Low Resistance TiAl Ohmic Contacts with Multi-Layered Structure for p-Type 4H–SiC

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The effect of the Al concentration and layer structure on the electrical and microstructural properties of TiAl Ohmic contacts for p-type 4H–SiC were investigated. The Al concentration was found to effect strongly on these contact properties, and the specific contact resistance of 1 × 10−5 Ω-cm2 was obtained for the TiAl contacts with the Al concentration higher than 77 at% after annealing at 1000°C. However, agglomeration of Al was observed after annealing, which caused the rough surface morphology. On the other hand, the TiAl contacts with the Al concentration lower than 75 at% showed non-Ohmic behavior and had smooth surface morphology after annealing at 1000°C. It was found from X-ray diffraction analysis that the interface structures were strongly influenced by the Al concentrations of the TiAl contacts. For the TiAl contact with high Al concentration, formation of Al3 Ti, Ti3 SiC2, and Al4 C3 was observed, and for the TiAl contact with low Al concentration, formation of AlTi, TiSiC2, and Ti3 C was observed. It was concluded that the electrical property of the TiAl contact was not affected by the number of TiAl layers and was very sensitive to the Al concentration in the TiAl contacts.

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1. Introduction

Silicon carbide (SiC) has been expected to be the key element for next generation devices for high power, high frequency, and high temperature applications, since it has excellent intrinsic properties such as a wide bandgap, a high thermal conductivity, and a high breakdown voltage.1–4) One of the materials-related issues is lack of low resistance Ohmic contact materials for p-type 4H- and 6H–SiC. Development of such the Ohmic contact is mandatory in order to manufacture these devices.5,6) TiAl contact was demonstrated by Tanaka et al. as the p-type Ohmic contact for SiC light emitting diodes with pn junction.7) TiAl has been expected to be one of low resistance Ohmic contact materials with specific contact resistance (ρc) lower than 10−5 Ω-cm2.8) The ρc values were reported by Crofton et al. to be from 5 × 10−6 to 3 × 10−5 Ω-cm2 for TiAl deposited on p-type 6H–SiC by a co-sputtering technique.9) Recently, Tanimoto et al. reported the extremely low ρc value (9.5 × 10−7 Ω-cm2) for the TiAl bilayered contact to p-type 4H–SiC with an acceptor concentration (N_A) of 1.2 × 1019 cm−3 by improving the cleaning procedure of the SiC surfaces.10) However, the rough surface morphology of the contact after annealing at 1000°C was our concern. It was believed that the rough surface morphology was caused by annealing at temperatures higher than 1000°C and using large amounts of Al.9,11) Lin et al. demonstrated TiAl multi-layered structures with a CrB2 cap-layer provided smooth surface morphology.11) They showed that the ρc values of medium-10−4 Ω-cm2 were obtained for the co-sputtered TiAl contacts with the Al concentrations of 94 and 81 at% (corresponding to 90 and 70 mass%, respectively) and that non-Ohmic characteristics were obtained for those with 73 and 29 at% (60 and 19 mass%, respectively). This result suggested that the high Al concentration was required to obtain the TiAl contacts with ρc lower than 10−3 Ω-cm2.

In this paper, we studied to select the most effective factor which has the strongest effect to reduce the ρc values of TiAl contacts to p-type 4H–SiC, such as the Al concentration in the contacts, the layer structures, and the annealing conditions by comparing the electrical properties with the microstructures. This information will provide a guideline to develop the thermally stable low resistance Ohmic contact materials for p-type 4H–SiC. Since it was expected that the multi-layered structure enhanced mixing of Al and Ti atoms compared with the bilayered structure, two step annealing was used to form thermally stable contact materials such as Al3 Ti intermetallic compound with high melting point of 1350°C.

2. Experimental Procedure

P-type 4H–SiC epilayers with a 5 μm thick and N_A of 1.0 × 1019 Al-cm−3 were grown on n-type 4H–SiC substrates with 8° off (0001) Si-face by Cree Research, Inc. After chemical cleaning the substrate using the RCA technique,12) the SiO2 sacrifice layer with about 10 nm thick was formed on the epilayer by dry oxidation at 1150°C for 60 min. After patterning electrodes on the surface by a photolithography process, the SiO2 layer was etched by dipping in diluted HF solution (H2O : HF = 50 : 1) for 60 s. Ti and Al layers were deposited in a high vacuum chamber by an e-beam evaporator and a resistance heater, respectively. The pressures before and during the deposition were about 1 × 10−5 and 1 × 10−4 Pa, respectively. Multi-layered contacts had 1, 5, or 6 pairs of a Ti/Al bilayered, where a “/” means the deposition sequence, and the first layer of one period was always Ti. The total thickness of the TiAl layers was 300 nm, and the Al concentrations were controlled to be 75, 77, and 80 at%. Table 1 lists microstructures of TiAl multi-layered contacts, where [Ti(13.3)/Al(36.7)] × 6 means the 6 repeated multi-layers of the Ti(13.3 nm)/Al(36.7 nm) couple. The thickness of de-
posited layers was measured by an in-situ thicknessmeter with a quartz oscillator and was also confirmed by a stylus surface profiler after the deposition. After lifting off the unnecessary TiAl on the photoresist by a chemical dissolution with acetone, the samples were annealed by two steps at 500°C for 30 min and then at 1000°C for 2 min in a ultra high vacuum chamber. The pressures before and during the annealing were under $1 \times 10^{-7}$ and $1 \times 10^{-4}$ Pa, respectively. We expected to form Al$_3$Ti (which was to be more thermally stable than single Al at 1000°C) at the first annealing step.

The current–voltage ($I$–$V$) characteristics were measured by a two-point probe method using circular patterns with spacing of 24$\mu$m. The $\rho_c$ values were measured by the transmission line model (TLM) using a four-point probe method, and multiple annular electrode patterns with spacing of 4, 8, 16, 24, and 32$\mu$m were used. Microstructural analysis was carried out by X-ray diffraction (XRD) with CuK$_\alpha$ radiation. Surface and interface morphologies were observed by a field emission scanning electron microscope (FE-SEM).

### 3. Results and Discussion

Figure 1 shows $I$–$V$ characteristics of TiAl bilayered and multi-layered contacts after two step annealing. The $I$–$V$ curves of samples 1, 2, and 3 (indicated by symbols “○”, “□” and “♦”, respectively) show Ohmic behavior. However, the $I$–$V$ curve of sample 4 (indicated by symbols “△”) shows non-Ohmic behavior. The $\rho_c$ values of samples 3 was in the ranged from $6.0 \times 10^{-6}$ to $2.2 \times 10^{-5}$ $\Omega$-cm$^2$. Note that the $\rho_c$ value lower than $10^{-5}$ $\Omega$-cm$^2$ was obtained for both the bilayered and multi-layered TiAl contacts with Al concentrations higher than 77 at% and non-Ohmic behavior was observed for sample with Al concentration less than 75 at%. This result agrees with that reported by Lin et al. for the TiAl contacts prepared on p-type SiC by the co-sputtering technique.

Figures 2(a), (b), and (c) show the SEM images taken from

### Table 1. Al concentrations and structures of TiAl contacts used in the present study.

<table>
<thead>
<tr>
<th>Sample structure (nm)</th>
<th>Al concentration (at%)</th>
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<tr>
<td>Sample 1 Ti(50.0)/Al(300.0)</td>
<td>87</td>
</tr>
<tr>
<td>Sample 2 [Ti(10.5)/Al(39.5)] × 6</td>
<td>80</td>
</tr>
<tr>
<td>Sample 3 Ti(21.0)/Al(79.0)/[Ti(10.5)/Al(39.5)] × 2/ Ti(13.3)/Al(36.7)/Ti(17.3)/Al(32.7)</td>
<td>77</td>
</tr>
<tr>
<td>Sample 4 [Ti(13.3)/Al(36.7)] × 6</td>
<td>75</td>
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Fig. 1 Current–voltage characteristics of Ti(50 nm)/Al(300 nm) bilayered (○), TiAl multi-layered with 80 at% Al (□), TiAl multi-layered with 77 at% Al (♦), and TiAl multi-layered with 75 at% Al (△) contacts for p-type 4H–SiC after two step annealing at 500°C and 1000°C.

Fig. 2. SEM images of surfaces of (a) TiAl bilayered, (b) multi-layered with 80 at%, Al and (c) multi-layered with 75 at%Al contacts for p-type 4H–SiC after two step annealing at 500°C and 1000°C, where the surface is observed by a glancing angle of 20°.
surfaces of samples 1, 2, and 4, respectively. The dark region in the image is the TiAl contact surface and the bright region is the SiO\textsubscript{2} surface on the p-type SiC epilayer. The surface morphology of the TiAl bilayered contact is extremely rough. In addition, agglomerations of Al with dimensions larger than 10 \(\mu\text{m}\) are observed on the surface (Fig. 2(a)), that was identified by electron prove micro analysis. The surface of sample 2 is also rough (Fig. 2(b)). Although the large agglomeration of Al is not observed, the agglomeration with dimensions smaller than a few \(\mu\text{m}\) is observed on the surface. Both bilayered and multi-layered contacts with the low \(\rho\text{c}\) value of \(1 \times 10^{-5} \Omega\text{-cm}\) show the rough surface morphology. On the other hand, the surface of sample 4 which showed non-Ohmic \(I-V\) characteristic is very smooth, and no agglomerations are observed on the surface (Fig. 2(c)).

The cross-sectional SEM images of sample 3 and 4 are shown in Figs. 3(a) and (b), respectively. The contact interface of sample 3 is constructed from small grains, and the interface morphology is very rough. On the other hand, for sample 4, large grains are observed to form at the interface, and the smooth interface is observed.

The microstructures of the TiAl contacts were investigated by XRD. After annealing at 500\degree C for 20 min, Al\textsubscript{2}Ti was observed in all samples and the reaction product formed between the TiAl layer and the SiC substrate was never observed. Figure 4 shows XRD profiles of the (a) sample 2 and (b) sample 4 after annealing at 1000\degree C. Formation of Al\textsubscript{3}Ti and Ti\textsubscript{3}SiC\textsubscript{2} is detected in all samples. The peaks corresponding to (000\textit{l}) Ti\textsubscript{3}SiC\textsubscript{2} are found, which indicates that the Ti\textsubscript{3}SiC\textsubscript{2} layer has a strongly oriented texture structure or an epitaxial relation with the 4H–SiC(0001) substrate. Getto, \textit{et al.} reported the formation of Ti\textsubscript{3}SiC\textsubscript{2} at the interface between the sputtered TiSi\textsubscript{x} and the 6H–SiC substrate after annealing at 1180\degree C for 90 s.\textsuperscript{10} Note that an Al\textsubscript{4}C\textsubscript{3} compound is detected for only low resistance TiAl contacts. The formation of Al\textsubscript{3}C\textsubscript{3} at the SiC/Ti interface was also reported in open literatures.\textsuperscript{17,18} On the other hand, for the non-Ohmic TiAl contact, a Ti\textsubscript{5}Si\textsubscript{3} compound is detected.

Table 2 shows summaries of the electrical and microstructural properties of TiAl multi-layered contacts. The electrical and microstructural properties of the TiAl contact after annealing at 1000\degree C was not affected by the number of layers of the TiAl contacts.

Figure 5 shows the schematic illustrations of structure changes of (a) bilayered and (b) multi-layered TiAl Ohmic contacts before and after annealing at 500\degree C, and (c) those after annealing at 1000\degree C were not affected by the number of layers of the TiAl contacts.
Table 2: Difference between Ohmic and non-Ohmic contacts.

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<th></th>
<th>Electrical properties</th>
<th>Ohmic</th>
<th>Non-Ohmic</th>
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<tr>
<td>Al concentration</td>
<td>87–77 at%</td>
<td>ALTi</td>
<td>75 at%</td>
</tr>
<tr>
<td>Microstructures</td>
<td></td>
<td>AL_{3}C_{3}, AL_{3}Ti, Ti_{3}SiC_{2}, Al</td>
<td>AL_{3}Ti, Ti_{3}SiC_{2}</td>
</tr>
<tr>
<td>Surface and interface</td>
<td></td>
<td>Rough</td>
<td>Smooth</td>
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<td>morphology</td>
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nealing at 500°C, the annealing temperature was high enough for Ti and Al atoms to intermix each other. The contact properties were very sensitive to the Al concentration in the TiAl contacts. From the present microstructural analysis, it was found that formation of compound at the contact interface was sensitive to the Al concentration and that the big change was observed TiAl contacts with the Al concentration higher than 75 at%. This critical Al concentration agreed with the stoichiometrical value of Al in Al_{3}Ti. We believed that Al higher than 75 at% was necessary to obtain low resistance TiAl contact but that the prevention of the rough morphology in the Ohmic contact was difficult. This result indicates that an excess amount of Al needs to form the Ohmic contact with low resistance after further formation of Al_{3}Ti. The excess Al may suppress the redistribution of Al from p-SiC substrate or diffuse to the substrate, those might form the heavily doped SiC region at the metal/SiC interface and reduce the contact resistivity. However, more experiments will be necessary to clarify the formation mechanism of low resistance contact in the TiAl/SiC system.

4. Conclusion

We have investigated the electrical and microstructural properties of the TiAl contacts with various Al concentrations and different structures of Ti and Al for p-type 4H–SiC. The TiAl contacts with the Al concentrations larger than 77 at% provided the \( \rho_c \) values lower than \( 1 \times 10^{-5} \) \( \Omega \)-cm\(^2\) and rough surface and interface morphologies after annealing at 1000°C. On the other hand, the TiAl contacts with the Al concentration lower than 75 at% provided the non-Ohmic behavior and the smooth surface morphology. The contact formed Al_{3}C_{3}, Al_{3}Ti, and Ti_{3}SiC_{2} for the contacts with Al concentrations higher than 75 at% and Al_{3}Ti, Ti_{3}SiC_{2}, and Ti_{3}Si_{3} for the contacts with lower Al concentrations. From the present results, we concluded that the electrical and microstructural properties of the TiAl contact were strongly affected by the Al concentration in the TiAl contacts, and weakly affected by the number of TiAl layers.

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