Electrical properties and structure of contact interface between Ti\textsubscript{3}SiC\textsubscript{2} and p-type GaN

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Abstract. The purpose of the present study is to investigate the electrical properties and structure of the contact interface between Ti\textsubscript{3}SiC\textsubscript{2} and p-type GaN. To form Ti\textsubscript{3}SiC\textsubscript{2} on GaN, a Ti-Si-C ternary film was deposited by radio-frequency magnetron sputtering and then annealed at 1073 K for a very short period. The electric conduction properties of the contact interface were examined. The as-deposited amorphous Ti-Si-C film on p-type GaN shows non-ohmic conduction with a Schottky barrier height (SBH) of 0.89 eV. The SBH is reduced to 0.70 eV by annealing to form Ti\textsubscript{3}SiC\textsubscript{2}. On the other hand, a prolonged Ar ion bombardment of the GaN surface during sputter cleaning reduces the SBH of the as-deposited Ti-Si-C film to 0.76 eV. However, the effect of ion bombardment is not retained after annealing.

1. Introduction
The new era of sustainable society will be established based on renewable energy sources, being independent from exhaustible energy sources such as fossil and nuclear power generation. The power generation method will shift from concentrated power plants to dispersed cells [1] and windmills combined with smart grids [2, 3]. Each cell requires high efficiency power electronic systems at the interface with the grid for conditioning the electricity [4, 5]. The power electronic devices in such applications have to be highly energy-efficient, and capable of handling high power with a long service life.

Today, most of power electronic devices are still made of silicon. However, due to limitations of the physical properties of silicon, it is important to replace the devices with better alternative materials for use in the future power electronics. Two of the most promising candidates for next-generation power electronic devices are gallium nitride (GaN) and silicon carbide (SiC). Both of these wide-bandgap semiconductors allow operation at higher temperatures, power densities, frequencies and voltages with lower leak currents than silicon-based devices [6].

To form an electric circuit, GaN and SiC have to be connected with metallic materials. The ideal contact between these semiconductors and metals is one that allows smooth transportation across the interface. Such an interface shows a constant resistance indicated by proportional current-voltage ($I$–$V$) characteristics obeying the Ohm’s law. Contact interfaces between semiconductors and metals with such properties are referred to as ohmic contacts. For p-type semiconductors, an ohmic contact can be
formed by connecting with a metallic material of which work function ($\phi_m$) is the same or higher than the electron affinity ($\chi$) and the bandgap ($E_g$) of the semiconductor, i.e.,

$$e\phi_m \geq \chi + E_g,$$  (1)

where $e$ is the elementary charge. However, the energy levels of the valence band edges ($\chi + E_g$) for p-type GaN and SiC are very deep: 7.50 and 6.46 eV, respectively. There is no pure metal element which satisfies condition (1). In the case that the work function of the connected metal is lower than the total of the electron affinity and the bandgap of the semiconductor, the electrons in the metal flow into the semiconductor until the Fermi levels of these two materials become equal, forming a depleted zone of carriers (holes) in the semiconductor under the contact. The zone interferes with carrier transportation across the interface. This interference is known as Schottky barrier. Carriers moving across such a contact interface require energy to get over the barrier. Thus, Joule heat is generated at the interface, which deteriorates the energy efficiency and the reliability of the device. Therefore, a technology is demanded to establish low-resistance ohmic contacts by lowering the Schottky barrier height (SBH) and/or by thinning the carrier depleted zone.

This problem has been researched actively worldwide and some important solutions have been reported. It was found that Ti$_3$SiC$_2$ formed adjacent to SiC provides a good ohmic contact for p-type SiC [7-12]. Ti$_3$SiC$_2$ is considered to work as a narrow-bandgap intermediate semiconductor layer which reduces the SBH [8, 9]. On the other hand, no appropriate material for low-resistance ohmic contacts to p-type GaN has been found so far. Jang et al. reported that low-resistance and thermally stable ohmic characteristic is achieved with a Au/Ni/Ru/Ag/Ni multilayered contact on p-type GaN [13]. In another paper, Chen et al. suggested that a low-resistance ohmic contact is achieved with the formation of NiO and a specific microstructure by annealing Au/Ni/p-type-GaN in an oxidative ambient [14]. However, most of the solutions are usually difficult to be reproduced by other researchers, even if the reported procedures are followed. This implies that the reported processes do not correspond only to the formation of the preferred structure at the contact interface. Therefore, a technology to control the interfacial structure has to be established based on knowledge of the formation mechanism of low-resistance ohmic interfaces between metals and GaN or SiC. This is a difficult task to tackle, since the suggested contacts are formed by complex interfacial reaction between the substrate and multilayered films [13].

GaN shows some degree of similarity with SiC in terms of lattice parameters, coefficient of thermal expansion and bandgap as shown in Table 1 [15-18]. These parameters are three of the most important factors which affect directly the formed contact structure and electrical properties. Therefore, there is a high possibility that Ti$_3$SiC$_2$ would also achieve an ohmic contact with p-type GaN. The present study demonstrates this idea by forming Ti$_3$SiC$_2$ on p-type GaN. To form a Ti$_3$SiC$_2$ layer on GaN, a Ti-Si-C ternary film with a composition stoichiometrically equivalent to Ti$_3$SiC$_2$ is deposited on GaN and then annealed at 1073 K.

**Table 1.** Properties of GaN and SiC.

| Properties                        | GaN       | 4H-SiC    |
|-----------------------------------|-----------|-----------|
| Crystal system                    | Hexagonal | Hexagonal |
| Lattice parameter, $a$ / nm       | 0.3189    | 0.3073    |
|                                  | 0.5186    | 1.0053    |
| Coefficient of thermal expansion, $\alpha$ / K$^{-1}$ | $5.59\times10^{-6}$ | $4.47\times10^{-6}$ |
| Bandgap, $E_g$ / eV               | 3.39      | 3.26      |
| Electron affinity, $\chi$ / eV    | 4.11      | 3.20      |
The SBH \( (e\phi_{SB}) \) at the interface between Ti\(_3\)SiC\(_2\) and p-type SiC is estimated as 1.39 eV by the Schottky-Mott model [19] described by

\[
e\phi_{SB} = \chi + E_g - e\phi_{Ti3SiC2}, \tag{2}
\]

where the work function of Ti\(_3\)SiC\(_2\) \( (\phi_{Ti3SiC2}) \) is taken as 5.07 eV [17]. This prediction shows that an ohmic contact cannot be formed by simply connecting Ti\(_3\)SiC\(_2\) and p-type SiC, but an additional mechanism is needed to compensate the SBH. The interfacial reaction between SiC and the deposition film, which consists of Ti and Al, to form Ti\(_3\)SiC\(_2\) is expected to bare the role: the reaction does not form only Ti\(_3\)SiC\(_2\), but also defects in SiC which lower the SBH by increasing the carrier density [8, 9].

On the other hand, the SBH at the interface between Ti\(_3\)SiC\(_2\) and p-type GaN is estimated as 2.43 eV. In contrast with the contact between Ti\(_3\)SiC\(_2\) and p-type SiC, the interfacial reaction between the deposited Ti-Si-C ternary film and GaN cannot be used for Ti\(_3\)SiC\(_2\) formation and defect introduction in GaN under the contact. In the present study, changing the carrier density is attempted by Ar ion bombardment during sputter-cleaning of the GaN surface just before the deposition. By performing a prolonged bombardment, it is expected that severe radiation damage is induced in the subsurface of the substrate. The damage corresponds to vacancy defect formation. Vacancies in GaN are known to act as dopants [19]. Thus, the increase in vacancy defect concentration results in an increase in carrier density. The effects of carrier density on the electrical properties of the contact have been discussed in several reports [19, 20].

The objective of the present study is to clarify the electrical properties and structure of the contact interface between Ti\(_3\)SiC\(_2\) and p-type SiC, including the effect of vacancy defects introduced by Ar ion bombardment.

2. Experimental procedure

A 2.0-µm-thick p-type GaN epitaxially grown on a 330-µm-thick sapphire (0001) wafer with a 2.3-µm-thick GaN buffer layer was used in the present study. The carrier density and the surface orientation were \( 3 \times 10^{17} \) cm\(^{-3} \) and the (0001) Ga-face, respectively. The wafer was cut into 4.0-mm-square substrates. The substrates were cleaned with acetone applying ultrasonic vibration just before the deposition. The substrates were fixed in a radio-frequency (RF) magnetron sputter deposition apparatus with 1.0-mm-wide Al masking ribbons. Before the deposition, careful sputter cleaning of the surfaces of the Ti-Si-C alloy target and substrates was performed. The bombardment of the substrates was performed during this process. Some of the substrates were subjected to 300 s of sputter cleaning to remove native oxide layer on the surfaces, whereas the other substrates were subjected to prolonged bombardment for 1800 s to remove the oxide layer and to introduce a high density of vacancy defects in the substrates. After the sputter cleaning, Ti-Si-C ternary films were deposited on the substrates. Both sputter cleaning and deposition were performed under 0.8 Pa of 99.9999% high-purity Ar and an RF power of 200 W. The target was a Ti-Si-C ternary alloy sintered disk with the composition of Ti\(_{65}\)Si\(_{22}\)C\(_{13}\). By performing deposition for 600 s with this target, 20-nm-thick films with the composition of Ti\(_{40}\)Si\(_{10}\)C\(_{33}\) were successfully deposited on all GaN substrates. The composition of the Ti-Si-C ternary films was close to the stoichiometric composition of Ti\(_3\)SiC\(_2\). After the deposition, some of the specimens were subjected to annealing at 1073 K in a vacuum of \( 1.3 \times 10^{-3} \) Pa. The specimens were cooled down immediately after reaching the temperature of 1073 K, i.e., the specimens were hold at 1073 K only for a very short time.

The structures and electrical properties of the as-deposited and annealed specimens were analyzed by X-ray diffraction (XRD) and direct current (DC) conduction test at room temperature.

3. Results and discussion

Figure 1 shows the structural change in the specimens caused by annealing at 1073 K. In the XRD pattern of the as-deposited specimen, only strong peaks of GaN and sapphire are identified, i.e., no peak related to the Ti-Si-C phases in the deposition film is found. It is likely that the deposition film is amorphous. The XRD pattern of the annealed specimen appears different from that of the as-deposited
specimen. Peaks corresponding to various crystallographic planes of Ti$_3$SiC$_2$ appear, indicating that the Ti$_3$SiC$_2$ has a randomly oriented polycrystalline structure. Thus, it is proven that the Ti$_3$SiC$_2$ layer can be formed on GaN by deposition of the Ti-Si-C ternary film stoichiometrically close to Ti$_3$SiC$_2$ and subsequent annealing at 1073 K.

![Figure 1. Structural change for specimens sputter-cleaned for 300 s (a) before and (b) after the annealing at 1073 K.]

![Figure 2. Electric conduction profiles of specimens sputter-cleaned for 300 s, in as-deposited and annealed state.]

![Figure 3. Electric conduction profiles of specimens sputter-cleaned for 1800 s, in as-deposited and annealed state.]

Figure 1. Structural change for specimens sputter-cleaned for 300 s (a) before and (b) after the annealing at 1073 K.

Figure 2. Electric conduction profiles of specimens sputter-cleaned for 300 s, in as-deposited and annealed state.

Figure 3. Electric conduction profiles of specimens sputter-cleaned for 1800 s, in as-deposited and annealed state.
Figure 2 shows the change in the electrical conduction profile by annealing of the specimens sputter-cleaned for 300 s. The curves of both the as-deposited and the annealed specimens show a non-linear relation between voltage and current, indicating that the contacts of both specimens are not ohmic. However, the difference in the rising voltage of the current indicates that the SBH is reduced by some amount by annealing to form Ti$_3$SiC$_2$. To evaluate the reduction of the SBH, the conduction profiles are analyzed by the thermionic emission model [21] given by

$$I_o = AA' T^2 \exp\left(-\frac{e\phi_{\text{SB}}}{kT}\right),$$

where $I_o$, $A$, $A'$, $T$ and $k$ are the saturated current, the contact area, the effective Richardson constant of 1.038×10$^6$ Am$^{-2}$K$^{-2}$ for p-type GaN [21], the absolute temperature of the specimen and the Boltzmann constant, respectively. The SBHs of the as-deposited and the annealed specimens are 0.89 and 0.70 eV, respectively. Thus, the reduction in SBH for 0.19 eV is attributed to the structural change in the contact film from amorphous to polycrystalline Ti$_3$SiC$_2$. Furthermore, the SBH of the interface between Ti$_3$SiC$_2$ and p-type GaN (the annealed specimen) is 1.73 eV lower than the value predicted by the Schottky-Mott model. Such lowering of the SBH is discussed in detail by Mohammad [19].

Figure 3 shows the change in the electrical conduction profile by annealing of the specimens sputter-cleaned for 1800 s. The profile and its change by annealing show a similar tendency with those shown in Figure 2: both the as-deposited and the annealed specimens are not ohmic. The SBHs of the specimens are 0.76 and 0.69 eV, respectively.

**Figure 4.** Effects of Ar ion bombardment and annealing on SBH reduction.

Figure 4 summarizes the effects of Ar ion bombardment and annealing on the reduction of the SBH. The extensive Ar ion bombardment for 1800 s prior to deposition reduces the SBH by 0.13 eV compared to the specimens subjected to conventional sputter-cleaning for 300 s. The reduction is considered to have been brought about by defects in the GaN sub-surface introduced by the bombardment. However, the difference between the SBH of the annealed specimens is negligible. It seems that the defects are recovered almost completely by annealing to form Ti$_3$SiC$_2$ and the effect of the defects on reduction of the SBH is weakened.

**4. Conclusions**

A Ti$_3$SiC$_2$ layer can be formed adjacent to p-type GaN by deposition of an amorphous Ti-Si-C ternary film stoichiometrically close to Ti$_3$SiC$_2$ and subsequent annealing at 1073 K for a short time. The SBH
of the Ti$_3$SiC$_2$ contact on p-type GaN is 0.70 eV, which is 1.73 eV lower than the theoretically predicted value. A prolonged Ar ion bombardment of the GaN surface reduces the SBH of the as-deposited Ti-Si-C film. However, the effect of ion bombardment is weakened by annealing to form Ti$_3$SiC$_2$.

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