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Comparison of Ni/Ti and Ni ohmic contacts on *n*-type 6H–SiC

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Abstract Ni (50 nm)/Ti (10 nm) and Ni (50 nm) contact structures were deposited by vacuum evaporation on *n*-type 6H–SiC with various doping level. Prior to deposition, part of the substrates had been subjected to plasma cleaning. To achieve ohmic character, the samples were annealed in vacuum. Electrical parameters of the contacts were determined by measuring specific contact resistances. The results were similar for both contact structures; we have not found any influence of plasma cleaning. The lowest value was $1.4 \times 10^{-4}\ \Omega\ cm^2$ for substrate with doping level of $1.9 \times 10^{19}\ cm^{-3}$. Using XPS depth profiling it was found, that the titanium layer was shifted upon annealing of the Ni/Ti structures from the interface towards contact surface and that this layer consists of TiC. Between the TiC layer and the substrate was a layer of nickel silicides and carbon. In the plasma-cleaned Ni/Ti/SiC samples, increased content of nickel at the expense of carbon was detected just below the TiC layer. We suggest the snowplow effect of dopants in the SiC substrate upon annealing of the structures as a main factor in ohmic contact formation.

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1 Introduction

Outstanding properties of silicon carbide make it a promising material for manufacturing of many semiconductor devices. Its properties like wide band gap (3.0 eV for 6H polytype), high breakdown electric field, thermal conductivity, saturated drift velocity and chemical stability are ideal e.g. for high temperature and high power/frequency applications [1]. It is also used as a substrate for epitaxial growth of some III–V semiconductors.

Stable ohmic contacts with low values of specific contact resistance are necessary for reliable device operation. Many metallizations have been studied as ohmic contact structures: Cu/Si, TiC, W, Ta–Si etc. [2–5], but Ni is the most common ohmic contact metal [6–11]. For fabrication of ohmic contacts on SiC, annealing process of Ni/SiC structure is performed at temperature around 1,000 °C, resulting in low specific contact resistance ($\sim 10^{-4}$–$10^{-6}\ \Omega\ cm^2$). This annealing process is accompanied by the reaction of Ni with SiC, nickel silicides (mainly Ni_2Si) are formed and free carbon is liberated. Carbon, which is identified mainly in graphitic state, has been reported to accumulate at the interface of contact and SiC substrate [7, 10], at the top of the contact [6], periodically within the contact structure [11], or into layers inside nickel silicide [9]; work [8] shows uniform carbon distribution within the contact layer. Several explanations of these phenomena have been given [11–13]. According to some authors, free carbon might be potential source of contact instability and there have been attempts to reduce its amount by adding silicon into the contact structure [6, 7, 14]. Silicon binds some nickel and reduces its reaction with SiC, thus less carbon is released. Another option is combination of nickel and titanium; because titanium has high affinity to carbon forming TiC,

an amount of free carbon is reduced as well. Taking into account high affinity of Ni to Si and Ti to C, the formation of a thermally stable contact consisting of Ni-silicides and Ti-carbide can be expected in the interaction between the Ni/Ti metallization and SiC. Recently, several studies have been made investigating reactions, ohmic contacts and Schottky diode properties [12, 13, 15] of Ni–Ti multilayer structures on 4H–SiC. Except for one work describing reaction of Ni–Ti alloy with 6H–SiC [16], no data are available on reactions and ohmic contact behavior of Ni–Ti metallization on 6H–SiC.

This work focuses on studying electrical and structural properties of as-deposited and annealed Ni/Ti contact structure on *n*-type 6H–SiC. Structure without titanium was taken for comparison. Influence of plasma cleaning on the contact structure is shown. Electrical properties have been evaluated by specific contact resistance measurements on substrates with different doping level, structural analyses have been carried out by means of XPS (X-ray photoelectron spectroscopy) depth profiling.

2 Experimental

The 6H–SiC substrates of *n*-type used for preparation of ohmic contacts were supplied by the North Caucasus State Technical University in Stavropol, Russia and were produced by the Lely method. Hall measurements were used to specify electron concentrations in the substrates: 4.5×10^{17}, 1.7×10^{18}, and 1.9×10^{19} cm^{-3}. Orientation of the SiC substrates (silicon and carbon face) was not followed when preparing the samples.

Prior to deposition, chemical cleaning of the substrates had been performed, consisting of the following steps: (a) degreasing in acetone (10 min in ultrasonic bath), rinsing in distilled water, (b) removing organic contamination in NH_4OH, H_2O_2 and H_2O mixture (5:1:1, 5 min in ultrasonic bath), rinsing in distilled water, (c) removing the surface oxide in concentrated HF (5 min), (d) immersing the substrates in boiling re-distilled water (10 min). After that, the samples were left in water and transported to the evaporating apparatus UNIVEX 450. They were blown dry using nitrogen and mounted to the heated substrate holder by nickel foil with regular openings, which served as a mask for creating contact structure patterns. Evacuation of the apparatus was commenced immediately afterwards. Some substrates were then cleaned by means of the Ar^+ ions in situ in the evaporation apparatus: after pumping down to 2×10^{-6} mbar, the apparatus was filled with argon to 1×10^{-1} mbar and a discharge was ignited by applying a positive potential of 1,000 V to the counter-electrode (the substrate holder was kept on the earth potential); discharge current was 50 mA and cleaning time was 20 min. Titanium (10 nm) and/or nickel (50 nm) were deposited using the electron gun at initial pressure 2×10^{-6} mbar and substrate holder temperature of 135 °C.

The samples with contact structures were annealed in the evaporating apparatus at pressure of 2×10^{-6} mbar, in the cavity of two-piece molybdenum annealing tray. Annealing temperature was specified by melting of the metals at the surface of the cover part of the tray (960 °C Ag, 1,065 °C Au), annealing time was 10 min.

The main followed parameters of the contact structures were specific contact resistance and the surface morphology. Specific contact resistance was measured by modified four-point method [17]. Surface morphology was examined by optical microscope JEVAVERT. The XPS analyses were done on the samples by means of the ESCAProbe P apparatus (Omicron Nanotechnology Ltd.) equipped with Al Kα (1486.6 eV) X-ray source and a hemispherical analyzer. The size of the analyzed area is approximately 1 mm^2. Ar ions of 5 keV energy were used for ion sputtering.

3 Results

3.1 Contact resistance

Structures Ni (50 nm)/Ti (10 nm) and Ni (50 nm) were evaporated on the substrates with three various doping levels. Chemical cleaning was done in case of all SiC substrates; additional plasma cleaning was done in case of medium and highly doped substrates for Ni/Ti metallization prior to deposition; for Ni metallization, only the medium doped substrate was plasma cleaned. All as-deposited Ni/SiC and Ni/Ti/SiC structures had the values of specific contact resistance in 10^{-2}–10^{-1} Ω cm^2 range, which indicates Schottky character of the as-deposited contacts. The structures were annealed to achieve ohmic character. The values of specific contact resistance (r_C) had decreased upon annealing; the results obtained in the process of repeated annealing are shown in Table 1 (repeated annealing means that the structures were annealed repeatedly, first at 960 °C, then at 1,065 °C). Figure 1 shows the values of specific contact resistance for both metallizations in dependence on the substrate doping level. The presented values are the lowest that were reached during all experiments and contain values obtained by both single and repeated annealing.

Morphology observed by the optical microscope was similar for both metallizations; the surface was smooth at all annealing temperatures. Sometimes, thin grooves caused probably by defects of the SiC substrate were present.

Table 1 Comparison of specific contact resistance values of Ni and Ni/Ti contact structures (deviations were calculated between the individual contacts on single samples)

Metallization	SiC doping [cm^{-3}]	r_C [Ω cm^2]	
		960 °C, 10 min	1,065 °C, 10 min
Ni/Ti	4.5×10^{17}	$(5.0 \pm 0.5) \times 10^{-3}$	$(1.8 \pm 0.1) \times 10^{-3}$
	1.7×10^{18}	$(4.8 \pm 0.3) \times 10^{-4}$	$(4.7 \pm 0.3) \times 10^{-4}$
	1.9×10^{19}	$(2.2 \pm 0.6) \times 10^{-4}$	$(2.0 \pm 0.7) \times 10^{-4}$
Ni	4.5×10^{17}	$(2.1 \pm 0.5) \times 10^{-3}$	$(2.5 \pm 0.9) \times 10^{-3}$
	1.7×10^{18}	$(4.2 \pm 0.2) \times 10^{-4}$	$(4.3 \pm 0.3) \times 10^{-4}$
	1.9×10^{19}	$(1.5 \pm 0.1) \times 10^{-4}$	$(1.4 \pm 0.1) \times 10^{-4}$

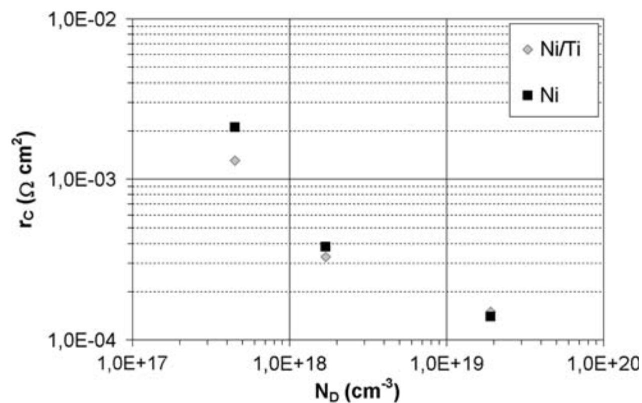

Fig. 1 Dependence of specific contact resistance (r_C) on doping for Ni/Ti and Ni contacts

3.2 XPS analysis

The composition of prepared structures was studied using the XPS analysis, including making depth profiles with utilization of ion sputtering. The results acquired on as-deposited and annealed samples are shown in Figs. 2–5, annealing before XPS analysis lasted 10 min at 960 °C. Figure 2 shows the depth profiles of the Ni/Ti/SiC structure (SiC substrate was not cleaned by Ar^+ plasma before deposition). Figure 3 shows the depth profiles of the same structure as the previous one, but the substrate was plasma cleaned before deposition. Figure 4 shows the depth profiles of the Ni/SiC structure [18] (where the substrate was plasma cleaned); in this profile sputtering time was replaced by depth. By measuring thicknesses of sputtered layers we experimentally found the sputtering rate of approximately 2 nm/min. Besides of composition we followed the XPS spectra of the individual elements and their variations during sputtering. Examples of spectra for carbon (C 1s) and silicon (Si 2s) are shown in Fig. 5; from these spectra we can estimate chemical bounds of these elements in both annealed and as-deposited metallizations.

The spectra show that contamination carbon bound from air was present on the surface of all samples (maximum of the C 1s peak at 284.6–285.0 eV); its concentration sharply decreased upon sputtering. From the depth profiles of all as-deposited metallizations it is obvious, that they contained high portion of carbon (10–20%), whose origin is so far unclear. Most probably it comes from the residual atmosphere in the deposition apparatus and builds into the layer upon evaporation by the electron gun. In as-deposited samples, nickel is most likely present as elementary (peak Ni 2p3/2 at 852.5–853.0 eV) and carbon as amorphous (peak C 1s at 284.8 eV). What is interesting is the presence of Ti partly in the form of carbide TiC (peak C 1s at 281.8 eV) in as-deposited Ni/Ti structures, which might be connected with carbon inbuilding upon deposition of the layers. Present oxygen follows titanium in the structures, however TiO_2 oxide hasn't been proved by XPS. It is not apparent that plasma cleaning influenced the composition and character of as-deposited contacts.

Annealing of the metallizations had principal impact on the character of their structure. In the metallization on the substrate, which was not plasma cleaned (Fig. 2b), the most significant change in the structure is transfer of the titanium layer towards the contact surface. The analysis of the carbon peaks in this area explicitly showed, that a portion of present carbon is bound to titanium as TiC (peak C1s at 281.5 eV) and this portion follows the content of titanium in the structure. Again, there is obviously increased content of oxygen in this layer. Ni and Si were present in substantial quantity especially close to the surface in the TiC layer. As evident by maxima of Si 2s peak at 150.5 eV, we could judge to nickel bound in the form of silicide (Ni_2Si). Under the layer containing TiC, there is nickel bound with silicon in the form of silicide, but the peak Si 2s is at the position 150.5–151.0 eV, which suggests also to the binding of Si to C mainly at the level of 30–35th min of sputtering. This fact is supported also by the shift of the C 1s peak towards lower energies and by lower nickel content compared to data from 40th min to 55th min of sputtering. Most of the carbon that is present here was however specified as free C (most probably graphite, peak C 1s at 284.5 eV). Deeper (70–110th min of

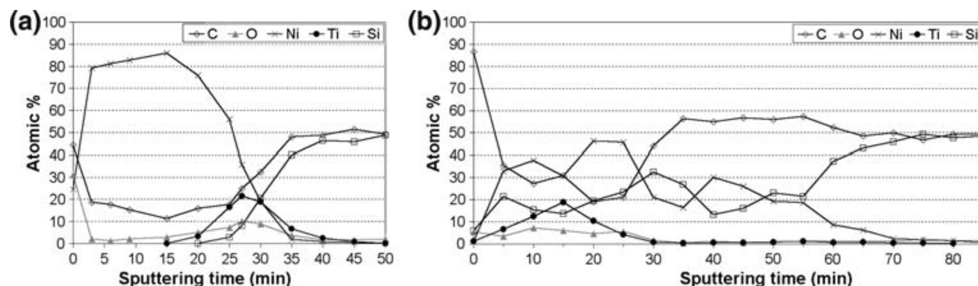

Fig. 2 XPS depth profiles: (**a**) as-deposited, (**b**) annealed Ni/Ti structure on SiC substrate without plasma cleaning

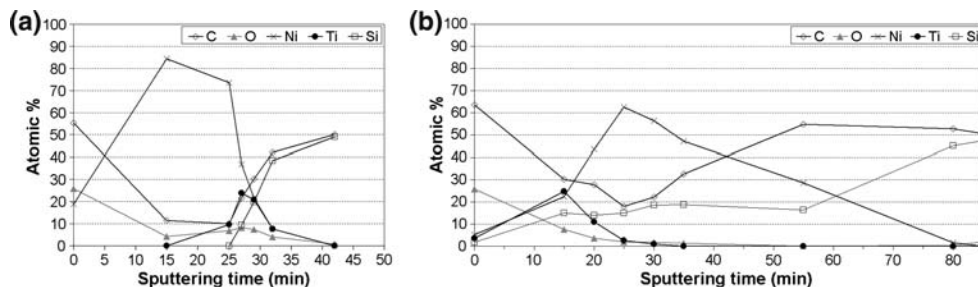

Fig. 3 XPS depth profiles: (**a**) as-deposited, (**b**) annealed Ni/Ti structure on the plasma-cleaned SiC substrate

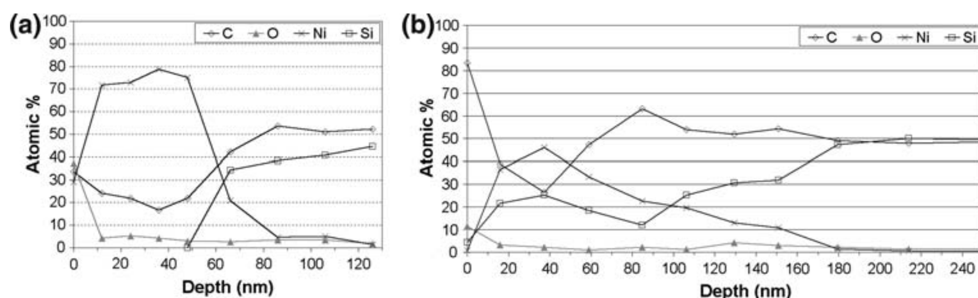

Fig. 4 XPS depth profiles: (**a**) as-deposited, (**b**) annealed Ni/SiC structure (plasma-cleaned substrate)

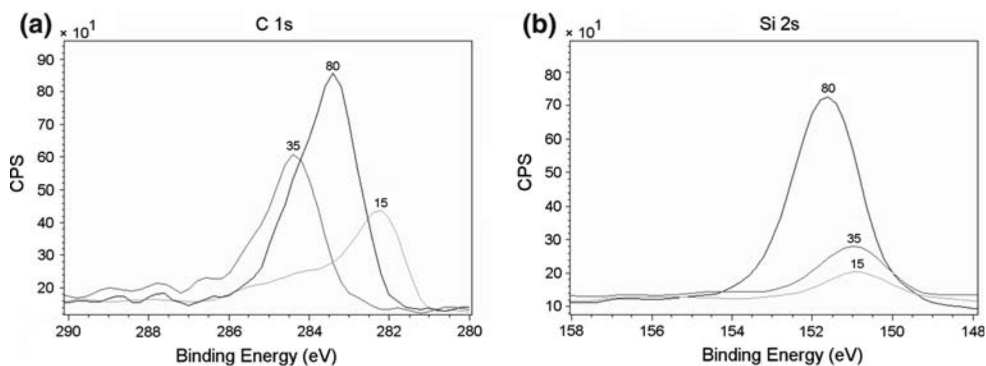

Fig. 5 XPS peaks of annealed Ni/Ti metallization on plasma-cleaned SiC—(**a**) carbon C 1s, (**b**) silicon Si 2s measured after 15, 35, and 80 min of sputtering

etching) SiC prevailed having identical peaks as SiC in as-deposited samples.

After annealing of the plasma-cleaned sample (Fig. 3 b), the layer containing titanium in the form of TiC (peak C 1s from 15th and 20th min in Fig. 5a) was located also close to the surface. Under this layer is however found more nickel at the expense of carbon, compared to the previous sample. Nickel is bound to silicon in the form of silicides; carbon is present most probably as graphite. The depth profile of the annealed nickel contact shown in Fig. 4b is very similar provided we neglect absence of the TiC layer.

4 Discussion

According to Table 1, for annealed Ni/Ti contacts we can see the influence of repeated annealing to decrease of the r_C value, while for the nickel contacts on low and medium doped substrates the r_C value has increased. Such behavior

may be caused by the presence of a layer containing titanium, which acts as a diffusion barrier and thus higher temperatures or longer annealing is needed to reach a balanced structure. Additional annealing at higher temperature however deteriorates nickel contacts. Plasma cleaning hasn't any significant influence onto the electrical parameters of as-deposited and annealed structures. When comparing the lowest r_C values in Fig. 1, the received values are quite similar; more significant difference in case of the least doped substrate might be caused by lower quality of the SiC material used for preparation of the Ni contacts. Although r_C decrease by several orders was expected for substrates with doping level of 1.9×10^{19} cm^{-3}, where the tunneling mechanism of conductivity with very low specific contact resistances should prevail, the lowest reached value was just 1.4×10^{-4} Ω cm^2 for nickel contacts. The reasons of such indistinctive decrease of specific contact resistance are not apparent, but may be related for example to the mechanism of ohmic contact formation as suggested further in this text.

Upon annealing, nickel diffuses through the thin layer containing titanium and reacts with SiC, creating nickel silicides and carbon; the remaining free titanium then reacts with a part of the released carbon. The TiC layer close to the contact surface is an advantage over contacts containing just carbon and nickel silicides, as it increases the oxidation immunity of the contacts at high temperatures, which was proved by ageing tests of the Ni/Ti and Ni structures up to 900 °C [19]. Moreover, creation of carbide in the structure surface lowers the content of free carbon. Increased content of oxygen was found in the titanium layer, however this does not prevent contact from reaching low r_C values. In the system containing Si, C and Ti there is also a possibility of forming of Ti_3SiC_2 ternary compound; this was however not detected by the XPS analysis.

Additional XRD (X-ray diffraction) analysis of annealed Ni (50 nm)/Ti (10 nm) contacts [19] confirmed nickel silicide content (orthorhombic Ni_2Si). Figure 6 shows selected part of the measured spectra that contains reflections of metallization. Reflections belonging to SiC are marked with the symbol S, reflections marked with the symbol N can be unambiguously assigned to the orthorhombic Ni_2Si; in the case of the peak at 45.72° this is a dominant reflection, the other smaller reflections were detected at 43.72°, 44.57°, and 49.05° [19]. Neither titanium compounds nor carbon were detected using this method.

The structural differences, which were found between the substrates with just chemical cleaning and those with additional plasma cleaning, could be also caused by different reactions of SiC polar faces. The differences between reactions on opposite faces of SiC were detected [20], but the contacts containing nickel are however

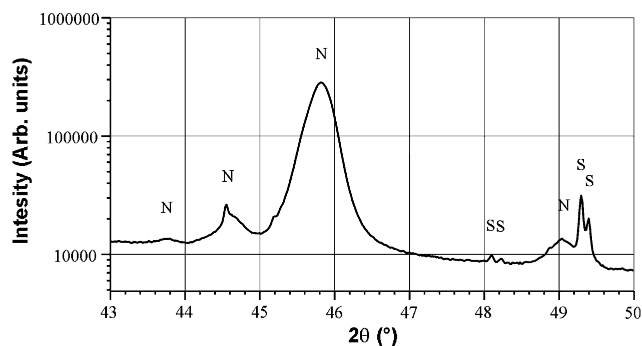

Fig. 6 X-ray diffraction pattern of annealed Ni/Ti/SiC contact structure (From: [19]. Copyright Elsevier (2007). Reproduced with permission.)

considered to be independent on substrate orientation [11]. High content of carbon in the evaporated structures and its influence on electrical and structural parameters of annealed contacts remains to be a problem. According to works of Lu et al. [21, 22], the carbon layer between the nickel metallization (thickness 200 nm) and 4H–SiC lowers annealing temperature necessary for occurrence of ohmic character; received optimal thickness was 2 nm, thicker C interlayers led to rather higher r_C values.

According to the observed changes after annealing of the contact structures, it is difficult to guess the mechanism of ohmic character formation. In the prepared Ni (50 nm)/Ti (10 nm) structures, the reaction between titanium and carbon plays just a side role and preferentially nickel reacts with the SiC substrate; the mechanism of formation of ohmic character will be thus similar to that of nickel contacts. Often stated possible reason is ohmic character of the interface between nickel silicides and SiC [7] or graphite and SiC [21]. Some authors consider creation of defects in the sub-contact SiC layer that have character of donors, increase doping level of SiC substrate and cause narrowing of the Schottky barrier [10]. High work function of both nickel silicides and carbon (approximately 5 eV [23, 24]) testifies against the first possibility, high dependence of the values of specific contact resistances on the SiC doping level testifies against the other possibility (occurrence of donor defects in the sub-contact area would be doping-independent and the r_C values would be rather similar). In the work of La Via et al. [9], measured Schottky barrier was 1.8 and 2.0 eV for nickel contacts on weakly doped SiC annealed at 600 and 950 °C, respectively. Although large increase of leakage current was detected after annealing at 950 °C, deep level transient spectroscopy has not shown occurrence of electrically active defects in the SiC substrate. The r_C values of the ohmic contacts after annealing are often dependent rather on SiC doping level than on used contact material. Therefore we suggest such mechanism that consists in

increasing of dopant concentration in the sub-contact SiC layer by the snowplow effect [25] of electrically active dopants present in SiC (namely nitrogen in the case of *n*-SiC). This would lead to narrowing of the Schottky barrier, resulting in increased probability of the charge carriers tunneling and thus to lowering of specific contact resistances. The relation between consumption of SiC by its reaction with the metallization and intensity of assumed snowplow effect at various annealing temperatures remains to be a question. Verification of the above mentioned hypothesis will be the subject of further research.

5 Conclusion

After annealing, similar values of specific contact resistance were measured for Ni/Ti and Ni contacts. The lowest reached value was $1.4 \times 10^{-4}\ \Omega\ \mathrm{cm}^2$ for SiC substrate with doping level of $1.9 \times 10^{19}\ \mathrm{cm}^{-3}$. The XPS analysis has shown that the layer containing titanium has shifted towards surface of annealed Ni/Ti metallization on both plasma cleaned and uncleaned substrates; further, we found that this layer consists of TiC. The layer between the SiC substrate and TiC consists of nickel silicides and carbon. Plasma cleaning of the SiC substrate before depositing of the metallization caused higher nickel content right under the TiC layer, without having influence on reached values of specific contact resistances. In case of Ni (50 nm)/Ti (10 nm) metallization, the main role is played by Ni reaction with SiC and mechanism of ohmic character formation than would be similar to that in nickel contacts. For formation of ohmic character we have suggested the snowplow effect of electrically active dopants in the SiC substrate upon annealing of the structures.

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