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Effect of Ti$_3$SiC$_2$ formation on p-type GaN by vacuum annealing on the contact properties

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Abstract. In the present study, after the formation of Ti$_3$SiC$_2$ on p-type GaN by depositing Ti-Si-C ternary film with a composition stoichiometrically close to Ti$_3$SiC$_2$ and subsequent annealing at temperatures of 973 K and 1073 K (lower than the annealing temperature for a contact between p-type SiC and Ti$_3$SiC$_2$), the resulting contact properties were analysed by X-ray diffraction, a direct-current conduction test, and a Hall-effect measurement test. The X-ray diffraction results reveal that the Ti$_3$SiC$_2$ phase is successfully formed after the annealing. The direct-current conduction test shows that ohmic-like contacts are achieved after the formation of Ti$_3$SiC$_2$. However, the Hall-effect measurement test reveals that the dominant carrier type of the specimens is inverted from p-type to n-type even after the annealing at 973 K. The N vacancy formation during the annealing is likely the cause of this change. The contact properties of the annealed specimens are discussed because it is difficult to achieve ohmic contact formation between n-type GaN and Ti$_3$SiC$_2$.

1. Introduction

Because gallium nitride (GaN) can operate at higher temperatures, frequencies, voltages, and power densities than silicon, it is one of the most promising candidates as an alternative material for next-generation power electronic devices [1]. However, in spite of the significant development in the single-crystal growth and processing technologies for light-emitting diodes (LED) and laser diodes (LDs), the realization of GaN-based power electronic devices is still being held back by some major problems.

One of the main problem is the difficulties in forming an ohmic contact to p-type GaN. In the search for appropriate contact materials for p-type GaN, many options have been considered based on p-type GaAs contact materials such as Ni, Au, Pd and Pt [2-3]. This is due to the fact that these contact materials have been empirically proven to form good electrical properties with p-type GaAs and have been used for a wide variety of devices [4]. Jang et al. suggested that with a Au/Ni/Ru/Ag/Ni multilayered contact on p-type GaN, low resistance and thermally stable ohmic characteristics are achieved [2]. 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 [3]. Despite the many p-type GaN ohmic contact solutions that have been reported, most of the solutions are difficult to reproduce, even if the procedures are exactly followed. This
suggests that the reported procedures are not solely responsible for the observed formations of the favoured contact interface structure.

On the other hand, a different approach to finding an appropriate contact material for p-type GaN has been used in the present study. GaN shows a higher degree of similarity with SiC than with GaAs in both crystallographic and electronic structures, as shown in Table 1 [5-8]. These are the most crucial factors which directly affect the formed contact structure and electrical properties. Thus, there is a high possibility that SiC contact materials are more suitable than GaAs contact materials for the formation of an ohmic contact to GaN.

The present study demonstrates this idea by forming Ti$_3$SiC$_2$ contacts on p-type GaN and examining the properties of the contacts. It has been reported that good ohmic contact has been achieved with p-type SiC and Ti$_3$SiC$_2$ contacts by annealing at 1273 K [9-14]. However, numerous investigations of p-type GaN have suggested that the elevated temperature during the contact formation can cause formation of N vacancies, which consequently reduce the hole concentration of the p-type GaN [15]. These vacancies are known to act as n-type dopant atoms with a donor level very close to the conduction band edge of n-type GaN [16]. Fujimoto et al. reported that Hall-effect measurements revealed that an n-type conductive layer was formed near the p-GaN surfaces by annealing at 1073 K in vacuum [17]. In this study, the formation of Ti$_3$SiC$_2$ is attempted by annealing at 973 K and 1073 K. Although there is possibility that the hole concentration of the p-type GaN is reduced by annealing at these temperatures, the investigation of the contact properties of p-type GaN and Ti$_3$SiC$_2$ is an important step to understand the practicality of this contact structure.

In the present study, Ti$_3$SiC$_2$ is formed on p-type GaN by 1) depositing a Ti-Si-C ternary film with a composition stoichiometrically equivalent to Ti$_3$SiC$_2$ on p-type GaN and 2) subsequent annealing. By forming Ti$_3$SiC$_2$ from the ternary film, no reaction is expected to occur between the deposited film and GaN, which would suppress the formation of N vacancies and lead to the preservation of the dominant carrier type of p-type GaN.

The direct-current conduction test and Hall-effect measurement is needed to examine the effect of the formation of Ti$_3$SiC$_2$ by annealing at 973 K and 1073 K. With the preservation of p-type carriers (holes) as the dominant carrier type, formation of an ohmic-like contact between p-type GaN and Ti$_3$SiC$_2$ is expected. However, with the dominant carrier type inverted from p-type to n-type, formation of a non-ohmic contact between the n-type GaN and Ti$_3$SiC$_2$ is expected.

In the present study, the effects of Ti$_3$SiC$_2$ formation on p-type GaN by annealing at 973 K and 1073 K and the relation of these effect to the contact properties are discussed.

Table 1. Properties of GaN, SiC and GaAs.

| Properties         | GaN  | 4H-SiC | GaAs |
|--------------------|------|--------|------|
| Crystal system     | Hexagonal | Hexagonal | Cubic |
| Lattice parameter, $a$ / nm | 0.3189 | 0.3073 | 0.5653 |
|                    | $c$ / nm |       |      |
|                    | 0.5186 | 1.0053 | -    |
| Bandgap, $E_g$ / eV | 3.39  | 3.26   | 1.42 |
| Electron affinity, $\chi$ / eV | 4.11  | 3.20   | 4.07 |

2. Experimental procedure

The substrates used in the present study were 2.0-$\mu$m-thick p-type GaN epitaxially grown on a 330-$\mu$m-thick sapphire (0001) wafer with a 2.3-$\mu$m-thick undoped GaN buffer layer. The surface orientation and carrier density of the substrate were (0001) Ga-face and $3\times10^{17}$ cm$^{-3}$, respectively. The wafer was cut into 4.0-mm-square substrates. Before the deposition process, the substrates were cleaned with acetone while applying ultrasonic vibration. Then, the substrates were fixed in a radio-frequency magnetron sputter deposition apparatus using 2.0-mm-wide Al masking ribbons to form 1.0-mm-square contacts at the corners of the substrates, as shown in figure 1. Before the sputter
deposition, the surfaces of the Ti-Si-C alloy target and the substrates were sputter-cleaned to remove the native oxide layer. The sputter deposition of Ti-Si-C ternary films on the substrates was performed immediately after the sputter cleaning. Both the sputter cleaning and sputter deposition were performed under 0.8 Pa of 99.9999% high-purity Ar under a radio-frequency power of 200 W. The target used in the sputter deposition process was a Ti-Si-C ternary alloy sintered disk with a composition of Ti-19mol%Si-17mol%C. Sputter deposition for 600 s with this target results in the successfully formation of a 200-nm-thick film with a composition of Ti-17mol%Si-33mol%C on all p-type GaN substrates. The composition of the ternary films was close to the stoichiometric composition of Ti$_3$SiC$_2$. Some of the deposited samples were subjected to annealing at 973 K or 1073 K in a vacuum pressure of $1.3 \times 10^3$ Pa. The specimens were cooled down immediately after reaching the targeted temperature. The heating rate and cooling rate between 600 K and 1073 K are approximately 0.2 K/s and 0.7 K/s, respectively.

The contact structure and electrical properties of the specimens were analysed by X-ray diffraction (XRD) and a direct-current (DC) conduction test at room temperature. The electrical conduction profiles of the specimens were measured between two adjacent contacts. Finally, the dominant carrier type of the annealed specimens was analysed by a Hall-effect measurement test using the van der Pauw method at room temperature.

Figure 1. Prepared specimens.

3. Results and discussion

Figure 2 shows the XRD patterns of the specimens in the as-deposited state and after the annealing at 973 K and 1073 K. In the XRD pattern of the as-deposited specimen shown in figure 2(a), a weak peak from Ti appears in addition to the strong peaks, which are identified as being from GaN and sapphire. Other than that, no peak related to Ti-Si-C phases was found. This analysis of as-deposited specimens indicates that the deposited film is in an amorphous state. The XRD for the annealed specimens appear different from that of the as-deposited specimen, as shown in figure 2(b) and (c). Peaks corresponding to various crystallographic planes of Ti$_3$SiC$_2$ were identified. As a result of reducing the annealing temperature to 973 K from 1073 K, the residual Ti phase appeared, and fewer peaks corresponding to crystallographic planes of Ti$_3$SiC$_2$ were identified. The structural change of each of the two annealed specimens indicates that the Ti$_3$SiC$_2$ has a randomly oriented polycrystalline structure for each of the specimens. This proves that the Ti$_3$SiC$_2$ phase 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 973 K or 1073 K.

It has been suggested that p-type SiC/Ti/Al needs to be annealed up to 1273 K for 120 s or longer to form Ti$_3$SiC$_2$ phase on SiC [14]. Hence, the Ti$_3$SiC$_2$ formation method applied in the present study has the advantages of lowering the annealing temperature and shortening the holding time. The lowering of the annealing temperature was achieved due to the fact that the deposited film is in a thermodynamically unstable state, resulting in the crystallization process that forms Ti$_3$SiC$_2$ phase being triggered at a lower temperature.
Figure 3 shows the changes in the electrical conduction profiles caused by annealing the specimens at 973 K or 1073 K. The curve of the as-deposited specimen shows a non-linear relation between voltage and current, indicating that the formed contact is non-ohmic. On the other hand, near-linear relations between voltage and current are observed for both of the annealed specimens, indicating that ohmic-like contacts have been successfully formed by the formation of Ti$_3$SiC$_2$ during annealing.

To investigate the dominant carrier type of the two annealed specimens, the Hall-effect measurement test has been performed at room temperature. The results revealed that the dominant carrier type of both specimens are n-type, i.e., the dominant carrier-type of the specimens changes from p-type to n-type as a result of the annealing at 973 K and 1073 K. The factor that is likely to be the cause of this change is the increasing of N vacancies in the p-type GaN subsurface resulting from the out-diffusion of N atoms during the annealing. These results indicate that the observed non-ohmic contact of the as-deposited specimen is formed between the p-type GaN and the deposited Ti-S-C ternary film. On the other hand, the observed ohmic-like contacts of the annealed specimens are formed between the n-type GaN (inverted from p-type GaN by annealing) and phases formed within the film during annealing. In the previous study, transmission electron microscopy revealed that other than the Ti$_3$SiC$_2$ phase, Ti$_5$Si$_3$ and TiSi$_2$ phases were also formed during the annealing [18].
high work function of Ti$_3$SiC$_2$ (5.07 eV), it is most likely that the observed ohmic-like contacts of the annealed specimens are formed between the n-type GaN and these byproducts. The work functions of Ti$_5$Si$_3$ and TiSi$_2$, which are respectively 3.71 eV and 4.10 eV, are lower compared to that of Ti$_3$SiC$_2$. In another study, Maeda et al. reported that with an enhanced interfacial reaction and the formation of N vacancies, ohmic contacts can be formed between n-type GaN and Ti even without annealing [19]. Thus, it is also possible that the observed ohmic-like contact of the annealed specimens is formed between n-type GaN and the residual Ti phase. Additionally, Mohammed reported that n-type GaN ohmic contacts can also be achieved by the formation of the TiN phase through the reaction between GaN and Ti film during the annealing [16]. Although the TiN phase was not found in the XRD patterns in this study, there is a possibility that the observed ohmic-like contacts of the annealed specimens are between n-type GaN and TiN.

To form a contact between p-type GaN and Ti$_3$SiC$_2$, a lower annealing temperature to form Ti$_3$SiC$_2$ is needed so that the dominant carrier type of the p-type GaN can be retained. For this purpose, an unconventional Ti$_3$SiC$_2$ formation method such as multilayer deposition by magnetron sputtering can be adopted [20].

4. Conclusions
A Ti-Si-C ternary film with a composition stoichiometrically close to Ti$_3$SiC$_2$ has been deposited on p-type GaN. By annealing the film at temperatures of 973 K and 1073 K, the Ti$_3$SiC$_2$ phase has been successfully formed. The direct-current conduction test shows that ohmic-like contacts have been achieved after the formation of Ti$_3$SiC$_2$. However, the Hall-effect measurement test reveals that the dominant carrier type of the specimens has changed from p-type to n-type even after the annealing at 973 K. The formation of N vacancies during the annealing is likely the cause of this change. The ohmic-like contacts are likely formed between n-type GaN and the byproducts of Ti$_3$SiC$_2$ formation (Ti$_5$Si$_3$ and TiSi$_2$), the residual Ti phase and/or the TiN phase. To form contacts between p-type GaN and Ti$_3$SiC$_2$, the annealing temperature to form Ti$_3$SiC$_2$ needs to be lowered so that the dominant carrier type of the p-type GaN can be retained.

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