Reaction between GaN and Metallic Deposition Films*

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The interfacial microstructures of two typical contact films for gallium nitride (GaN) have been investigated by transmission electron microscopy. One is a 300-nm-thick Ni single-layer deposited on p-type GaN and then annealed at 873 K. Ni5Ga3 is formed at the interface by the post-deposition anneal. As the other product of the interfacial reaction, N2 voids are formed bulging to the Ni-side. The other contact film consists of four layers: Ti, Al, Ni, and Au, at the initial state. By annealing at 873 K for 300 s, the reactions proceed between GaN and Ti and also among the layers. The reaction at the GaN/Ti interface forms a thin layer of TiN adjacent to GaN. The layered structure disappears completely due to the interlayer reaction and subsequent growth of the reaction product grains.

Key Words: Gallium nitride, single- and multi-layered contacts, interfacial reaction and microstructure, transmission electron microscopy

1. Introduction

The development of blue light-emitting diodes with gallium nitride (GaN), a wide band-gap III-V compound semiconductor, has opened a break-through to solid-state illumination1). Recently, intensive research and development of GaN devices are being implemented worldwide, achieving considerably high light-source efficiency2) and long service life3) which are both essential for saving consumption of energy and resources. Therefore, to expand the application of GaN devices replacing conventional incandescent and fluorescent lamps will benefit human society facing on global environmental problems.

GaN devices have to be connected with metallic materials to form electric circuits. However, the wide band-gap of GaN being 3.39 eV (5.43×10 –19 J) forms high Schottky barrier at the interface between GaN and metal, which interferes the transportation of carriers across the interface. Especially in p-type GaN, the Fermi level being 7.50 eV (1.20×10–18 J) under the vacuum level indicates that no contacts of pure metals can avoid the formation of the barrier4). This phenomenon generates Joule heat at the interface and deteriorates the energy efficiency and the reliability of the system. A number of researchers are competing to develop low-resistance Ohmic contacts on GaN5-7). The reported contact properties are, however, usually difficult to reproduce by outsiders of the research groups even by tracing the reported procedures. This implies that the processes on the reports do not correspond only to the formation of preferred contact structure. Thus, a technology to control the interfacial structure between GaN and metals has to be established. However, neither the interfacial reaction behavior nor the metal-gallium-nitrogen ternary phase diagrams for some important systems are clarified8).

The present study has been implemented to clarify two typical contact microstructures for p-type and n-type GaN using transmission electron microscopy (TEM). The knowledge obtained from the results will be essential for controlling the interfacial microstructure.

2. Experimental procedure

GaN samples were 1.5-µm-thick epitaxially grown films on (1120) surface planes of sapphire substrates. The surface of GaN films was (0001) Ga-face. Every GaN samples were cleaned chemically by buffered hydrofluoric acid and then by hydrochloric acid prior to the deposition. In addition, some of the p-type GaN samples were surface-treated with induction-coupled plasma (ICP) etching followed by annealing at 1173 K for 1200 s in ammonia gas and then at 1123 K for 300 s in nitrogen. These sequential surface treatments were performed to remove the oxide surface layer on GaN and then to eliminate nitrogen vacancy defects formed in subsurface area of GaN by ICP etching. As mentioned in the introduction, lowering the Schottky barrier height at contact interface on p-type GaN is very difficult. Thus, thinning of the barrier by forming heavily-doped region is commonly applied as the second best method. It is known that gallium vacancies in GaN act as p-type dopant atoms which form acceptor level near the valence-band edge, while nitrogen vacancies form donor level near the conduction-band9). Therefore, the elimination of nitrogen vacancies would leave gallium vacancies under the surface of GaN. To investigate the effect of the surface treatment on the formation of the interfacial microstructures, p-type GaN samples both with and without the surface treatment were used.

On the p-type GaN samples, 300-nm-thick single layer of Ni was formed by electron-beam deposition. On the n-type GaN...
samples, layers of Ti, Al, Ni, and Au of which thicknesses were 20, 200, 40, and 50 nm, respectively, were deposited sequentially by multi-source electron-beam deposition. This combination of metals in four-layered precursor is commonly applied for Ohmic contact formation on n-type GaN\textsuperscript{10-12}. The deposited samples were then annealed at 873 K for 300 s in nitrogen atmosphere.

The interfacial microstructures of the contacts after annealing were analyzed by TEM. The TEM observation was carried out at an acceleration voltage of 200 kV. Focused ion beam micro-sampling technique was used for TEM sample preparation.

3. Results and discussion

3.1 Interfacial microstructure between p-type GaN and Ni after annealing

Figure 1 depicts the interfacial microstructure between surface-treated GaN and Ni after annealing at 873 K for 300 s in nitrogen. In the bright field image (BFI) shown in Fig. 1(a), GaN appears as bright tone area with bend contours in the bottom, while the contact film appears with medium-gray tone in the center. As indicated in the figure with arrows, voids are formed at the interface between GaN and the contact film. The interface between GaN and the voids are flat. The voids grow only by bulging to the contact film. The size and shape of the voids are not uniform: some appear with spheroidal shape, while the other as flat plates or pyramids with facets.

Figure 1(b) shows the selected-area electron diffraction (SAED) pattern corresponding to Fig. 1(a). The indices of the appearing diffraction spots are superimposed on the figure. The diffraction pattern consists of GaN \( [00\overline{1}\overline{0}] \), Ni \( [\overline{2}1\overline{2}] \), and Ni\textsubscript{5}Ga\textsubscript{3} \( [\overline{1}\overline{0}\overline{1}] \) zone axis net-patterns. This result indicates that GaN and Ni reacts to form Ni\textsubscript{5}Ga\textsubscript{3} at 873 K. Unfortunately, the distribution of the Ni\textsubscript{5}Ga\textsubscript{3} phase has not been analyzed due to the technical difficulties. Figure 1(b) reveals also the crystallographic relation among GaN, Ni, and Ni\textsubscript{5}Ga\textsubscript{3} as follows:

\[
\begin{align*}
0001_{\text{GaN}} & \parallel 1\overline{1}1_{\text{Ni}} \parallel 1\overline{1}0_{\text{Ni5Ga3}}, \\
\overline{1}2\overline{1}0_{\text{GaN}} & \parallel \overline{1}\overline{1}0_{\text{Ni}} \parallel 001_{\text{Ni5Ga3}}.
\end{align*}
\]

Since the surface of GaN is parallel to (0001), Ni and Ni\textsubscript{5}Ga\textsubscript{3} are formed facing their (111) and (110) planes, respectively, to the interface. On the other hand, GaN \( (\overline{1}\overline{2}10) \), Ni \( (\overline{1}\overline{1}0) \), and Ni\textsubscript{5}Ga\textsubscript{3} \( (001) \) are perpendicular to the interface. Their interplanar distances are 0.1595, 0.2492, and 0.3770 nm, respectively, indicating that a severe misfit exist at the interface.

The result shown in Fig. 1 has revealed that the reaction proceeding at the interface during annealing at 873 K can be described as follows:

\[
6 \text{GaN} + 10 \text{Ni} = 2 \text{Ni}_{5}\text{Ga}_3 + 3 \text{N}_2. \quad (2)
\]

The N\textsubscript{2} generated by the reaction has to dissolve into GaN, Ni, or Ni\textsubscript{5}Ga\textsubscript{3} or to form voids at the interface. The phase diagrams of Ga-N\textsuperscript{13}, Ni-N\textsuperscript{14}, and Ni-Ga-N\textsuperscript{8} indicate that GaN, Ni, and Ni\textsubscript{5}Ga\textsubscript{3} hardly dissolve nitrogen. Therefore, N\textsubscript{2} has no way but to form voids at the interface. The voids observed in Fig. 1(a) should be originally filled with N\textsubscript{2} gas generated by the reaction.

In the same way, the interfacial microstructure between GaN without the surface treatment and Ni after annealing at 873 K for 300 s in nitrogen has been analyzed as shown in Fig. 2. Almost the same interfacial microstructure as that between surface-treated GaN and Ni appears in the BFI shown in Fig. 2(a): voids are formed at the interface. The SAED pattern in Fig. 2(b) indicates that GaN, Ni, and Ni\textsubscript{5}Ga\textsubscript{3} exist in the vicinity of the interface. The crystallographic relations among the phases are...
also the same as that described in relation (1).

The results shown in Figs. 1 and 2 indicate that the surface treatment of GaN does not affect the interfacial reaction between GaN and Ni at 873 K.

3.2 Interfacial microstructure of GaN/Ti/Al/Ni/Au multilayered contact after annealing

Figure 3 shows the interfacial microstructure of a GaN/Ti/Al/ Ni/Au multilayered contact after annealing at 873 K for 300 s in N$_2$ atmosphere. In the BFI shown in Fig. 3(a), GaN appears as bright tone area with bend contours in the bottom, while the contact film appears as regions with various tones in the center. The aspect of the contact film indicates that the film has equiaxial polycrystalline microstructure. The average grain diameter is 60 nm, being considerably large for the 320-µm-thick contact film. The grains are distributed randomly in the film. No traces of original four layered film can be recognized. The microstructure of the contact film proves that the annealing has induced the reaction among the layers and the grain growth of the reaction products.

Figure 3(b) shows a high magnification BFI of the interface between GaN and the contact film. Between them, a uniform 4.1-nm-thick layer with dark tone is observed. This layer indicates that an interfacial reaction between GaN and the contact film has occurred during annealing. Contrastive to the interfaces

Fig. 2 Interfacial microstructure between GaN without the surface treatment and Ni after annealing at 873 K for 300 s in N$_2$ atmosphere. (a) BFI, (b) corresponding SAED pattern.

Fig. 3 Interfacial microstructure of a GaN/Ti/Al/Ni/Au multilayered contact after annealing at 873 K for 300 s in N$_2$ atmosphere. (a) BFI, (b) close-up BFI of the interface, (c) SAED pattern taken from the area shown in Fig. 3(a), (d) DFI of the same place shown in Fig. 3(b) using diffractions of $111_{TiN}$ and $0002_{GaN}$ shown in Fig. 3(c).
between GaN and Ni shown in Figs. 1 and 2, no voids are formed. Therefore, the reaction at this interface does not form N\textsubscript{2} gas.

The SAED pattern taken from the area corresponding to Fig. 3(a) is shown in Fig. 3(c). The diffraction pattern consists of GaN [1210], TiN [011], Al\textsubscript{2}Au [011] zone axis net-patterns. In SAED patterns taken from other areas, NiAl has also been identified. However, patterns of pure Ti, Al, Ni, or Au have not been detected. This result indicates that layers of pure Ti, Al, Ni, and Au have completely consumed by the interfacial and interlayer reactions to form TiN, Al\textsubscript{2}Au, or NiAl. Among these reaction products, Al\textsubscript{2}Au and NiAl are the products of interlayer reactions. On the other hand, TiN is the product of the interfacial reaction between GaN and the neighboring Ti layer. There is a crystallographic relation between GaN and TiN being

\begin{equation}
0001_{\text{GaN}} // 111_{\text{TiN}}.
\end{equation}

Therefore, the thin layered reaction product adjacent to GaN observed in Fig. 3(b) is considered to be TiN. To verify this analysis result, dark field observation of the interface using the diffractions of 111\textsubscript{TiN} and 000\textsubscript{2}\textsubscript{GaN} has been implemented. Figure 3(d) shows the dark field image (DFI) of the same position shown in Fig. 3(b). In Fig. 3(d), GaN and the thin layered reaction product appear with bright tone, confirming that the layer is TiN. In addition, the TiN layer is not a single crystal. While the major part of the TiN layer appear with bright tone in Fig. 3(d), the rest appear with dark tone, indicating that they are different grains with different crystal orientation. The average size of TiN grains in the direction parallel to the interface is 8.9 nm.

TiN has been identified as the product of the interfacial reaction described as

\begin{equation}
\text{GaN + Ti} = \text{TiN + Ga.}
\end{equation}

Although Ga is also produced by the reaction (4), Ga is not detected as the pure substance nor an intermetallic compound. Therefore, Ga has to be dissolved in GaN, TiN, Al\textsubscript{2}Au or NiAl. The phase diagrams of Ga-N\textsuperscript{39} and Ti-Ga-N\textsuperscript{39} indicate that GaN and TiN hardly dissolve Ga. Furthermore, no report has dealt with the solubility of Ga in Al\textsubscript{2}Au. On the other hand, NiAl can dissolve a large amount of Ga, substituting Al in NiAl by Ga\textsuperscript{39}. In this way, Ga produced by the reaction (4) is considered to be dissolved in NiAl.

4. Conclusions

Two typical contact microstructures, Ni single layer and Ti/Al/Ni/Au multilayer for p-type and n-type GaN, respectively, were analyzed using TEM. The following points were clarified.

1. GaN reacts with Ni during annealing at 873 K to form voids and Ni\textsubscript{5}Ga\textsubscript{3}. The voids are considered to be filled with N\textsubscript{2} gas generated by the interfacial reaction. The voids are formed adjacent to GaN bulging to the contact layer. The morphology and location of Ni\textsubscript{5}Si\textsubscript{3} are still unclear.

2. Surface treatments of GaN consisting of ICP etching and subsequent annealing under NH\textsubscript{3} and N\textsubscript{2} atmospheres scarcely affect the reaction behavior between GaN and Ni at 873 K.

3. TiN is formed as a thin layer adjacent to GaN by the interfacial reaction between GaN and Ti / Al / Ni / Au multilayer at 873 K. The TiN layer has polycrystalline structure which retains a crystal orientation between GaN being 000\textsubscript{1}\textsubscript{GaN} // 111\textsubscript{TiN}.

4. No voids are formed at the GaN / Ti / Al / Ni / Au interface. The strata of the as-deposited multilayer are lost by annealing at 873 K. Equiaxial coarse grains of Al\textsubscript{2}Au and NiAl are formed by the interlayer reaction and subsequent grain growth.

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References

4) S. N. Mohammad: Contact mechanisms and design principles for alloyed Ohmic contacts to p-type GaN, Philosophical Magazine, 84-24 (2004), 2559-2578.

7) S.-C. Lee, J.-C. Her, S.-M. Han, K.-S. Seo and M.-K. Han: Low-resistance Ti/Al/Ni/Au ohmic contact of GaN employing silicon diffusion by XeCl excimer laser irradiation, Electrochemical and Solid-State Letters, 8-6 (2005), G135-G136.


