Research Article

Influence of Carbon Layer on the Properties of Ni-Based Ohmic Contact to n-Type 4H-SiC

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Nickel-based contacts with additional interfacial layer of carbon, deposited on n-type 4H-SiC, were annealed at temperatures ranging from 600 to 1000°C and the evolution of the electrical and structural properties were analyzed by *I-V* measurements, SIMS, TEM, and Raman spectroscopy. Ohmic contact is formed after annealing at 800°C and minimal specific contact resistance of about $2.0 \times 10^{-4} \Omega \text{ cm}^2$ has been achieved after annealing at 1000°C. The interfacial carbon is amorphous in as-deposited state and rapidly diffuses and dissolves in nickel forming graphitized carbon. This process activates interfacial reaction between Ni and SiC at lower temperature than usual and causes the formation of ohmic contact at relatively low temperature. However, our results show that the specific contact resistance as well as interface quality of contacts was not improved, if additional layer of carbon is placed between Ni and SiC.

1. Introduction

Owing to its excellent intrinsic properties such as high thermal conductivity, high electric field breakdown strength, and high saturation, electron silicon carbide (SiC) is well recognized as an attractive material for application in highpower devices operating in high-temperature environment [1]. Much effort has been undertaken to master the SiC growth, both in form of ingots and of the epitaxial thin films, and important progress has been made in these fields during last two decades. However, in order to fully exploit this potential it is still necessary to overcome several technical issues related to the semiconductor processing and fabrication of power electronic devices; development of reliable ohmic contacts is one of the key problems in this respect [2].

The fabrication of ohmic contacts to SiC may be achieved by using various metallization schemes; as for the n-type SiC, Ni, and Ni-based contacts are the most commonly used ones. They are formed by high temperature annealing at temperatures in the range 950–1050°C for time of 2– 15 minutes [3–6]. Although many experimental works have been performed in order to understand the mechanism of ohmic contact formation and different models were proposed to explain Schottky to Ohmic transition, the final picture is still far from completeness.

There is no doubt that Ni very easily react with SiC forming the whole spectrum of nickel silicides, depending on details of ohmic contact fabrication. On the other hand there is a strong evidence that fabrication of silicides, via contact reaction of Ni with SiC or via deposition of the specific silicide does not provide solely an ohmic contact with low specific resistance. This is especially true for Ni₂Si which was early proposed as responsible for ohmic behaviour but later shown to form Schottky barriers with height of 1.62-1.75 eV [7]. Also a question arises about the fate of the remaining carbon which may segregate in the contact region.

As the silicide formation occurs at much lower temperatures (typically 400–600°C [8, 9]) than the transition to ohmic behaviour it has been suggested that formation of interfacial graphite layer is responsible for the ohmic contact. This hypothesis was supported by the observation of ohmic behaviour of graphitized carbon on SiC [10]. On the other hand it has been shown that [11] even if elemental C atoms may be present at semiconductor-silicide interface at low temperatures, that is, when silicide forms, further high-temperature treatment necessary for ohmic formation activates carbon atoms to outdiffuse towards the silicide surface. This observation has lead to a hypothesis that carbon outdiffusion produces C vacancies below the contact, acting as donors for electrons and increasing the net electron concentration below the contact thus reducing the barrier thickness. While the redistribution of interfacial carbon after silicide formation and its movement from the interface towards the contact surface was proven by Calcagno et al. [12], the DLTS measurements were not able to reveal the presence of a donor level related to $V_{\rm C}$, that is, located at 0.5 eV below the conduction-band edge [13]. Consequently, it seems that the role of carbon in ohmic contact formation is still unclear.

In our earlier works [14, 15] we have investigated various Ni- and Ni/Si-based contacts to SiC and reported on their electrical and structural properties while the characterisation was performed by XRD, RBS, and SIMS. These have shown that the best results in terms of ohmic contact formation are obtained by using Si/Ni/Si/Ni metallization scheme with thickness of Si and Ni films enabling to produce stoichiometric Ni₂Si. In this work, to go further and to clarify in more detail the effect of carbon phase on ohmic contact formation we have modified our metallization scheme by inserting an additional carbon layer at metal/SiC interface. To investigate carbon behaviour we have chosen Raman spectroscopy, as this technique was demonstrated to be an effective technique to investigate the structural states of carbon and the degree of structural order in different carbon materials [16].

2. Experimental

Ohmic contacts were fabricated on nitrogen doped n-type epitaxial wafers, purchased from Cree Research Inc., with a carrier concentration $n \sim 1 \times 10^{19} \text{ cm}^{-3}$ and a thickness 2.97 μ m grown on 4H-SiC substrates. Prior to the deposition of contact structures the wafers were degreased in hot organic solvents (trichloroethylene, methanol, and acetone) and subjected to chemical etching: (i) 10 min. in NH₄OH:H₂O₂:H₂O = 1:1:5 at 65°C, (ii) 10 min. in H₂O₂:HCl:H₂O = 1:1:5 at 70°C; (iii) 2 min. in buffered HF (HF:NH₄F:H₂O = 2:7:1). After every etching step the samples were rinsed in deionized water and dried under nitrogen flow.

Contact structures consisting of the sequence of C(3 nm)/Ni(30 nm)/Si(33 nm)/Ni(30 nm)/Si(33 nm) thin films were deposited in high-vacuum Gamma 1000C system by magnetron sputtering at room temperature from elemental targets of 99.99% purity in Ar plasma. Various sputtering modes were applied for specific materials, namely, DC for nickel, RF for silicon, and pulsed DC for carbon. Two-step annealing in nitrogen was applied to fabricate ohmic contacts: first step at 600°C for 15 min. to form Ni₂Si,

and second at temperature from 800 to $1000^\circ\mathrm{C}$ for 10 min. to form ohmic contact.

Electrical characterization involved measurements of current-voltage (*I-V*) characteristics and of the specific contact resistance. *I-V* characteristics were measured by Keithley 2400 Source-Meter using an automated setup. A circular transmission line model (c-TLM) method was used to measure specific contact resistance. The c-TLM pattern prepared by *lift-off* photolithography consists of inner contact pads with a diameter of 100 μ m and a metallized area separated by rings with a space of 10, 20, 30, 45, and 60 μ m.

The composition and structure were evaluated using secondary ion mass spectroscopy (SIMS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). SIMS measurements were carried out by using Cameca IMS 6F microanalyser, applying Cs⁺ ion beam. JEOL JEM2100 microscope was used for TEM analysis, and SEM images were obtained using Helios NanoLab.

The Raman spectra were obtained on MonoVista Raman microspectrometer (Spectroscopy and Imaging GmbH, Germany) using excitation line $\lambda = 488 \text{ nm from Ar}^+$ laser (INOVA 90C FREED). The power of the laser beam on the sample was equal to ~1 mW for each fundamental wavelength. The micro-Raman spectrometer makes use of Olympus BX51 microscope; images from microscope are recorded with TM 2040GE camera (JAI, Japan) with 16 bit AD image conversion. The spectral part of the micro-Raman spectrometer makes use of SpectraPro 2750 spectrograph (Princeton Instruments, USA); the detection was done with CCD camera Spec-10 System (Princeton Instruments). Maximum efficiency of the camera was at 250 nm. The x, y, z motor driven (Ludl Electronics, USA) stage allowed positioning with 20 nm step in *x* or *y* direction and 50 nm in *z* direction. Raman spectra were recorded with the grating having 1800 lines/mm and the objective of magnification equal to 100x. The Ar laser beam was at normal incidence to the samples, illuminating sample surface from the metallization side.

3. Results and Discussion

The current-voltage characteristics of C/Ni/Si/Ni/Si contacts on n-type 4H-SiC, annealed at different temperatures (600, 800, 950, and 1000°C) are shown in Figure 1. The I-V curves have been measured between two pads of TLM structure with spacing of $30 \,\mu\text{m}$. After annealing at 600°C the I-V characteristics show a rectifying behavior, while after annealing at 800°C an ohmic contact is obtained. When the annealing temperature increase up to 950°C, the slope of the I-V curve negligible increases and only after annealing at 1000°C the significant reduction in resistance is observed. The specific contact resistance was 3.9×10^{-4} , 3.4×10^{-4} , and $2.0 \times 10^{-4} \,\Omega \,\mathrm{cm}^2$ after annealing at 800, 950, and 1000°C, respectively. The reported results are comparable with our further values of $4\,\times\,10^{-4}\,\Omega\,\text{cm}^2$ obtained for 4H-n-SiC/Ni₂Si contacts on substrate with doping level of $\sim 10^{17} \text{ cm}^{-3}$ annealed at 1050°C [14, 15].



10 4H-n-SiC/C/Ni/Si/Ni/Si 10 105 10 10^{3} Interface 10^{2} SIMS signal (a.u.) As-deposited 10^{1} 0 0.1 0.2 0.3 0.4 (a) 10^{7} 106 105 10^{4} 103 102 1000°C/10 min. 10^{1} 0 0.1 0.2 0.3 0.4 Depth (µm) 58Ni 28Si 12C (b)

FIGURE 1: Current-voltage characteristics of as-deposited and annealed up to 1000°C 4H-n-SiC/C/Ni/Si/Ni/Si contacts. Inset: microscope image of the c-TLM pattern.

Figure 2 shows SIMS depth profiles for the as-deposited and ohmic n-SiC/C/Ni/Si/Ni/Si contacts. For the asdeposited contact (Figure 2(a)), variations of the measured signal well correspond to thickness of distinct specific layers and the position of interface between the metallization and the substrate is detected at a depth of $0.12 \,\mu$ m. The apparent "tail" of the Ni profile extending to $0.3 \,\mu$ m is due to the degradation of the depth resolution which is a typical effect observed when polycrystalline materials are sputtered. SIMS profiles for ohmic contact after annealing at 1000°C (Figure 2(b)) indicate strong interfacial reaction involving Ni and Si, while carbon layer is still visible at a depth of about 0.05 μ m from the surface.

The TEM micrographs of as-deposited n-SiC/C/Ni/ Si/Ni/Si contact are shown in Figures 3(a) and 3(b). These confirm multilayer structure and give evidence that carbon and silicon layers are amorphous while both Ni layers are polycrystalline. The total thickness of the deposited structure is about 100 nm. SEM image (Figure 3(c)) shows flat and uniform surface of the sample. Annealing at 600°C causes nonuniformity of contact structure, its surface, and interface (Figures 3(d) and 3(e)). The upper part of the contact consists of small crystalline grains surrounded by the amorphous phase. An increase of contact nonhomogeneity and of the surface roughness is observed for ohmic contacts annealed at 1000°C (Figures 3(f) and 3(g)).

Figure 4 shows Raman spectra measured for 4H-n-SiC/C/Ni/Si/Ni/Si structures after annealing at temperatures

FIGURE 2: SIMS depth profiles of 4H-n-SiC/C/Ni/Si/Ni/Si contacts: (a) as-deposited; (b) annealed at 1000°C for 10 min.

of ohmic contact formation. It is well known that the pair of G- and D-bands is the best diagnostic feature for polycrystalline graphitic materials [16]. This is why the range from 1300 to 1850 cm^{-1} , where D and G bands of carbonic structures are observed, was selected in our analysis. The G-band around $1590-1600 \text{ cm}^{-1}$ correspond to single-crystal graphite, while D-band at 1350 cm^{-1} and satellite band with maximum at about 1620 cm^{-1} are associated with the disordered or defective hexagon graphitic plane structures [16].

The spectra in Figure 4 indicate that an increase of annealing temperature causes a decrease of intensity of Dand satellite-bands, as well as an increase of intensity of G-band. These suggest that an increase of the annealing temperature results in the formation of more graphitized and less disordered carbon structures.

The size of graphitic crystallites (*L*) can be estimated from the ratio of D and G peak intensities by using the relation $L = C \times (I_G/I_D)$ in which the constant C = 3.5 nm for excitation wavelength of 488 nm [16, 17]. Taking this into consideration, the increase of the size of graphitic crystallites can be deduced as 2.8, 3.1, and 3.8 nm, after annealing at 800, 950, and 1000°C, respectively.



FIGURE 3: TEM cross-section and SEM images of 4H-n-SiC/C/Ni/Si/Ni/Si contacts: ((a), (b), (c)) as-deposited; ((d), (e)) annealed at 600°C for 15 min.; ((f), (g)) annealed at 1000°C for 10 min.

4. Conclusions

In this paper we have reported on electrical and structural properties of Ni-based contacts to n-type 4H-SiC having additional interfacial layer of carbon. Our results show that no improvement of specific contact resistance was obtained in this way, contrary to some suggestions in the literature [18, 19]. The general picture of contact reaction is that interfacial carbon is amorphous in as-deposited state but rapidly diffuses and dissolves in nickel forming graphitized carbon. Raman spectroscopy was useful method in characterizing evolution of graphitic phases and has proven that annealing at higher temperatures required for ohmic contact with low specific resistance increases the amount of graphitized carbon. The driving force for the graphitization process can be related to the decrease of free energy by the conversion of amorphous carbon to graphitized carbon [20]. Finally, an important finding of our work is that interaction of interfacial amorphous C and Ni activates interfacial reaction between Ni and SiC at lower temperature than usual. These, however, have negative effect on the quality of interfacial region. Consequently, in our future work we plan to investigate the effect of interfacial carbon layer in contact metallization C/Si/Ni/Si/Ni having silicon as a first layer.



FIGURE 4: Raman spectra of 4H-n-SiC/C/Ni/Si/Ni/Si ohmic contacts formed after annealing at 800°C, 950°C, and 1000°C for 10 min.

Conflict of Interests

A. Kuchuk one author signing on behalf of all coauthors of the paper and I inform that there is no direct financial relation with the commercial identity Cree Research Inc., mentioned in the paper and no any possible conflict of interests.

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