

Ohmic Contact Mechanism of Titanium-based electrodes on n-type Gallium Nitride[†]

MAEDA Masakatsu*, YAMASAKI Takao** and TAKAHASHI Yasuo***

Abstract

Electrical properties at the interface between n-type gallium nitride (GaN) and Ti-based contact layers formed by radio-frequency magnetron sputter deposition under various conditions were investigated to clarify the mechanism to achieve ohmic contacts. TiN contacts deposited using N₂ gas are non-ohmic. Therefore, formation of TiN adjacent to GaN is not a necessary condition for achieving ohmic properties. On the other hand, Ti contacts deposited using Ar gas are ohmic in the as-deposited state, even though a layer of Ti₂N is formed between GaN and Ti during the deposition. It is also shown that Ti deposition on undoped GaN produces ohmic contacts. The nitrogen vacancies increased in the sub-interface of GaN are essential for ohmic properties. The interfacial reaction between Ti and GaN to form nitrogen vacancies is affected by the partial pressure of N₂ during the deposition.

KEY WORDS: (Ohmic contact), (n-type GaN), (Wide-bandgap compound semiconductor), (Interfacial reaction), (nitrogen vacancy), (TiN), (Schottky barrier)

1. Introduction

Gallium nitride (GaN) is a direct transition wide band-gap III-V compound semiconductor commonly used in light-emitting and laser diodes that exhibit high luminous efficacy and long service life^{1,2}. In addition, its high electron mobility, breakdown voltage and saturated electron drift velocity make GaN suitable for high-frequency operated power electronic devices^{3,4}. However, several problems have to be overcome to realize GaN-based power electronic devices. One of the major problems is to form low-resistance ohmic contacts at the interfaces between GaN and metallic outer circuits. The difference in electronic structure of the materials can form a Schottky barrier. The barrier interferes with charge transportation across the interface and generates Joule heat. By suppressing the heat generation, the reliability and the energy efficiency of the devices can be improved. Therefore, forming low-resistance ohmic contacts is important. To form low-resistance ohmic contacts on GaN, it is necessary to reduce the height and/or width of the Schottky barrier. An appropriate contact material has to be formed adjacent to GaN to lower the barrier. The work function of the contact metal has to be shallower than the conduction-band edge of n-type GaN, which is 4.11 eV below the vacuum level⁵. TiN is one of those materials with a sufficiently shallow

work function of 3.74 eV⁵. 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 nitrogen vacancies in GaN, which work as donors at an energy level close to the conduction band edge of GaN. Therefore, TiN is formed adjacent to GaN generally by interfacial reaction between GaN and multilayered metallic film containing Ti layer⁵⁻⁸. However, the factor dominating the ohmic properties is scarcely studied.

Luther et al. have investigated the evolution of Ti, TiN and Ti/TiN contact resistances by annealing in Ar or N₂⁹. They concluded that the presence of TiN adjacent to GaN is a necessary condition for ohmic contact formation and that the interfacial reaction assists in lowering the contact resistance. However, their results indicate that TiN contacts formed directly on n-type GaN fail to be ohmic in the as-deposited state. The contact became ohmic after annealing at 673 K for 60 s in Ar. On the other hand, the Ga-Ti-N ternary phase diagram indicates that TiN can equilibrate with GaN¹⁰, *i.e.*, no interfacial reaction takes place during annealing. Therefore, the appearance of ohmic properties by annealing cannot be correlated with the interfacial reaction between GaN and TiN. On the contrary, Lin et al. have argued that nitrogen

[†] Received on June 18, 2012

* Assistant Professor

** Graduate Student

*** Professor

Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

Ohmic Contact Mechanism of Titanium-based electrodes on n-type Gallium Nitride

vacancies produced in GaN under the Ti contact play the main role in development of ohmic conduction and that the ohmic behavior cannot be attributed to the presence of TiN, based on their XPS analysis of Ti/GaN interfaces¹¹⁾. However, they failed to form N–Ti bonds in the as-deposited state even though the GaN surfaces were free of oxide films. Thus, the factor dominating the development of ohmic conduction is still unclear.

The present study clarifies the dominating factor for ohmic properties of contact interfaces on n-type GaN. It is also demonstrated that ohmic contacts can be formed on n-type GaN without annealing by employing deposition conditions that enhance the mechanism dominating ohmic conduction.

2. Experimental procedure

Two types of GaN substrates were used in the present study. One was a monolithic single crystal wafer of n-type GaN of which the thickness and carrier density were 350 μm and $4.8 \times 10^{18} \text{ cm}^{-3}$, respectively. The other was a 6.5- μm -thick undoped GaN single crystal layer formed epitaxially on the (0001) plane of sapphire. The surface orientation of the undoped GaN was the (0001) Ga-face. Therefore, only the (0001) Ga-face was used also with the n-type GaN. The substrates were cut to 4.0 mm square and were degreased by acetone applying ultrasonic vibration.

The substrates were placed on a water-cooled copper holder of a radio-frequency (RF) magnetron sputter deposition apparatus. 1.0-mm-wide aluminum ribbons were used to fix the substrates on the holder. The ribbons also work as deposition masks. The deposition chamber was first evacuated to 4.0×10^{-5} Pa. High-purity Ar or N₂ gas was then introduced into the chamber up to 8.0 Pa. Immediately after careful sputter-cleaning of the surfaces of targets and substrates at the RF power of 200 W and the sputtering time of 600 and 300 s, respectively, deposition was implemented using Ti or TiN targets. The samples used in the present study are listed in Table 1. The preparation condition for Sample 1 was set to form TiN directly on GaN suppressing the interfacial reaction between GaN and the deposited film. Therefore, the donor density in GaN is hardly expected to increase under this deposition condition. On the contrary, the condition for Sample 2 was set to suppress the formation of TiN by the reaction between Ti and the atmosphere. Nitrogen atoms dissolved into and/or reacted with the Ti film will be supplied only from the GaN substrate. Thus, the donor density in GaN sub-interface is expected to increase by these interfacial interactions. The condition for Sample 3 was set to suppress the initial donor density in the GaN substrate. Since the condition, except for the substrate, is the same as that for Sample 2, the electrical properties of Sample 3 will reveal the interfacial interactions during the deposition.

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.

Table 1 Samples and their preparation conditions.

Sample No.	Substrate	Target	Atmosphere
1	n-type GaN	TiN	N ₂ , 8.0 Pa
2	n-type GaN	Ti	Ar, 8.0 Pa
3	undoped GaN	Ti	Ar, 8.0 Pa

Electrical properties were estimated by direct-current conduction test at 273 K.

3. Results and discussion

The deposited films of Sample 1 appear in gold color, implying that TiN is successfully formed in the films. To confirm the formation of TiN, the sample was analyzed by XRD. Fig. 1 shows the XRD pattern of Sample 1. In the pattern, only one peak corresponding to TiN 200¹²⁾ appears with strong peaks of GaN¹³⁾ and a weak peak of αTi ¹⁴⁾. Therefore, the contact film consists of TiN and αTi . Formation of αTi will occur due to the atomic detachment of Ti atoms from the TiN target by sputtering. The lack of all other peaks than 200 of TiN indicates that TiN in the film has been formed epitaxially on the GaN substrate. The existence of such a relation implies the formation of TiN adjacent to GaN.

The electrical conduction profile between two 1.0-mm-distant contact films on Sample 1 is shown in Fig. 2. The profile shows a non-linear current-voltage relation, *i.e.*, the contacts are non-ohmic. In particular, the current drops to a nearly negligible level at voltages below 0.5 V. The Schottky barrier height derived from the conduction profile is 0.46 eV^{15, 16)}. This barrier height agrees well with that of the TiN contact formed by annealing of Ti on n-type GaN reported by Lin et al.¹¹⁾. The result clearly shows that the contact cannot be ohmic only by forming TiN adjacent to GaN. The interfacial reaction between Ti and GaN to form nitrogen vacancies in GaN under the contact will be necessary for developing ohmic

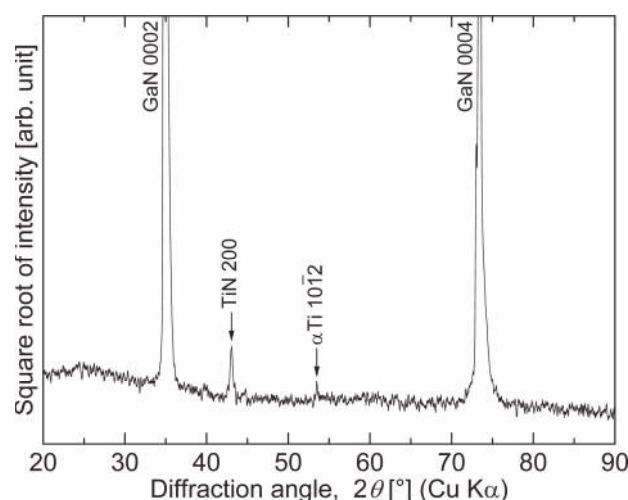


Fig. 1 XRD pattern of Sample 1 prepared using TiN target and N₂ gas. The deposition was performed at an RF power of 300 W for 1800 s, which resulted in a film thickness of 90 nm.

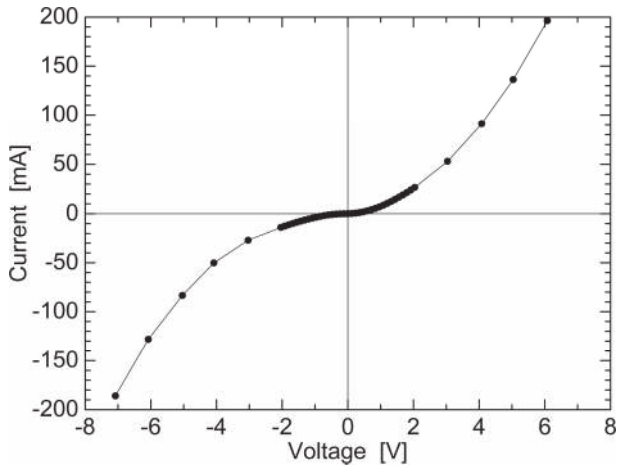


Fig. 2 Current-voltage profile taken from Sample 1, on which two 1-mm-distant TiN contacts are formed.

conduction at TiN / n-type GaN contact interface rather than the TiN formation itself.

Fig. 3 shows the cross-sectional structure of the contact interface formed on Sample 2. In the bright-field image shown in Fig. 3(a), a 12-nm-thick layer is observed adjacent to GaN. The electron diffraction pattern taken from this area shown in Fig. 3(b) consists of net patterns of GaN and Ti₂N. In the dark-field image of the same area using the Ti₂N 020 diffraction shown in Fig. 3(c), only the layer adjacent to GaN appears bright. Therefore, it is confirmed that a thin layer of Ti₂N is formed adjacent to GaN during the deposition of Sample 2. Since the nitrogen constituting Ti₂N originates only from the GaN substrate, a considerable amount of nitrogen vacancies must be formed in the GaN just under the contact.

Ti₂N is not suitable for ohmic contact formation with n-type GaN. The Fermi level of Ti₂N is approximately 2 eV deeper than that of TiN¹⁷⁾, i.e., Ti₂N forms a Schottky barrier 2 eV higher than TiN. As shown in Fig. 2, the contact fails to be ohmic due to the formation of a 0.46-eV-high Schottky barrier. Therefore, a significant interference to electrical conduction by the barrier will be expected. However, the electrical conduction profile of

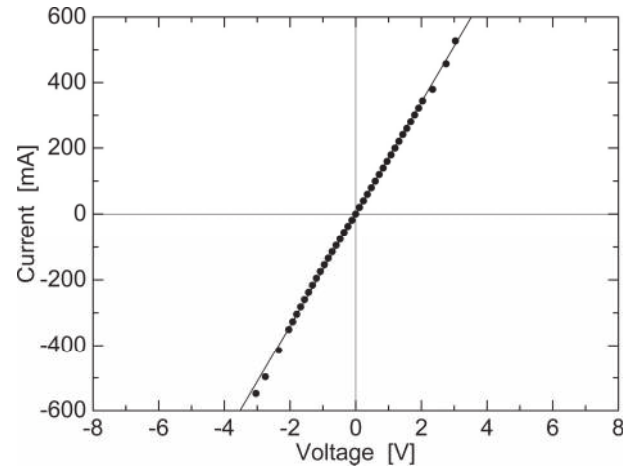


Fig. 4 Current-voltage profile taken from Sample 2.

Sample 2 shown in Fig. 4 indicates that the contacts are ohmic even though a layer of Ti₂N is formed. Ohmic conduction in the presence of a high Schottky barrier can occur by tunneling mechanism. Since tunneling requires thinning of the barrier by introducing a high carrier density in the GaN sub-interface, the achievement of ohmic conduction with Sample 2 indicates that the interfacial reaction to form Ti₂N has introduced a sufficient amount of nitrogen vacancies in GaN just under the contact.

To confirm the formation of a high carrier density zone in GaN by the interfacial reaction during the deposition, Sample 3 was prepared with undoped GaN under the same deposition condition as Sample 2. The initial carrier density in undoped GaN must be very low at 273 K, since it is a wide-bandgap intrinsic semiconductor in which only a small amount of thermally activated carriers exist. Therefore, the increase in carriers is all attributed to the increase in nitrogen vacancies due to the interfacial reaction. The electrical conduction profile of Sample 3 is shown in Fig. 5. Although the electrical conductivity of Sample 3 appears approximately one-eighteenth that of Sample 2, the contacts are ohmic. This result indicates that a high

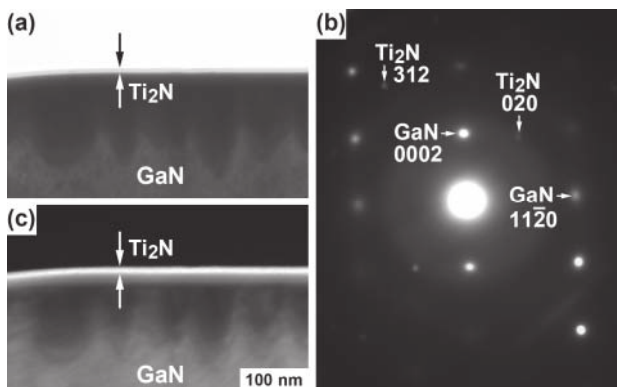


Fig. 3 Interfacial structure of the contact formed on Sample 2. (a) bright field image; (b) electron diffraction pattern corresponding to the area shown in (a); (c) dark field image of the same area as (a) using Ti₂N 020.

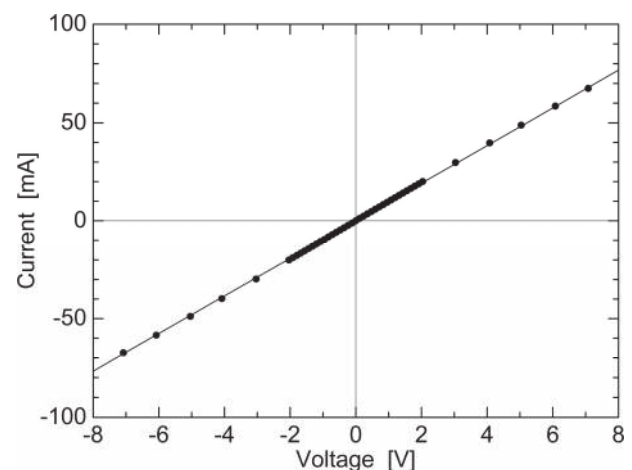


Fig. 5 Current-voltage profile taken from Sample 3.

Ohmic Contact Mechanism of Titanium-based electrodes on n-type Gallium Nitride

carrier density sufficient for ohmic conduction has been achieved in the GaN sub-interface. The interfacial reaction during the deposition has introduced such a high density of nitrogen vacancies. The low electrical conductivity of Sample 3 will be attributed to the high specific resistance in the undoped GaN substrate.

Interfacial reaction between the deposited film and GaN plays an essential role in the formation of ohmic contacts on n-type GaN. The reaction has to be controlled to achieve the optimum performance of the contacts. Luther et al.⁹⁾ and Lin et al.¹¹⁾ reported that Ti contacts require annealing to be ohmic. In the present study, however, Samples 2 and 3 successfully achieve ohmic conduction in the as-deposited state. The difference in sample preparation between the previous reports and the present study is the surface treatment before deposition. The previous studies used chemical etching. Although the native oxides on the surfaces of GaN can be removed by aqua regia, exposure to air after the treatment reforms the oxides. The oxides will prevent the reaction until the sample is annealed. Thus, the role of annealing in development of ohmic conduction is not only to initiate the interfacial reaction, but also to remove these layers. On the other hand, the samples prepared in the present study were cleaned by substrate sputtering and the deposition was conducted immediately without exposing the cleaned surfaces to air. The present study has shown that the surface of GaN becomes reactive by sputter-cleaning enough to form Ti₂N during the deposition of Ti, as shown in Figure 3. The sputter-cleaning removes oxide films on the surfaces of GaN and introduces defects in the GaN subsurface. The former point enhances the interfacial reaction to generate nitrogen vacancies in GaN, since the surface of GaN free of oxide films can react directly with the deposited Ti. With regard to the latter point, the amount of defects formed by sputter-cleaning at the RF power of 200 W for 300 s is considered to be negligible since Sample 1 which was also sputter-cleaned under the same condition fails to be ohmic even though TiN is better than Ti₂N as an ohmic contact material for n-type GaN. Therefore, ohmic contacts can be formed on n-type GaN without annealing by preparing a clean and reactive surface of GaN, which enhances the interfacial reaction during the deposition of Ti and generates nitrogen vacancies in GaN.

4. Conclusions

Ti-based contact films are formed on GaN under various conditions to investigate the dominant factor to develop ohmic conduction. The following points are revealed.

- 1) TiN formed directly on n-type GaN shows non-ohmic conduction indicating that the formation of TiN is not essential for development of an ohmic contact.
- 2) Ti deposited on n-type GaN shows ohmic conduction, even though Ti₂N is formed at the interface during the deposition process by the reaction between Ti and GaN. Nitrogen vacancies are formed and the carrier (donor) density is increased by the reaction.
- 3) Ti deposited on undoped GaN shows ohmic conduction, indicating that a significant increase in carrier density is achieved due to the interfacial reaction. This result supports the idea that the ohmic contact is developed by the formation of nitrogen vacancies.
- 4) Ohmic contacts for n-type GaN can be formed without annealing by preparing a clean and reactive surface of GaN, which enhances the interfacial reaction and generates nitrogen vacancies in GaN.

References

- 1) S. Nakamura, T. Mukai and M. Senoh: *Jpn. J Appl. Phys.* 30 (1991) L1998-L2001.
- 2) I. Akasaki: *J. Cryst. Growth* 300 (2007) 2-10.
- 3) M. Asif Khan, Q. Chen, M. S. Shur, B. T. Dermott, J. A. Higgins, J. Burm, W. J. Schaff and L. F. Eastman: *Solid-Stat. Electron.* 41 (1997) 1555-1559.
- 4) R. J. Trew, M. W. Shin and V. Gatto: *Solid-Stat. Electron.* 41 (1997) 1561-1567.
- 5) S. N. Mohammad: *J. Appl. Phys.* 95 (2004) 7940-7953.
- 6) Z. Fan, S. N. Mohammad, W. Kim, Ö. Aktas, A. E. Botchkarev and H. Morkoç: *Appl. Phys. Lett.* 68 (1996) 1672-1674.
- 7) L. L. Smith, R. F. Davis, R.-J. Liu, M. J. Kim and R. W. Carpenter: *J. Mater. Res.* 14 (1999) 1032-1038.
- 8) M. Maeda, N. Matsumoto, H. Hatakawa and Y. Takahashi: *Quart. J. Jpn. Weld. Soc.* 27 (2009) 204s-208s.
- 9) B. P. Luther, S. E. Mohny and T. N. Jackson: *Semicond. Sci. Technol.* 13 (1998) 1322-1327.
- 10) S. E. Mohny, B. P. Luther and T. N. Jackson: *Mater. Res. Soc. Symp. Proc.* 395 (1996) 843-848.
- 11) Y.-J. Lin, Y.-M. Chen, T.-J. Cheng and Q. Ker: *J. Appl. Phys.* 95 (2004) 571-575.
- 12) Powder Diffraction Files, ICDD, 38-1420.
- 13) Powder Diffraction Files, ICDD, 50-0792.
- 14) Powder Diffraction Files, ICDD, 44-1294.
- 15) Y. Koyama, T. Hashizume and H. Hasegawa: *Solid-Stat. Electron.* 43 (1999) 1483-1488.
- 16) J.-S. Jang, S.-J. Park and T.-Y. Seong: *Phys. Stat. Sol. A* 194 (2002) 576-582.
- 17) R. Eibler: *J. Phys.: Condens. Matter* 5 (1993) 5261-5276.