Effect of Argon Ion Irradiation on Ohmic Contact Formation on n-type Gallium Nitride

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This paper describes electrical properties at the interface between n-type GaN and Ti contact layers formed by RF magnetron sputter deposition under various time of Ar⁺ irradiation. The conductance increases proportionately to the extension of the Ar⁺ irradiation time, indicating that Ar⁺ irradiation enhances the formation of nitrogen vacancies and consequently Schottky barrier width is narrowed. On the other hand, extensive Ar⁺ irradiation for 3600 s and longer does not show further increase of conductance. Extensive selective sputtering of nitrogen atoms out of GaN has induced the phase transformation from GaN to Ga at the surface of GaN. The Ga phase enhances the formation of Ga–Ti compounds during the deposition of Ti, and it increases the height and width of the Schottky barrier.

1. Introduction

Gallium nitride (GaN) is applied in solid-state illumination devices and has a breaking-through potential as high-frequency-operated power electronic devices.¹) These applications need low-resistance ohmic contact at interfaces between GaN and outer (metallic) circuits. However, to form such a contact on GaN is difficult.²) Even the mechanism of ohmic conduction across the interface between the wide-bandgap semiconductor and the contact material is not sufficiently understood.

To form low-resistance ohmic contacts on GaN, it is necessary to reduce the height and width of the Schottky barrier. In the case of n-type GaN, the work function has to be shallower than the conduction-band edge of GaN, which is 4.11 eV below the vacuum level. TiN is known as one of those materials with a sufficiently shallow work function of 3.74 eV.³,⁴)

On the other hand, to make the Schottky barrier thin, it is effective to increase the carrier density in the GaN just under the contact material. The density can be increased by implantation of dopants. Formation of TiN by interfacial reaction between GaN and Ti generates N-vacancies in GaN, which work as donors at an energy level close to the conduction band edge of GaN.⁴) Therefore, TiN is formed adjacent to GaN by interfacial reaction between GaN and multilayered metallic film containing Ti layer.⁴)–⁸) Furthermore, Maeda et al. have reported that N-vacancies formed in the sub-interface of GaN by interfacial reaction between GaN and contact metal, instead of the formation of TiN adjacent to GaN, play an essential role in developing ohmic properties.⁹) Generally, the vacancies are formed by interfacial reactions between the deposited film and the GaN substrate during the contact formation process. However, the interfacial reaction is not the only method to form N-vacancies. The present study demonstrates another route to form N-vacancies in GaN sub-interface: Ar⁺-irradiation-induced vacancy formation during extensive sputter-cleaning of the GaN surface.

2. Experimental Procedure

Substrates of n-type GaN were prepared from a 350-μm-thick, 51-mm-diameter single crystal wafer by cutting to 4.0-mm-square chips. The surface orientation, the electron mobility and the carrier density of the substrates were (0001) Ga-face, 1.6 × 10⁶ m²/Vs and 5.1 × 10¹⁴ m⁻³, respectively. Single layer of Ti was deposited on the substrates by radio-frequency (RF) magnetron sputtering through the following process. The substrates were fixed in the deposition chamber using 1.0-mm-wide Al ribbons. The ribbons work also as deposition masks. After evacuation of the chamber to 4.0 × 10⁻⁵ Pa, high-purity Ar of 8.0 Pa was introduced as the discharging gas. The surfaces of the target and the substrates were sputter-cleaned consecutively. The RF power for sputter-cleaning of both the target and the substrates was 200 W. The sputter-cleaning time for the target was fixed at 300 s, whereas that for the substrates was varied from 300 to 5400 s. Finally, a layer of Ti was deposited under the RF power of 200 W and deposition time of 600 s.

The microstructures of the deposited films and the interfaces were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The TEM samples were prepared by focused ion beam machining. Direct-current electric conductivity was measured at 273 K by probing between 1.0-mm-distant Ti contacts on a GaN substrate.

3. Results and Discussion

Figure 1 shows the electric conductivity profiles of Ti/n-GaN specimens which were formed after Ar⁺ irradiation of the substrate for 300, 1200, 2400, 3600 and 5400 s. All profiles show linear current–voltage relation, indicating that all contacts are ohmic. On the other hand, the gradients of the profiles (i.e., the electrical conductance) change depending on the Ar⁺ irradiation time. It indicates that sputter-cleaning affects the ohmic conductivity. However, the I–V profiles of the samples sputter-cleaned for 3600 s and longer do not show improvement in electrical conductance from that sputter-cleaned for 2400 s.
Figure 2 shows the effect of sputter-cleaning time on the electrical conductance of the contacts. Except the samples sputter-cleaned for 3600 s and longer, the conductance increases proportionately to the extension of the sputter-cleaning time. The increment of the electrical conductance by the sputter-cleaning time is approximately $6.1 \times 10^{-2} \text{ S s}^{-1}$.

The Ar$^+$ irradiation on the n-GaN surface enhances the formation of N-vacancies. Due to the formation of N-vacancies, the carrier density of n-GaN is increased and the Schottky barrier width is narrowed, as indicated by the conductance of the samples subjected to sputter-cleaning for 300 to 2400 s. Extensive Ar$^+$ irradiation time over 2400 s does not show further increasing of conductance. It is likely that extensive selective sputtering of N-atoms out of GaN has induced the phase transformation from GaN to Ga at the surface of GaN. The Ga phase enhances the formation of Ga–Ti compound during the deposition of Ti. The Ga–Ti compounds will increase the height and width of the Schottky barrier.

Figure 3 shows a cross-sectional structure of the contact interface formed on GaN irradiated by Ar$^+$ for 5400 s. In the bright-field image (BFI) shown in Fig. 3(a), a 250-nm-thick layer is observed adjacent to GaN. The electron diffraction pattern (EDP) taken from this area is shown in Fig. 3(b). It consists of a [1100] zone axis net pattern of GaN and Debye–Scherrer rings of Ti, TiN and Ga$_5$Ti$_3$. In the dark-field image (DFI) of the same area using the Ga$_5$Ti$_3$ [211] diffraction shown in Fig. 3(c), some grains adjacent to GaN and columnar grains of Ti appear bright, indicating that some crystal of Ga$_5$Ti$_3$ is formed adjacent to GaN during the deposition of Ti. Figure 4 shows the XRD patterns of samples irradiated for 300, 2400 and 3600 s. In all patterns, the peaks corresponding to Ga$_5$Ti$_3$ appear. Especially, the peaks of Ga$_5$Ti$_3$ appear much stronger in the pattern of the sample irradiated for 3600 s than the other samples.

From the results shown in Figs. 3 and 4, it is confirmed that Ga$_5$Ti$_3$ is formed at the interface of the samples irradiated for 3600 s and longer. Therefore, the lowering of the electrical conductance by extensive Ar$^+$ irradiation for 3600 s and longer is attributed to the formation of Ga$_5$Ti$_3$ adjacent to GaN. On the other hand, the patterns of the samples irradiated for 300 and 2400 s do not show distinct
differences. Therefore, the change in the electrical conductance by Ar\textsuperscript{+} irradiation up to 2400 s is attributed only to the reduction of the Schottky barrier width.

In the present study, a model to estimate the Schottky barrier width is developed. The origin of the Schottky barrier is the depleted zone of carriers formed by the difference in the electronic structure between the semiconductor and the contacting metal. In n-type semiconductors, the carrier electrons in the vicinity of the contact electrode are evacuated to the metallic electrodes. Therefore, the electrons have to conduct through the barrier by tunneling and/or thermionic emission mechanisms. These two mechanisms are competitive and the dominating mechanism is determined by the carrier density.\textsuperscript{4) In the case of the present study, the carrier density being 5.1 \times 10^{18} \text{ cm}^{-3} makes the tunneling mechanism dominant. Thus, the conduction by thermionic emission mechanism is omitted out of further consideration. The tunneling current \( I \) is expressed as

\[
I = qA\nu_{th}n \exp[-8\pi w/3h(2qm_{e}\phi_{B})^{1/2}],
\]

where the symbols and their values are listed in Table 1. The Schottky barrier height \( \phi_{B} \) is derived from the Schottky-Mott model which is described as

\[
\phi_{B} = \phi_{M} - \chi_{S}.
\]

Although some mechanisms to lower the Schottky barrier height such as band-gap narrowing and image force lowering are proposed,\textsuperscript{4) these mechanisms were neglected in the present study for simplification. Indeed, it is very difficult to estimate the Schottky barrier height quantitatively.

From the eqs. (1) and (2) and the values shown in Table 1, the Schottky barrier width \( w \) is expressed as

\[
w = \frac{23.50 - \ln(I)}{1.368} \times 10^{-9}.
\]

Figure 5 shows the Schottky barrier width derived using eq. (3) and its change by Ar\textsuperscript{+} irradiation up to 2400 s. A distinct narrowing of the Schottky barrier is observed. The barrier is narrowed down for 0.3 nm by Ar\textsuperscript{+} irradiation for 2400 s.

### 4. Conclusion

Ti contact films were formed on n-GaN under various sputtering condition to investigate effect of Ar\textsuperscript{+} irradiation to develop ohmic conduction. The following points are clarified.

1. The conductance of Ti/n-GaN contact is increased by Ar\textsuperscript{+} irradiation.
2. Extensive Ar\textsuperscript{+} irradiation for 3600 s and longer does not show further improvement of the conductance.
3. Ga\textsubscript{5}Ti\textsubscript{3} is formed at the interface of Ti/n-GaN contact extensively irradiated by Ar\textsuperscript{+}. The formation of Ga\textsubscript{5}Ti\textsubscript{3} at the interface reduces the conductance of the interface.
4. Schottky barrier is narrowed down for about 0.3 nm by Ar\textsuperscript{+} irradiation time for 2400 s.
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