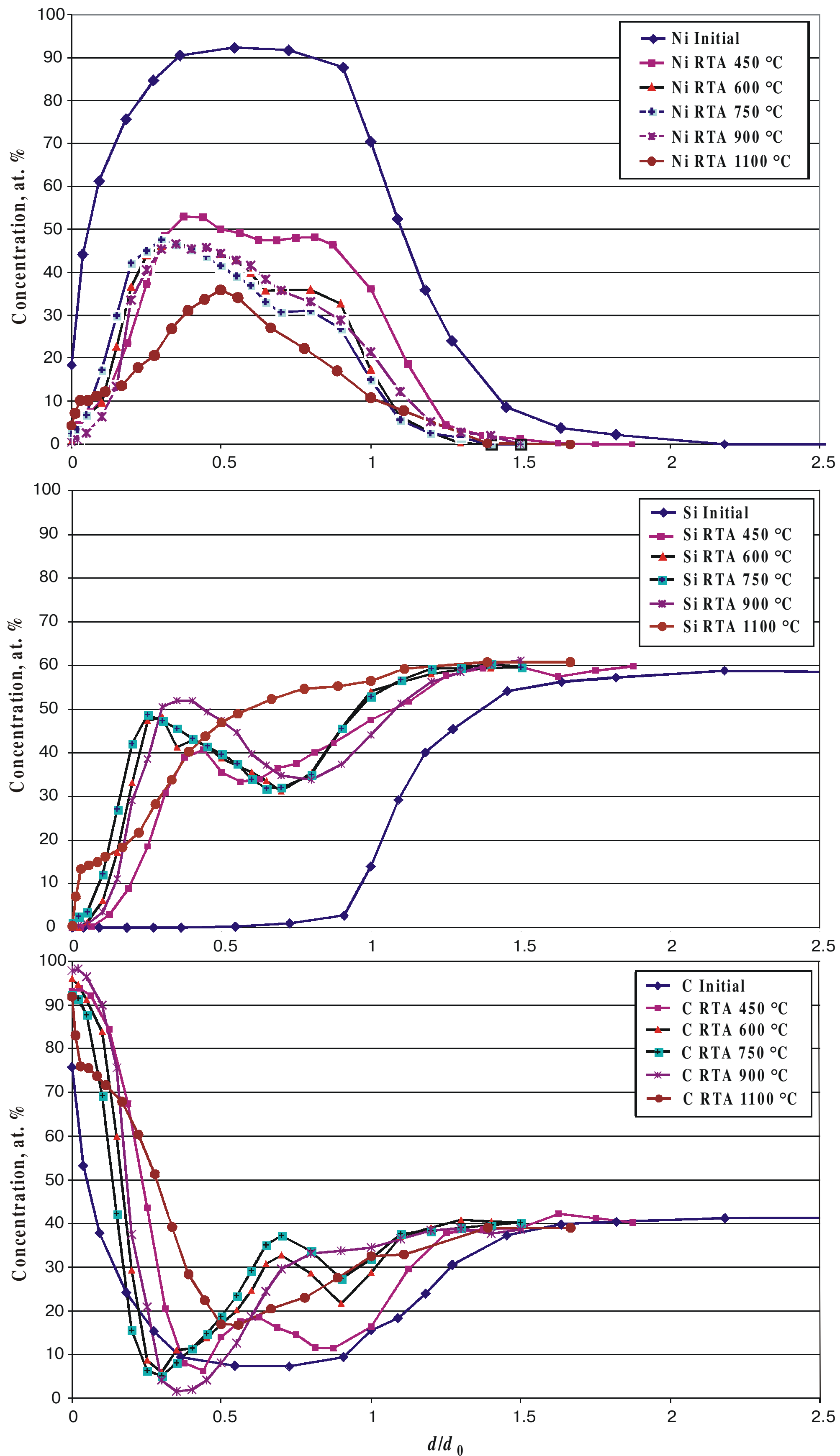

Fig. 3. Auger concentration depth profiles of the components of Ni/SiC system (Si side) after RTA.

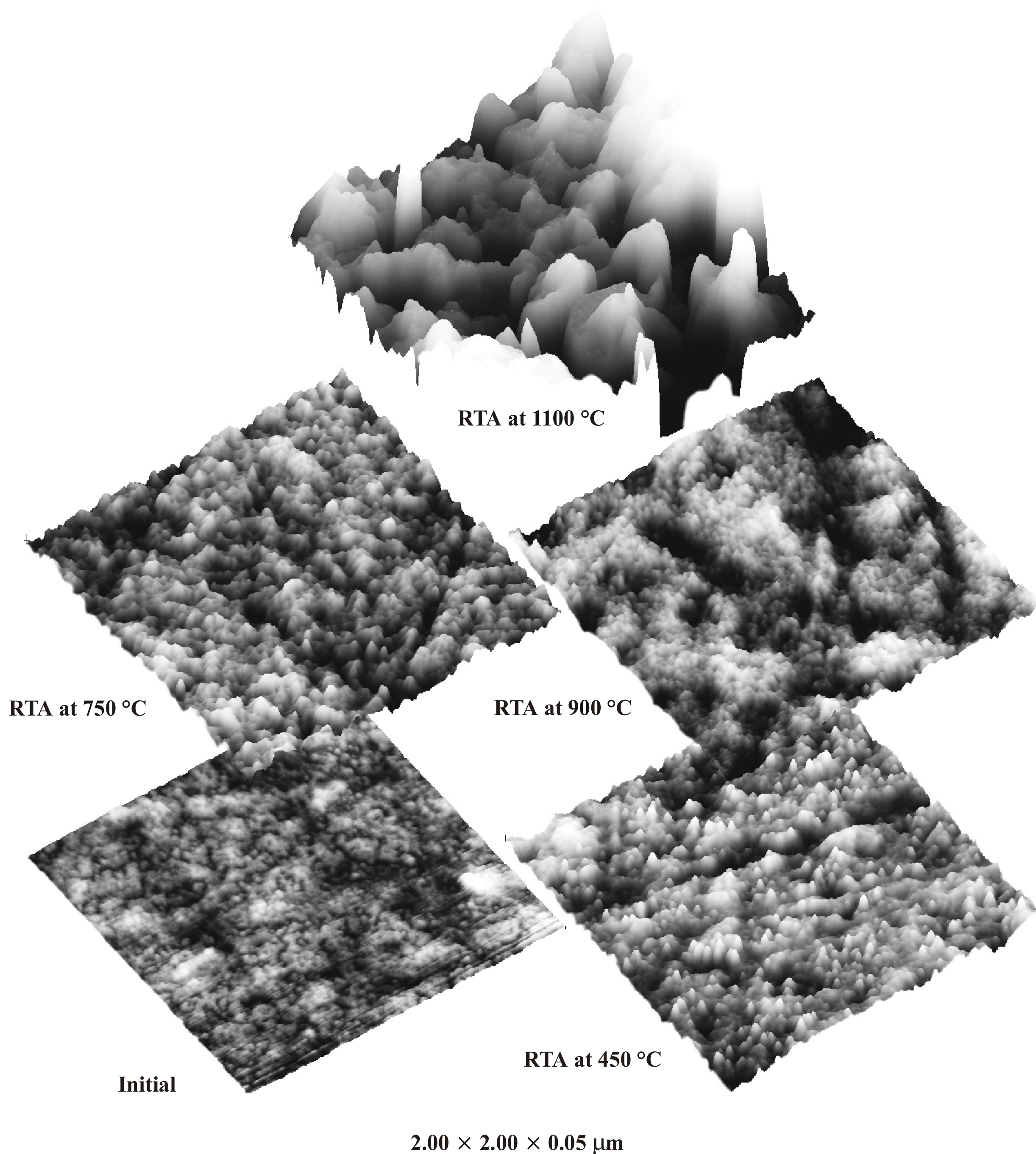

Fig. 4. Surface microrelief of Ni film after RTA at different temperatures.

phases, $NiSi_2$ and Ni_2Si, separated with a carbon interlayer.

We believe that the above results of structural investigations agree with those of electrophysical studies. One can assume that the Ni/SiC structure after RTA is a set of areas of different barrier heights connected in series, with an ohmic component that becomes predominant after RTA at 750, 900 and 1100 °C.

The forward branches of *I-V* curves for the contact structures studied are given in Fig. 6. One can see that *I-V* curve of the initial structures and those after RTA at T = 450 and 600 °C may be analytically presented as $j = j_0 \exp\left(\frac{qV}{nkT} - 1\right)$. Here j is contact current density, j_0 is saturation current density, q is electron charge, V is applied voltage, n is ideality factor, and k is Boltzmann constant. $j_0 = A^* T^2 \exp\left(-\frac{q\varphi_B}{kT}\right)$, where φ_B is Schottky barrier height and A* is Richardson constant.

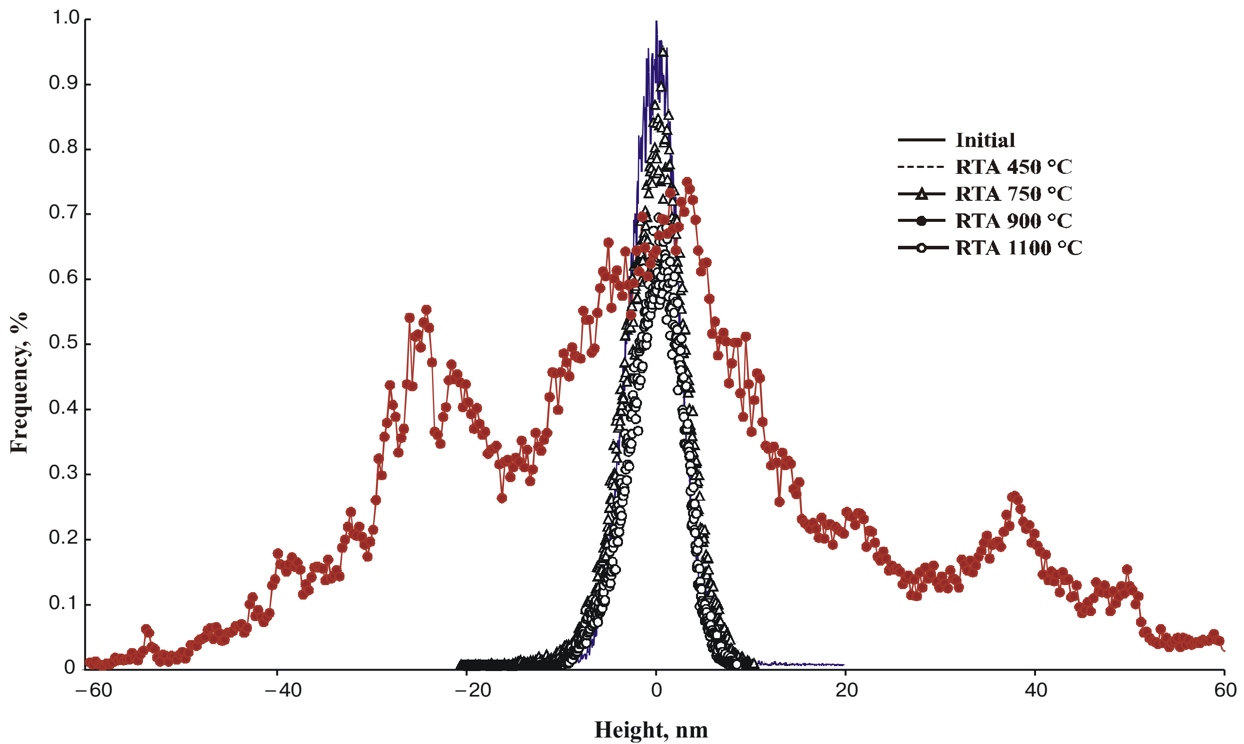

Fig. 5. Histograms of Ni film surface points after RTA.

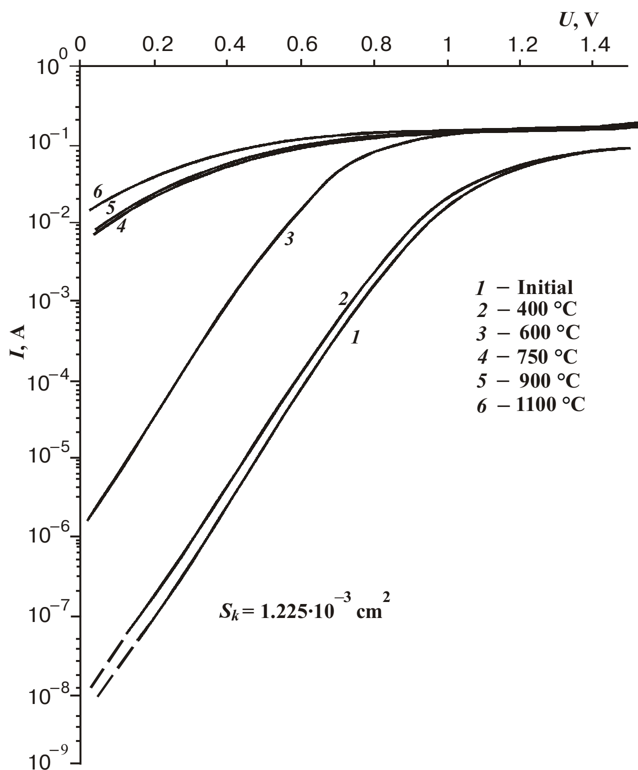

Fig. 6. Forward *I-V* curves of Ni/SiC contacts (Si side) after RTA.

Using the above expression for the forward branch of *I-V* curve, we determined the Schottky barrier height as $\varphi_B = \frac{kT}{q}\ln\left(\frac{A^* T^2}{j_0}\right)$ and ideality factor as $n = \frac{q}{kT}\left(\frac{\partial V}{\partial(\ln j)}\right)$. The j_0 was found by extrapolating current to zero voltage. The barrier structure parameters obtained in such way are given in Table 1. One can see from this Table and Fig. 6 that contact retains its barrier properties after RTA at 450 °C. The fact that ideality factor $n \geq 2$ indicates at domination of recombination processes in the current flow mechanism. One can see from Fig. 6 that RTA at higher (750, 900 and 1100 °C) lead to evolution of barrier contact to ohmic one.

Both structural and electrophysical parameters of Ni/SiC contacts indicate at formation of two different interfaces after RTA. One of them appears after RTA at 450 and 600 °C (barrier contact), while another is formed by RTA at 750, 900 and 1100 °C (ohmic contact). It should be noted also that contact evolution has been predetermined, to a great extent, by the initially nonuniform interface that was formed during Ni deposition onto the SiC substrate heated up to 300 °C.

Table 1. The parameters of Ni/*n*-21R-SiC (0001) barrier structures: current density *j*, Schottky barrier height φ_B, surface resistance of Ni film ρ and ideality factor *n*.

	Temperature of RTA, °C					
	initial sample	450	600	700	900	1100
j, A/cm^2	$4.8 \cdot 10^{-6}$	$1.2\ 10^{-5}$	$1.2 \cdot 10^{-2}$	3.7	5.1	4.7
φ_B, V	0.72	0.69	0.52	0.37	0.36	0.36
ρ, Ω/□	3.95	1.30	2.83	4.48	3.56	1.01
n	2.3	2.3	2.5	4.7	5.7	4.7

4. Concluding remark

It is found that RTA at 450÷1100 °C result in intense processes of structural-phase ordering of the initially nonuniform interface of the Ni/*n*-21R-SiC contact. These processes gradually decrease the Schottky barrier over the whole RTA temperature range. Finally the (previously) barrier contact becomes ohmic after RTA at temperatures over 750 °C. These results should be taken into account when developing manufacturing technology for electronic devices operating at high temperatures.

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