Nickel-titanium-based contact for n-type silicon carbide to combine high ohmic conductivity and mechanical properties

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Abstract. This paper reports a method to improve mechanical properties retaining the electrical properties of Ni-based ohmic contact material for n-type 4H-SiC. Ni/Ti bilayered films varying only in the thickness of the Ti layer were deposited on SiC substrates and annealed at 1273 K for a very short time in vacuum. The interfacial structures were analyzed by X-ray diffraction. The electrical and mechanical properties were measured by DC conduction test and constant-load scratch test, respectively. An appropriate thickness of the Ti layer on Ni improves the mechanical properties retaining the electrical properties by forming TiC instead of the free carbon.

1. Introduction

Silicon carbide (SiC) is a wide-bandgap compound semiconductor expected in application to heavy-duty power electronic devices [1]. Replacement of conventional Si-based power electronic devices with SiC-based ones can provide significant improvement in energy efficiency, service life, and total mass of the power electronic system. To realize the devices, however, several problems have to be overcome. One of them is to form a reliable and low-resistance ohmic electrode on SiC [1-3].

On n-type SiC, the ohmic contact is commonly formed by deposition of Ni on SiC and subsequent annealing at temperatures higher than 1173 K [2-5]. The interfacial reaction during the heat treatment forms NiSi adjacent to the SiC. However, NiSi is not the only phase produced by the reaction. The most fatal product of the reaction is the free carbon, consisting of graphite and/or amorphous carbon. The free carbon deteriorates the mechanical properties of the contact. To suppress the formation of the free carbon, an element X that has a high affinity with carbon should be added in the deposited layer to form X-carbide instead of the free carbon. A candidate for element X is Ti. Ti is a strong carbide former [6]. Furthermore, TiC has a low work function [7], which is favorable for an ohmic contact on n-type SiC. Although several papers reported Ni-Ti contacts on SiC [8, 9], the mechanical properties are rarely discussed [9].

The present study reports the mechanical properties of Ni-Ti contacts on n-type 4H-SiC in relation with the electrical properties. TiC contact on SiC is also examined.

2. Control of interfacial reaction among SiC, Ni, and Ti

The interfacial reaction between SiC and Ni is considered based on the Ni-Si-C ternary phase diagram. Figure 1 shows the isotherm at 1173 K [10]. SiC and Ni cannot coexist in equilibrium. Therefore, the interfacial reaction proceeds during annealing to establish local equilibrium. Since Ni does not form...
any stable carbides nor dissolve carbon, the interfacial reaction produces Ni-Si compounds and the free carbon. Therefore, the formation of the free carbon is inevitable when only Ni reacts with SiC. The addition of Ti overcomes this problem. Formation of TiC proceeds spontaneously, since the formation significantly reduces the chemical potential of carbon in the system. However, it has to be noted that Ti can also react with Si.

Naka et al. reported that the reaction between SiC and pure Ti forms Ti$_3$Si$_2$C$_x$ and Ti$_3$SiC$_2$ at the interface [11]. To avoid the formation of these products, the chemical potential of Ti at the reaction interface has to be lowered to a sufficient level. The chemical potential can be reduced by forming compound phases and/or by diluting Ti at the reaction interface. Thermodynamic calculations suggest that the formation of NiTi and Ni$_3$Ti intermetallic compounds lowers down the chemical potential of Ti to an appropriate level [12, 13]. On the other hand, it is effective to dilute Ti by placing a Ti-source at a portion distant from the reaction interface, suppressing the diffusion flux of Ti through the phase adjacent to the SiC. The Ni layer should be thick for this purpose, since the thickness of the Ni layer determines the chemical potential gradient and diffusion flux of Ti. Consequently, the Ti layer was formed on the Ni layer in the present study in order to make Ti form Ni-Ti intermetallic compounds and to supply Ti to the interface by diffusion of Ti through the intermetallic compound. In the present study, the thickness was set to 100 nm as a pilot case.

The phase diagram shown in Figure 1 presents another concern. Fukai et al. reported that the interfacial phase sequence of a SiC/Ni diffusion pair becomes SiC/(Ni$_3$Si + C)/(Ni$_3$Si$_{12}$ + C)/Ni$_3$Si/Ni by annealing at 1273 K for 3600 s [14]. The sequence corresponds to the diffusion path indicated on Figure 1 with a broken line. The diffusion path indicates that NiSi cannot be formed while Ni exists as the end-member of the diffusion pair. Two methods to overcome this problem are considered. One is to change the annealing temperature at which SiC, NiSi, and C coexist in equilibrium. However, the three-phase equilibrium cannot be achieved at temperatures below the eutectic of Ni and Ni$_3$Si at 1416 K [15]. The other method to form NiSi adjacent to SiC is to make Ni$_3$Si react with SiC by reducing the chemical potential of C. The addition of Ti in the film reduces the chemical potential significantly by forming TiC instead of the free carbon. Figure 2 shows the original and modified diffusion paths on the Ni-Si-C ternary chemical potential diagram at 1173 K [12, 16]. It is clearly understood that the diffusion path reported in the literature goes through a high chemical potential of C. Due to this, NiSi is kept away from formation. By preventing the formation of the free carbon, the diffusion pair is
allowed to take a direct path with monotonous chemical potential gradients of all constituent elements. In addition, the formation of a Ni-Ti intermetallic compound reduces the chemical potential of Ni at one of the end-members, which magnifies the driving force to establish a diffusion path through a low chemical potential of C.

Therefore, the key point of the contact formation process proposed in the present study is to control the interfacial reaction behavior of Ti, i.e., to facilitate TiC formation in order to eliminate the free carbon, preventing the formation of other Ti-Si-C byproducts.

3. Experimental procedure
SiC substrates used in the present study were N-doped n-type 4H-SiC substrates cut to a square shape of 5.0 mm on each side from a 360-µm-thick wafer of which surface was inclined 8° from the (0001) crystallographic plane toward [0 0 2 1 1]. The inclination is commonly given to SiC single-crystal wafers for controlling the polytype of epitaxial layers stacked on the substrate to form a semiconductor device. Although the surface is different from the exact crystallographic plane, it is conventionally treated the same as the (0001) plane, based on the fact that most of the surface consists of the (0001) facet. Only the (0001) Si-face of the SiC substrates was used. Ni and Ti were deposited consecutively on the substrates by radio-frequency magnetron sputtering. The thickness of the Ni layer was kept constant at 100 nm, whereas that of the Ti layer was varied from 0 to 640 nm. The samples were then heated to 1273 K in a vacuum of 3×10⁻³ Pa and immediately cooled down after reaching the target temperature (hereinafter described as the annealing time of 0 s). For comparison, a TiC contact was formed on some SiC substrates by deposition of a C/Ti bilayer and subsequent annealing at 1273 K for 0 s in vacuum. Since this process can form TiC on the substrate without an interfacial reaction between the contact film and the substrate [17], Ti-Si-C byproducts were not formed at the interface.

The interfacial structures were analyzed by X-ray diffraction (XRD). The electrical properties were measured by direct-current conduction test. The mechanical properties were evaluated by constant-load scratch test. A Rockwell-C indenter was plunged into the contact layer with a force of 5.0 N and swept along the surface of the layer. The depth of the trench formed by the scratch was measured by atomic force microscopy at a position 1.0 mm distant from the start point of the scratch test. The reciprocal value of the trench depth was used as the strength index of the contact layer.
4. Results and discussion

Figure 3 shows the XRD patterns of the samples with various thicknesses of Ti layers after annealing. The initial thicknesses of the Ti layers for the patterns (a), (b), (c), and (d) are 0, 16, 80, and 640 nm, respectively. The pattern (a) consists of the peaks of SiC and Ni$_2$Si. The peaks of NiSi and the free carbon do not appear in the pattern. Failure of detection of the NiSi layer indicates that the layer is very thin, which agrees with previous reports [4, 5]. On the other hand, the free carbon will not appear if it is amorphous. The pattern (b) also consists of the peaks of SiC and Ni$_2$Si, which is quite similar to the pattern (a). The initial thicknesses of the Ni and Ti layers of this sample were 100 and 16 nm, respectively, which corresponds approximately to the composition of Ni-10 mol%Ti. Therefore, the peaks of NiSi, TiC, and Ni$_3$Ti are expected to appear, in addition to the peaks appearing in the pattern. It is likely that the Ti layer is consumed by the interlayer reaction before the Ni adjacent to the SiC changes to Ni$_3$Ti. SiC reacts with this unchanged Ni. In this way, the XRD pattern of the sample is almost the same as that of pattern (a).

In the pattern (c) of Figure 3, a peak of TiC appears at the diffraction angle of 41.88°, indicating that a considerable amount of TiC is successfully formed at the interface and thus the formation of the free carbon is suppressed. Even in this pattern, however, the peaks of Ni-Ti intermetallic compounds are not found. It is hardly expected that a film of which total thickness is 180 nm is completely consumed by the reaction with SiC. Further analysis is needed to clarify the interfacial phenomena during annealing and the resultant structure.

The interfacial reaction fails to form Ni-Si compounds and TiC when the Ti layer is very thick. In the pattern (d) of Figure 3, Ti$_5$Si$_3$ and Ti$_3$SiC$_2$ are detected instead of TiC. Furthermore, the film after annealing is easily peeled off the substrate, even with careful handling. Therefore, the electrical and mechanical properties of this sample could not be measured.

The results shown in Figure 3 suggest that there is an optimum thickness of the Ti layer and/or an optimum thickness ratio between the Ti and Ni layers to facilitate the TiC formation. Among the samples shown in Figure 3, the sample with a 100-nm-thick Ni layer and an 80-nm-thick Ti layer seems to be the closest to the optimum condition. The composition of the film corresponds approximately to Ni-33 mol%Ti. The Ni-Ti binary phase diagram suggests that Ni$_3$Ti and NiTi are stable at this composition [15], i.e., the results agree with the thermodynamic consideration described in the previous section.

Figure 4 shows the electrical current–voltage profiles of the SiC/Ni, SiC/Ni/Ti (16 nm), SiC/Ni/Ti (80 nm), and SiC/C/Ti samples after annealing at 1273 K for 0 s. The plots of each sample lie on a...
first-order least-square line in good agreement, indicating that all samples show ohmic conduction. Among the samples, the highest electrical conductance is obtained with the SiC/Ni/Ti (80 nm) and SiC/Ni samples. On the other hand, the lowest electrical conductance is obtained with the SiC/C/Ti samples. Although it is proven that TiC is an ohmic contact former for n-type SiC, NiSi contacts exhibit higher electrical conductance. Nevertheless, TiC is an indispensable phase for improving both the electrical and mechanical properties of the contact interface by eliminating the free carbon phase.

The electrical conductance of SiC/Ni/Ti (16 nm) appears lower than that of the SiC/Ni samples. Since the phase formed adjacent to SiC is considered to be the same as that of the SiC/Ni interface, the degradation of the conductance is attributed to the formation of a Ni-Ti intermetallic compound at the Ni/Ti interface. It should be noted that Ni-Ti intermetallic compounds are also formed at the interface of the SiC/Ni/Ti (80 nm) sample. It is considered that the degradation of the conductance in the film is compensated for by reducing the contact resistance, i.e., by replacing the non-ohmic SiC/free-carbon interface with an ohmic SiC/TiC interface.

Figure 5 shows the mechanical indices of the samples against their electrical conductance. The highest mechanical index is obtained with the SiC/C/Ti samples. This result evinces the successful formation of TiC at the interface, i.e., it is likely that the high hardness of TiC made the trench formed
by scratching shallow. In addition, the adhesion between the contact electrode and the substrate is strong and ductile enough to endure the scratch test. The SiC/Ni/Ti (80 nm) sample also endures the scratch test. Although its mechanical index appears lower than those of the SiC/C/Ti samples, it achieves high electrical conductance and mechanical strength simultaneously. On the other hand, the mechanical indices of the SiC/Ni and SiC/Ni/Ti (16 nm) samples are almost one order of magnitude lower than those of the other two samples. The contact films on these samples are completely removed by scratching, i.e., the depths of their trenches are the same as the thicknesses of the contact films. Therefore, the fact that the mechanical index of the SiC/Ni/Ti (16 nm) sample is lower than that of SiC/Ni has no meaning, but the contact film of SiC/Ni/Ti (16 nm) is thicker than that of SiC/Ni. However, it should be noted that an inappropriate combination of thicknesses of the Ti and Ni layers deteriorates both the mechanical and electrical properties. The interfacial phenomena during the formation process and the resultant performance of the contact film are very sensitive to the thicknesses of the Ti and Ni layers.

5. Conclusions
The present paper proposed and demonstrated the improvement of the mechanical properties of a Ni-based ohmic contact for n-type SiC by the addition of a Ti layer. The following points became clear.
(1) SiC/Ni samples achieve low-resistance ohmic contact after annealing at 1273 K for a short time. However, the mechanical properties are significantly deteriorated by the annealing.
(2) SiC/C/Ti samples become ohmic after annealing at 1273 K for a short time. The contact films perform high mechanical properties. However, the electrical conductance is lower than that of SiC/Ni contacts after annealing.
(3) SiC/Ni/Ti samples also become ohmic after annealing at 1273 K for a short time. Appropriate thicknesses of the Ti and Ni layers significantly improve the mechanical properties, retaining high electrical conductivity. On the other hand, inappropriate setting of the thicknesses deteriorates both the mechanical and the electrical properties.

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