Interfacial Nanostructure and Electrical Properties of Ti₃SiC₂ Contact on p-Type Gallium Nitride

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In the present study, the interfacial nanostructure and electrical properties of Ti₃SiC₂ formed by depositing a Ti–Si–C ternary film with a composition stoichiometrically equivalent to Ti₃SiC₂ on p-type GaN and subsequent annealing at 1073 K were analyzed by X-ray diffraction, transmission electron microscopy and direct current conduction test. The results reveal that structural changes occur by the annealing. Polycrystalline Ti₃SiC₂ is formed at most of the contact interface area and single crystal Ti₃SiC₂ at small area of the contact interface. Furthermore, other than Ti₃SiC₂ phase, polycrystalline Ti₅Si₃ and TiSi₂ with different grain sizes are also formed, resulting in a formation of three-layered film after the annealing. By all these structural change, the electric conduction profiles show that the Schottky barrier height (SBH) is reduced. The estimated SBH of the Ti₃SiC₂ contact on p-type GaN is 0.70 eV, which is 1.73 eV lower than the theoretically predicted value.

1. Introduction

Due to the physical limitation of silicon, which is still used in most of today’s power electronic devices, it is important to seek for better alternative materials for use in the next-generation power electronic devices. Gallium nitride (GaN) is one of the most promising candidates. Compared with silicon, this wide band-gap semiconductor can be operated at higher temperatures, frequencies, voltages and power densities with lower leak current.¹ With all these advantages, GaN-based power electronic devices are promising higher energy efficiency with capability of handling higher power and longer service life compared to silicon-based power electronic devices. However, in spite of having a significant development in the growth and processing technology of light emitting diodes (LED) and laser diodes (LDs), the application of GaN semiconductor as power electronic devices is still far from real.

One of the main problems in realizing GaN-based power electronic devices is related to the fact that the only effective p-type dopant known for GaN is magnesium. Although some decent annealing methods were developed²,³ after the breakthrough discovery of Mg-activation by electron-beam irradiation,⁴ not much recent development of p-type GaN conductivity has been accomplished. It is known that only approximately one percent of doped magnesium atoms are activated during Mg-activation.⁵,⁶ To achieve reasonable p-type conductivity, a relatively high Mg-doping level is needed. However, such high level of impurities in GaN leads to growth disturbances such as stacking faults, which consequently degrade the quality of crystalline.

The other important problem is the difficulties in formation of low resistance ohmic contact to p-type GaN. GaN have to be connected with metallic materials to form an electric circuit. However, due to the very deep valance band edge for p-type GaN (7.50 eV under the vacuum level), there is no pure metallic element which can directly form ohmic contact with p-type GaN. Without the formation of ohmic contact, the interference of carrier will occur at the contact interface, which generates Joule heat and deteriorates the energy efficiency and the reliability of the devices. Hence, to form an efficient and reliable power electronic device, a clear understanding on formation of low-resistance ohmic contact between semiconductors and metallic materials by lowering the Schottky barrier height (SBH) and/or by thinning the carrier depleted zone at the contact interface is needed.

Unfortunately, there is no appropriate contact material for p-type GaN to form low-resistance ohmic contact has been recognized so far. Jang et al. suggested that with a Au/Ni/Ru/Ag/Ni multilayered contact on p-type GaN, low-resistance and thermally stable ohmic characteristic is achieved.⁷ 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.⁸ Despite a lot of p-type GaN ohmic contact solutions have been reported, most of the solutions are difficult to be reproduced, even if the procedures are exactly followed. This suggests that the reported procedures do not correspond solely to the formation of the favored contact interface structure. Thus, it is important to establish a technology to control the interfacial structure based on knowledge of the mechanism of low-resistance ohmic contacts formation between p-type GaN and contact materials. However this is a difficult subject: the suggested contacts are formed by complex interfacial reaction between the p-type GaN and multilayer contact materials.⁹

In researches related to p-type GaN contacts, to seek for appropriate contact materials, a lot of considerations are made based on p-type GaAs contact materials such as Ni, Au and Pt. 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 such as optoelectronic devices, metal semiconductor field-effect transistors, heterojunction FET and heterojunction bipolar transistors.⁹ However, in this study, a different approach to seek an appropriate contact material for p-type GaN has been used. Compared with GaAs, GaN shows more similarity with SiC, as shown in Table 1.¹⁰-¹³ GaN shows close similarity with SiC in
Table 1 Properties of GaN, GaAs and 4H-SiC.

<table>
<thead>
<tr>
<th>Properties</th>
<th>GaN</th>
<th>GaAs</th>
<th>4H-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Hexagonal</td>
<td>Cubic</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Lattice parameter, ( a/\text{nm} )</td>
<td>0.3189</td>
<td>0.5653</td>
<td>0.3073</td>
</tr>
<tr>
<td>( c/\text{nm} )</td>
<td>0.5186</td>
<td>—</td>
<td>1.0053</td>
</tr>
<tr>
<td>Coefficient of thermal expansion, ( \alpha/\text{K}^{-1} )</td>
<td>( 5.59 \times 10^{-4} )</td>
<td>( 6.00 \times 10^{-4} )</td>
<td>( 4.47 \times 10^{-4} )</td>
</tr>
<tr>
<td>Band gap, ( E_g/\text{eV} )</td>
<td>3.39</td>
<td>1.42</td>
<td>3.26</td>
</tr>
<tr>
<td>Electron affinity, ( \chi/\text{eV} )</td>
<td>4.11</td>
<td>4.07</td>
<td>3.20</td>
</tr>
</tbody>
</table>

The lattice parameters, coefficient of thermal expansion and band gap, which are the three most important factors which directly affect the contact structure and electrical properties of the formed contact. Hence, there is a high possibility that, SiC contact materials are more suitable than GaAs contact materials for formation of low resistance ohmic contact to SiC.14

In the present study, Ti3SiC2 is formed on p-type GaN by depositing a Ti–Si–C ternary film with a composition stoichiometrically equivalent to Ti3SiC2 on p-type GaN and subsequent annealing at 1073 K.

2. Experimental Procedure

Substrates used in the present study were 2.0-μm-thick, 4.0 mm-square p-type GaN epitaxially grown on a 330-μm-thick sapphire (0001) wafer with a 2.3-μm-thick GaN buffer layer. The surface orientation and carrier density of the substrate were (0001) Ga-face and 3 \( \times 10^{17} \) cm\(^{-2} \), respectively. Before the deposition process, the substrates were cleaned with acetone applying ultrasonic vibration. Then, the substrates were fixed in a radio-frequency (RF) magnetron sputter deposition apparatus using 1.0-mm-wide Al masking ribbons. Before the sputter deposition, the surfaces of Ti–Si–C alloy target and the substrates were sputter-cleaned. The sputter deposition of Ti–Si–C ternary films on the substrates was performed immediately after the sputter-cleaning. Both of sputter-cleaning and sputter deposition were performed in 0.8 Pa of 99.9999% Ar under the RF power of 200 W. The target used in the sputter deposition process was a Ti–Si–C ternary alloy sintered disk with the composition of Ti0.8Si1.2C1.3. Sputter deposition for 600 s with this target forms a 500-nm-thick film with the composition of Ti0.8Si1.2C1.3 on all p-type GaN substrates. The composition of the ternary films was close to the stoichiometric composition of Ti3SiC2. Some of the deposited samples were subjected to annealing at 1073 K in vacuum of 1.3 \( \times 10^{-3} \) Pa. The specimens were cooled down immediately after reaching the temperature of 1073 K.

The contact structure and electrical properties of the as-deposited and annealed specimens were then analyzed by X-ray diffraction (XRD), transmission electron microscopy (TEM) and direct current (DC) conduction test at room temperature.

3. Result and Discussion

Figure 1 shows the structural change of the specimens by annealing at 1073 K. In the XRD pattern of the as-deposited specimens, all the identified peaks correspond to GaN and sapphire. No other peak related to the Ti–Si–C phase in the as-deposited film is identified. This analysis indicates that the deposited film consists only of an amorphous phase. The XRD pattern of the specimens after the annealing appears different from that of the as-deposited specimen. Peaks corresponding to various crystallographic planes of Ti3SiC2 are identified, indicating that Ti3SiC2 has a randomly oriented polycrystalline structure. Hence, it is proven that the Ti3SiC2 can be formed on p-type GaN substrates by deposition of the Ti–Si–C ternary film stoichiometrically close to Ti3SiC2 and subsequent annealing at 1073 K. On the other hand, it is suggested that p-type SiC/Ti/Al need to be annealed up to 1273 K for 120 s or longer to form Ti3SiC2 phase on p-type SiC.14–19 Therefore, the Ti3SiC2 formation method employed in the present study has advantages in lowering the annealing temperature and shortening the holding time. The lower annealing temperature was achieved due to the fact that the deposited film is in thermodynamically unstable state, triggering the crystallization process to form Ti3SiC2 phase at lower temperature. Lowering of the annealing temperature is strongly demanded, in order to prevent surface roughening of the contact and deterioration of capacitances of gate insulation layers. Furthermore, processes with lower annealing temperature and shorter hold time are preferred for production cost suppression.

The structure change during annealing has been analyzed further by TEM. Figure 2 shows the structure of the as-deposited specimen. Figure 2(a) shows a bright field image (BFI) of the specimen. In the image, the deposited film of which thickness is approximately 500 nm appears in a monotonous contrast showing no grain boundaries within the film. Figure 2(b) shows the selected area electron diffraction (SAED) pattern of the specimen. The SAED pattern consists of [1100] zone axis net pattern corresponding to GaN single crystal and a halo ring corresponding to amorphous phase. The results indicate that the deposited Ti–Si–C ternary film is in amorphous state, which agrees with the XRD pattern.
shown in Fig. 1. Figure 3 shows the structure of the specimen after annealing at 1073 K. In the BFI shown in Fig. 3(a), the dislocation line of p-type GaN stops near the contact interface, indicating that the p-type GaN substrate near the contact interface have structurally transformed by annealing at 1073 K, forming a layer of intermediate-phase. The high-magnification BFI shown in Fig. 3(b) clearly shows that the single-layer Ti-Si-C ternary film of the as-deposited specimen has changed into three-layered film, distinguished by the grain sizes. The grain sizes increase from coarse-grained near the contact interface to fine-grained near the film surface, indicating that the structural change of the film such as crystallization and nucleation start form near the contact interface. Figure 3(c) shows the SAED pattern taken from the area shown in Fig. 3(a). This pattern consists of net patterns of GaN and Ti3SiC2 single crystals and Debye–Scherrer rings of Ti5Si3 and TiSi2 polycrystals. The net pattern of GaN and Ti3SiC2 show a close correlation with each other as

\[(0002)\text{GaN} // (1102)\text{Ti}_3\text{SiC}_2\]  
and

\[(11\overline{2}0)\text{GaN} // (11\overline{2}0)\text{Ti}_3\text{SiC}_2\]  

Therefore, it is considered that the Ti3SiC2 is formed adjacent to GaN epitaxially. On the other hand, the Debye–Scherrer rings of Ti5Si3 and TiSi2 appear differently. The rings corresponding to Ti5Si3 are continuous, indicating that the grains of Ti5Si3 are very fine. The rings corresponding to TiSi2 appear as discontinuous scattered spots, indicating that only a few grains of TiSi2 are involved in the diffraction.

Contrary with the analysis from XRD pattern, which shows that the film is consisting of polycrystals Ti3SiC2, the TEM observation shows that the selected area of the specimen shown in Fig. 3(a) is consisting of single crystal Ti3SiC2. These observations reveal that most of the formed Ti3SiC2 in the film is polycrystalline Ti3SiC2. Single crystal Ti3SiC2 failed to be formed in most of the contact interface area likely due to the mismatch in lattice parameter between p-type GaN and Ti3SiC2.

Figure 4 shows the profile of electrical conduction and its change by annealing at 1073 K. The relations between voltage and current for both as-deposited and annealed specimens are indicated by non-linear curves. This result shows that both specimens fail to achieve ohmic contact. However, the voltage to raise the current is lowered by the annealing. The change indicates that the SBH is reduced by some amount after the annealing, i.e., after the formation of Ti3SiC2 on the p-type GaN. To evaluate the reduction of SBH after the formation of Ti3SiC2, the conduction profiles are analyzed by the thermionic emission model \(^{(20)}\) given by

\[I_0 = A A^* T^2 \exp\left(\frac{e\phi_{SB}}{kT}\right), \quad (3)\]

where \(I_0, A, A^*, T \) and \(k \) are the saturated current, the work function of Ti3SiC2, the absolute temperature of the specimen and the Boltzmann constant, respectively. The estimated SBH of the as-deposited and annealed specimens are 0.89 and 0.70 eV, respectively. Therefore, a reduction of 0.19 eV of SBH is attributed to the structural change in the contact film from the amorphous to polycrystalline Ti3SiC2. In addition to that, compared to the value predicted by Schottky–Mott model \(^{(21)}\) given by

\[e\phi_{SB} = \chi + E_g - e\phi_{\text{Ti}_3\text{SiC2}}, \quad (4)\]

where the work function of Ti3SiC2 (\(\phi_{\text{Ti}_3\text{SiC2}}\)) is taken as 5.07 eV \(^{(18)}\) the SBH of the p-type GaN and Ti3SiC2 interface (the annealed specimen) is 1.73 eV lower. Mohammad have discussed such lowering of the SBH in detail, and suggested that such lowering of the SBH is caused by band gap narrowing and image force lowering effects. \(^{(21)}\)

4. Conclusion

The interfacial nanostructure and electrical properties of Ti3SiC2 formed by depositing a Ti–Si–C ternary film with a composition stoichiometrically equivalent to Ti3SiC2 on p-type GaN and subsequent annealing at 1073 K were analyzed by XRD, TEM and DC conduction test. The following points were clarified:

(1) Ti3SiC2 phase can be formed adjacent to p-type GaN by deposition of an amorphous Ti–Si–C ternary film stoichiometrically close to Ti3SiC2 and subsequent annealing at 1073 K for a short time.

Fig. 2 Structure of an as-deposited specimen. (a) BFI, (b) SAED pattern.

Fig. 3(a), the dislocation line of p-type GaN stops near the contact interface between the p-type GaN and deposited film, indicating that the p-type GaN substrate near the contact interface have structurally transformed by annealing at 1073 K. In the BFI shown in Fig. 3(b) clearly shows that the single-layer Ti–Si–C ternary film of the as-deposited specimen has changed into three-layered film, distinguished by the grain sizes. The grain sizes increase from coarse-grained near the contact interface to fine-grained near the film surface, indicating that the structural change of the film such as crystallization and nucleation start form near the contact interface. Figure 3(c) shows the SAED pattern taken from the area shown in Fig. 3(a). This pattern consists of net patterns of GaN and Ti3SiC2 single crystals and Debye–Scherrer rings of Ti5Si3 and TiSi2 polycrystals. The net pattern of GaN and Ti3SiC2 show a close correlation with each other as

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The XRD and TEM results reveal that the structural changes during the annealing occur. Polycrystalline Ti3SiC2 is formed at most of the contact interface area and single crystal Ti3SiC2 at small area of the contact interface.

The TEM results reveal that other than Ti3SiC2 phase near the interface, polycrystalline Ti5Si3 and TiSi2 with different grain sizes are also formed, resulting in a formation of three-layered film after the annealing.

The electric conduction profiles show that the SBH is reduced by the formation of Ti3SiC2 phase at the contact interface. The SBH of the Ti3SiC2 contact on p-type GaN is 0.70 eV, which is 1.73 eV lower than the theoretically predicted value.

Acknowledgement

The authors express their gratitude to Prof. Em. H. Mori and Mr. E. Taguchi for their kind permission and assistance to use facilities in the Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Japan.

REFERENCES