electroscope

Reactions of nickel-based ohmic contacts with n-type 4H silicon carbide

B. Barda, P. Macháč
Department of Solid State Engineering, Institute of Chemical Technology, Prague,
Technická 5, 166 28 Prague 6, Czech Republic
E-mail: Bohumil.Barda@vscht.cz, Petr.Machac@vscht.cz

Abstract:
We directly compared three nickel-based metallizations on Si-face of n-type 4H-SiC: pure nickel and nickel silicides prepared by the evaporation of nickel and silicon layers with overall composition corresponding to NiSi and Ni_2Si. The degree of interaction between the metallizations and silicon carbide was determined by the AFM (Atomic Force Microscopy) scanning of the SiC substrate after the selective etching of the metallizations. The optimal annealing temperature was 960°C for all the metallizations; the values of contact resistivity were $6–7\times10^{-5}\ \Omega\ cm^2$. The morphology of Ni (50 nm) contacts was free of defects at all annealing temperatures, but the reaction during annealing consumed approximately 60 nm of SiC. NiSi and Ni_2Si metallizations altered the surface of the SiC substrate, but no significant decomposition was detected by AFM. NiSi contacts had unsatisfactory droplet-like morphology after annealing at 960 and 1065°C. Annealed Ni_2Si contacts contained pores, but their formation was prevented by increasing the heating up rate of annealing. Due to suppressed interaction with SiC and good morphology, Ni_2Si is the most suitable metallization for shallow silicon carbide structures.

INTRODUCTION

Silicon carbide is a promising semiconductor material suitable for high temperature and high power applications because of its wide band gap (3.2 eV for 4H-SiC polytype), high thermal conductivity, breakdown electric field and electron saturation velocity [1]. For the utilization of these unique properties of SiC, stable ohmic contacts with low contact resistivity are necessary. Nickel is the most common contact material for n-type SiC. As-deposited nickel contacts have to be annealed at temperatures about 950°C to achieve ohmic behavior. During annealing, Ni reacts with SiC and nickel silicides together with free carbon (graphite) are created as a result [2, 3, 4]. Thus, a certain region of subcontact SiC is decomposed and the consumption of SiC by the reaction can influence behavior of the whole semiconductor structure. In addition, the contact structure is not homogenous and usually contains multiple bands of nickel silicides and graphite together with voids, which results in quick degradation under stressing [5]. The addition of silicon into the nickel metallization can reduce the reaction with SiC during annealing and minimize the decomposition of SiC [6, 7, 8]; also the homogeneity and conductivity should be superior to the nickel contacts.

The aim of this contribution is the investigation and optimization of pure nickel contacts and contacts prepared by deposition of different Ni/Si multilayers on n-type 4H-SiC. Testing of their interaction with the SiC substrate after annealing was performed by the wet etching of the metallizations, followed by the AFM analysis of the SiC substrate left after the etching.

EXPERIMENTAL

Substrates cleaved from an n-type 4H-SiC wafer (supplied by SiCrystal, AG) with the doping level of $4.2\times10^{18}\ cm^{-3}$ were used in our experiments. The substrates were chemically cleaned by a standard process [9]. Then the substrates were dried with nitrogen and transferred into an evaporation apparatus UNIVEX 450. The contact patterns for electric measurements were defined by a shadow mask. The deposition of contact materials was carried out on the Si-face of the substrates by an e-gun at pressure 2×10^{-6} mbar; the temperature of the substrates was 135°C during the deposition. The annealing of the samples was carried out in vacuum (3×10^{-6} mbar) in the cavity of two-piece resistively heated molybdenum annealing tray at temperatures 750, 850, 960 and 1065°C. Temperature was estimated by the melting of special materials at the surface of the cover part of the tray (750 and 850°C – temperature indicator material Thermomelt from LA-CO Industries, Inc.; 960°C – Ag; 1065°C – Au). Standard annealing time was 10 min. Electrical characterization was performed by measuring contact resistivity (r_C) using modified four-point method [10]. At least 10 groups of four contact pads with dimensions 150×200 μm and 1 mm distance were measured on each sample and values were averaged to obtain the final value of contact resistivity.

Initially, three types of Ni-based metallizations were prepared: pure nickel contact Ni(50), Ni(13)/Si(12)/Ni(13)/Si(12) and Ni(8.8)/Si(16.2)/Ni(8.8)/Si(16.2) sequence with overall composition corresponding to stoichiometry of Ni_2Si and NiSi silicide, respectively (numbers in parentheses represent the thickness of deposited layers in nanometers). Pure Ni contacts had the highest Ni content, Ni_2Si medium and NiSi contacts the lowest. For the etching of nickel silicides in annealed contact structures, two solutions of concentrated acids were used: HF + HNO_3 (1:3) and HCl + HNO_3 (3:1); etching lasted for 10 min in both solutions. For the etching of graphite present in annealed nickel contacts a conc. solution of $KMnO_4$ in the 10% water solution of KOH was used (1–3 days duration of etching). Surface morphology was examined by an optical microscope JEVAVERT. An AFM investigation was performed in a contact mode under ambient conditions on a Digital Instruments CP II set-up.

RESULTS AND DISCUSSION

Electrical properties and contact morphology

As-deposited contacts and contacts annealed successively at 750 and 850°C had their contact resistivity values higher than $1\times10^{-3}\ \Omega\ \mathrm{cm}^2$. After annealing at 960°C, the contact resistivity of all metallizations dropped to the values of approximately $6\times10^{-5}\ \Omega\ \mathrm{cm}^2$ – see the second column of Tab. 1, and decreased only negligibly after annealing at 1065°C. Ni contacts had stable and defect-free morphology at all annealing temperatures. After annealing at 960°C pores appeared in Ni_2Si contacts, and completely discontinuous droplet-like morphology developed in the case of the NiSi metallization. However, the temperature of 960°C is necessary to achieve the ohmic behavior with low values of r_C, so it was chosen as optimal and as-deposited samples of all tested structures were annealed at this temperature for 10 minutes to compare their properties after single annealing. The contact resistivity values achieved after the single annealing are shown the third column of Tab. 1.

Table. 1: Values of the contact resistivity of tested metallizations obtained after annealing at 960°C for 10 min

	r_C [Ω cm^2]	
	Successive annealing at 750–960°C	Single annealing at 960°C
Ni	$(6.9 \pm 1.1)\times10^{-5}$	$(6.4 \pm 0.6)\times10^{-5}$
Ni_2Si	$(5.5 \pm 1.9)\times10^{-5}$	$(5.8 \pm 0.9)\times10^{-5}$
NiSi	$(6.6 \pm 1.1)\times10^{-5}$	$(6.2 \pm 1.2)\times10^{-5}$
Ni_2Si, 100 nm	$(8.4 \pm 0.7)\times10^{-5}$	$(6.8 \pm 0.7)\times10^{-5}$

After single annealing, the morphology of Ni and NiSi metallizations was similar to the morphology of the successively annealed metallizations, but in Ni_2Si contacts much lower number of pores was present. Examples of contact morphology are shown in Fig. 1 (a), (b) and (c), respectively. The best values of contact resistivity were achieved by Ni_2Si metallization after both successive and single annealing, however the disadvantage of this metallization was its imperfect morphology (pores).

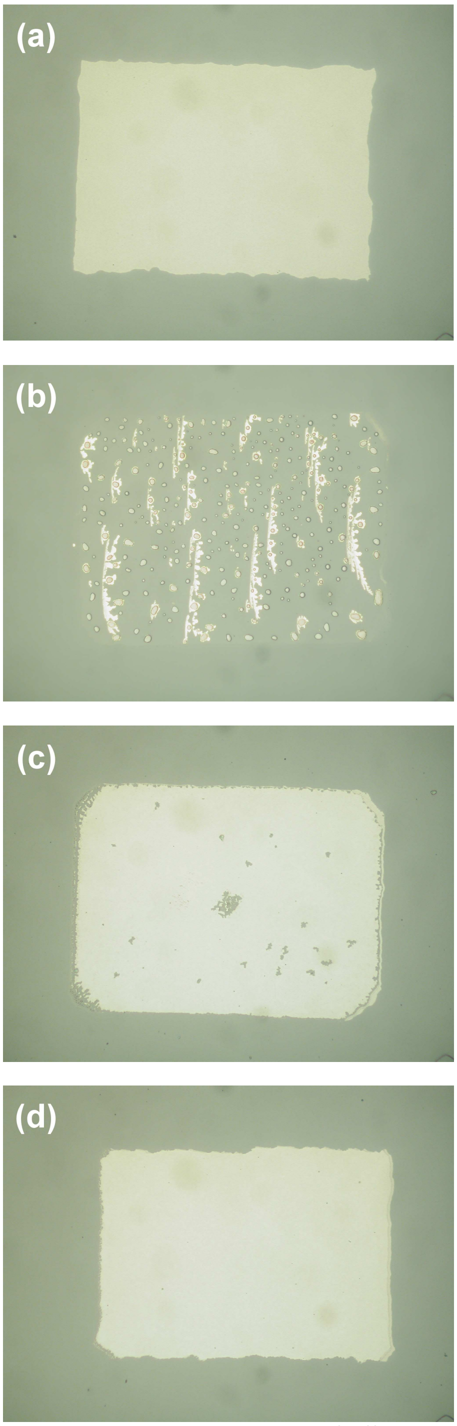

Fig. 1: Optical microscopy photographs of different contact structures (150×200 µm) annealed at 960°C for 10 minutes: (a) Ni, (b) NiSi, (c) Ni_2Si (standard heating up rate), (d) Ni_2Si (increased heating up rate)

We tested two approaches to improve the morphology of the Ni_2Si metallization: preparation of a thicker metallization, and shortening the annealing period at the optimal temperature (960°C).

The thicker metallization was prepared by the deposition of Ni and Si layers with doubled thicknesses, so the total thickness of the structure was 100 nm. The values of contact resistivity after successive and single annealing were however higher than the values achieved by 50 nm metallization – see the bottom line of Tab. 1. Most contacts on the single-annealed sample were free of pores but several contacts contained some pores. The morphology of the successively annealed 100 nm metallization was identical to the morphology of 50 nm thick metallization.

For the testing of the time dependence of contact morphology and resistivity a set of four 50 nm Ni_2Si samples was prepared and annealed at 960°C for 2.5, 5, 7.5 and 10 min, respectively. The values of r_C are depicted in Fig. 2. It is apparent that annealing even for 2.5 min is sufficient for achieving low values of r_C, and there is a slight decrease of r_C after annealing for 7.5 and 10 min. The standard deviation intervals of all samples from the annealing time dependence overlap. The morphology of all samples including the sample annealed for 10 minutes was free of pores, see Fig. 1. (d). This shows that another factor might play a role in the formation of Ni_2Si contact morphology. The only difference between the processing of Ni_2Si samples for the comparison of the metallization with different Si content, and the samples used for the time dependence of r_C, was modification of the heating up rate during annealing. A manually controlled heating up rate was approximately doubled upon annealing of the samples for the time dependence of r_C because the dependence included short annealing times (i.e. heating up time was decreased to approximately 1–1.25 minute from standard time of 2–2.5 minutes). This increased heating up rate was kept similar for all annealing times in the time dependence investigation. When also considering the fact that the successively annealed samples contained much more pores than the samples annealed only at 960°C, it is probable that the heating up rate influences kinetics of nickel silicide formation from evaporated Ni and Si layers. In this way the morphology of contacts can be affected.

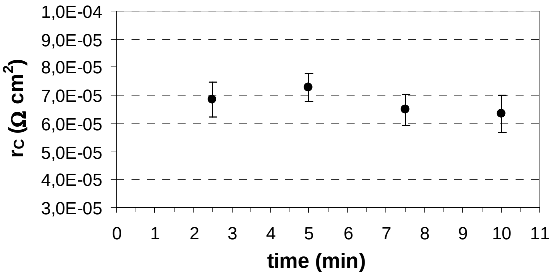

Fig. 2: Dependence of contact resistivity (r_C) of Ni_2Si metallization on the time of annealing at 960°C

Etching of contact metallizations

All three types of metallization were selectively etched off in order to reveal the penetration of the metallizations into the SiC substrate during annealing. Etchants were alternately applied until no remains of metallizations were visually found on the substrate. From the AFM surface profiles across the substrate area, where contact pad edges had been located, we found the degree of interaction between metallizations and the SiC substrate. The AFM images of etched Ni and Ni_2Si contacts, which were annealed successively at 750–1065°C, are shown in the Fig. 3 (a) and (b). We found that approximately 60 nm of SiC were consumed by the reaction with Ni (50 nm) contacts both in the case of successive annealing at 750–1065°C and single annealing at 960°C for 10 min. On the contrary, virtually no penetration was found in the case of Ni_2Si and NiSi contacts. The surface morphology of the substrate located below former silicide contacts was altered due to the interaction between nickel silicides and silicon carbide at high temperatures, but no groove distinguishable by AFM was found.

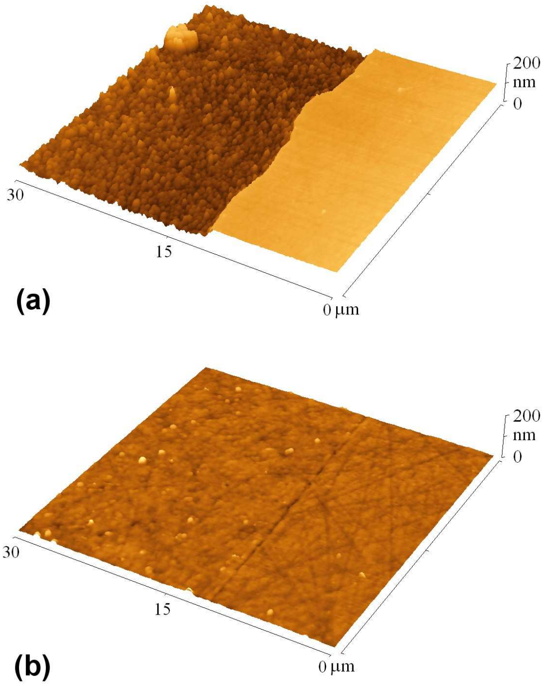

Fig. 3: AFM images of substrate after etching of successively annealed contacts: (a) Ni contact, (b) Ni_2Si contact. Pristine 4H-SiC surfaces are on the right-hand side and the areas of etched contact are on the left-hand side of the images.

CONCLUSIONS

The optimal annealing temperature was 960°C for all metallizations and the achieved values of contact resistivity were $6–7\times10^{-5}\ \Omega\ cm^2$. The morphology of Ni contacts was free of defects and independent on annealing temperature, but the reaction during annealing consumed approximately 60 nm of SiC. NiSi and Ni_2Si metallizations altered the surface of the SiC substrate, but no significant decomposition was detected by AFM after the etching of the contacts. NiSi silicide contacts had unsatisfactory droplet-like morphology after annealing. Annealed Ni_2Si silicide contacts contained pores, which were prevented by increasing the heating up rate during annealing. With an appropriate annealing regime, the Ni_2Si metallization is adequate replacement of usually used Ni contacts, especially in the case of shallow SiC semiconductor structures.

ACKNOWLEDGMENTS

The work was supported by the internal grant No. 126089006 of the Institute of Chemical Technology, Prague, Czech Republic.

REFERENCES

[1] Y. S. Park (editor). *SiC Materials and Devices*. San Diego, Academic Press, 1998.

[2] A. Kakanakova-Georgieva, T. Marinova, O. Noblanc, C. Arnodo, S. Cassette, C. Brylinski, "Characterization of ohmic and Schottky contacts on SiC", Thin Solid Films 637–641, pp. 343–344, 1999.

[3] B. Pécz, G. Radnóczi, S. Cassette, C. Brylinski, C. Arnodo, O. Noblanc, "TEM study of Ni and Ni_2Si ohmic contacts to SiC", Diamond and Related Materials 6, pp. 1428–1431, 1997.

[4] P. Macháč, B. Barda, J. Maixner, "Structural characterization of nickel–titanium film on silicon carbide", Applied Surface Science 254, pp. 1691–1693, 2008.

[5] B. P. Downey, J. R. Flemish, B. Z. Liu, T. E. Clark, S. E. Mohney, "Current-Induced Degradation of Nickel Ohmic Contacts to SiC", Journal of Electronic Materials 38 (4), pp. 563–568, 2009.

[6] M. W. Cole, P. C. Joshi, M. Ervin, "Fabrication and characterization of pulse laser deposited Ni_2Si Ohmic contacts on n-SiC for high power and high temperature device applications", Journal of Applied Physics 89 (8), pp. 4413–4416, 2001.

[7] T. Nakamura, M. Satoh, "Schottky barrier height of a new ohmic contact $NiSi_2$ to n-type 6H-SiC", Solid-State Electronics 46, pp. 2063–2067, 2002.

[8] A. Kuchuk, V. Kladko, M. Guziewicz, A. Piotrowska, R. Minikayev, A. Stonert, R. Ratajczak, "Fabrication and characterization of nickel silicide ohmic contacts to n-type 4H Silicon Carbide", Journal of Physics: Conference Series 100, 042003, 2008.

[9] B. Barda, P. Macháč, M. Hubičková, J. Náhlík, "Comparison of Ni-Ti and Ni ohmic contacts on n-type 6H–SiC. Journal of Materials Science", Materials in Electronics, 1039–1044, 2008.

[10] J. Genzer, P. Macháč, V. Myslík, "Modifikovaná čtyřbodová metoda pro měření kontaktních odporů", Slaboproudý obzor 52, 130–132, 1991.