Effect of interfacial reaction on electrical conduction across the interface between n-type gallium nitride and contact materials

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Abstract. The present paper reports electrical properties at the interface between n-type GaN and Ti-based contact layers formed by radio-frequency magnetron sputter deposition under various conditions. TiN contacts deposited using N\(_2\) gas are non-ohmic, i.e., formation of TiN adjacent to GaN is not a necessary condition for developing ohmic properties. On the other hand, Ti contacts deposited using Ar gas are ohmic in the as-deposited state, even though a layer of Ti\(_2\)N 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 developing ohmic properties. The interfacial reaction between Ti and GaN to form nitrogen vacancies is affected by the partial pressure of N\(_2\) during the deposition.

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]. Power electronic devices are widely installed in electrical and electronic facilities to manage power flow and to improve energy efficiency. Owing to these functions of the devices, the facilities achieve reduced energy consumption without deteriorating their performance. Recently, the devices are considered as one of the key for establishing dispersed renewable power systems [5] and, as a further goal, a sustainable society. The emerging applications demand high power capability, high energy efficiency and long service life. Furthermore, all power electronic devices have to exhibit extremely high reliability, since only one failure can halt the entire system. Replacing conventional Si-based power electronic devices with GaN-based ones will improve the functions of power electronic systems, i.e., the demands can be satisfied by putting GaN-based power electronic devices into practical use. 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, similar to a resistor or a capacitor, and it generates Joule heat. The heat generation rate becomes high under high power and...
frequency operation, which corresponds to the field to which GaN-based power electronic devices are going to be applied. Repetitive thermal expansion and shrinkage induced by the heat deteriorate the reliability of the interface. 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 width of the Schottky barrier. An appropriate contact material has to be formed adjacent to GaN to lower the barrier. One of the requirements for the appropriate contact material is its work function. In the case of n-type GaN, it has to be shallower than the conduction-band edge of GaN, which is 4.11 eV below the vacuum level. TiN is one of those materials with a sufficiently shallow work function of 3.74 eV [6, 7]. 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 layer [7-10]. However, this method has a problem. Interlayer reactions during heat treatment form several intermetallic compounds in the film [10]. The compounds have high electric resistances and brittle nature. Thus, it is preferred to form TiN retaining the rest of the contact film metallic. However, it is difficult due to the high miscibility and diffusivity of nitrogen in Ti [11-13]. Recently, Maeda et al. have developed a method to form Ti(C, N), an alternative contact material to TiN, by which ohmic conduction properties were obtained preventing the formation of intermetallic compounds [13]. The results raise a new question regarding which factor dominates the ohmic conduction properties: the formation of TiN adjacent to GaN or the increase in donor density by the interfacial reaction.

Luther et al. have investigated the evolution of Ti, TiN and Ti/TiN contact resistances by annealing in Ar or N2 [6]. 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 GaN [14], 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 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 interfaces [15]. 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 has been implemented to clarify the dominating factor for ohmic conduction of contact interfaces on n-type GaN: whether it is the formation of TiN itself or the increased nitrogen vacancy in the GaN sub-interface. Various deposition conditions were employed to form TiN or Ti contact films on GaN. Electrical conduction profiles and interfacial structures were analyzed to investigate the effects of interfacial reactions between GaN and the films during the deposition on the electrical conduction properties. 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 4.8×10^{18} 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 set on a water-cooled copper holder to suppress the temperature increase and the reactions between the contact film and the substrate during the deposition. 1.0-mm-wide aluminum ribbons were employed to set the substrates on the holder of a radio-frequency (RF) magnetron sputter deposition apparatus. The ribbons also work as deposition masks. The distance between the target and the substrates was 50 mm. The deposition chamber was first evacuated to \(4.0 \times 10^{-5}\) Pa. High-purity Ar or \(\text{N}_2\) 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 thickness of the deposited films was varied in the range of 30–90 nm to fit the analysis to be conducted with the samples by controlling the RF power and the deposition time. The preparation condition for Sample 1 was employed to form TiN directly on GaN suppressing the interfacial reaction between GaN and the contact 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 employed 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 employed 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 conditions for Samples 4 and 5 were employed to compare the effect of the target material and the atmosphere on the development of ohmic conduction.

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

### Table 1. Samples and their preparation conditions.

| Sample No. | Substrate     | Target | Atmosphere |
|------------|---------------|--------|------------|
| 1          | n-type GaN    | TiN    | \(\text{N}_2\), 8.0 Pa |
| 2          | n-type GaN    | Ti     | Ar, 8.0 Pa |
| 3          | undoped GaN   | Ti     | Ar, 8.0 Pa |
| 4          | n-type GaN    | Ti     | \(\text{N}_2\), 8.0 Pa |
| 5          | n-type GaN    | TiN    | Ar, 8.0 Pa |

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 set on a water-cooled copper holder to suppress the temperature increase and the reactions between the contact film and the substrate during the deposition. 1.0-mm-wide aluminum ribbons were employed to set the substrates on the holder of a radio-frequency (RF) magnetron sputter deposition apparatus. The ribbons also work as deposition masks. The distance between the target and the substrates was 50 mm. The deposition chamber was first evacuated to \(4.0 \times 10^{-5}\) Pa. High-purity Ar or \(\text{N}_2\) 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 thickness of the deposited films was varied in the range of 30–90 nm to fit the analysis to be conducted with the samples by controlling the RF power and the deposition time. The preparation condition for Sample 1 was employed to form TiN directly on GaN suppressing the interfacial reaction between GaN and the contact 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 employed 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 employed 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 conditions for Samples 4 and 5 were employed to compare the effect of the target material and the atmosphere on the development of ohmic conduction.

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. 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. Figure 1 shows the XRD pattern of Sample 1. In the pattern, only one peak corresponding to TiN 200 [16] appears with strong peaks of GaN [17] and a weak peak of \(\alpha\text{Ti}\) [18]. Therefore, the contact film consists of TiN and \(\alpha\text{Ti}\). Formation of \(\alpha\text{Ti}\) will occur due to the atomic detachment of Ti atoms from TiN target by sputtering. Missing of all other peaks than 200 of TiN indicates that TiN in the film has been formed retaining a crystallographic relation with the GaN substrate being

\[
100_{\text{TiN}} // 0001_{\text{GaN}}.
\]

Although the relation is different from that observed in previous reports [10, 13], the existence of such a relation implies the formation of TiN adjacent to GaN.
The electric conduction profile between two 1.0-mm-distant contact films on Sample 1 is shown in Figure 2. The profile shows a non-linear current-voltage relation. Especially, the current drops to a nearly negligible level at voltages below 0.5 V, i.e., the contacts are non-ohmic. The Schottky barrier height derived from the conduction profile is 0.46 eV [19, 20]. 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. [15]. The result clearly shows that an ohmic contact cannot be developed only by forming TiN adjacent to GaN. Therefore, the interfacial reaction between Ti and GaN to form nitrogen vacancies in GaN under the contact will be rather necessary for developing ohmic conduction at TiN / n-type GaN contact interface than the TiN formation itself.

Sample 2 was prepared to enhance the formation of nitrogen vacancies in GaN by suppressing the interaction between Ti and the atmosphere. Figure 3 shows the cross-sectional structure of the contact interface formed on Sample 2. In the bright-field image (BFI) shown in Figure 3(a), a 12-nm-thick layer is observed adjacent to GaN. The electron diffraction pattern (EDP) taken from this area shown in Figure 3(b) consists of net patterns of GaN and Ti₂N. In the dark-field image (DFI) of the same area using the Ti₂N 020 diffraction shown in Figure 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 Ti$_2$N originates only from the GaN substrate, a considerable amount of nitrogen vacancies must be formed in the GaN just under the contact. Ti$_2$N is not suitable for ohmic contact formation with n-type GaN. The Fermi level of Ti$_2$N is approximately 2 eV deeper than that of TiN [21], i.e., Ti$_2$N forms a Schottky barrier 2 eV higher than TiN. As shown in Figure 2, the contact fails to be ohmic due to the formation of 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 Sample 2 depicted in Figure 4 clearly shows a proportional relation between the current and voltage, i.e., the contacts are ohmic even though a layer of Ti$_2$N 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 Ti$_2$N has introduced a sufficient amount of nitrogen vacancies in GaN just under the contact.

**Figure 3.** Interfacial structure of the contact formed on Sample 2. (a) BFI; (b) EDP corresponding to the area shown in (a); (c) DFI of the same area as (a) using Ti$_2$N 020.

**Figure 4.** Current-voltage profile taken from Sample 2. Ohmic conduction is obtained even though Ti$_2$N is formed adjacent to n-type GaN.
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 Figure 5. Although the electrical conductivity of Sample 3 appears approximately one-eighth that of Sample 2, the relation between the current and voltage is proportional, i.e., the contacts are ohmic. This result indicates that a high carrier density sufficient for developing ohmic conduction has been achieved in the GaN sub-interface. The interfacial reaction during the deposition has introduced a high density of nitrogen vacancies.

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. [6] and Lin et al. [15] 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, i.e., the surfaces are exposed to ambient air after drying. The native oxides on the surfaces of GaN can be removed by aqua regia [15]. However, exposure to air after the treatment reforms the oxides; otherwise the surfaces of GaN are covered by radicals which terminate the surface dangling bonds of GaN and protect from oxidation. These surface layers will prevent the reaction until the sample is annealed, i.e., 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. Therefore, the present study has shown that the surface of GaN free of the surface layers reacts with Ti even during the deposition.

In the present study, the effects of the target and the atmosphere selection on the interfacial reaction are investigated using the reactive surface of GaN. Figure 6 shows the electrical conduction profiles of Samples 4 and 5. A distinct difference in electrical conduction properties is observed: the contacts on Sample 4 are non-ohmic, whereas those on Sample 5 are ohmic. The difference between the samples is the partial pressure of N2. The partial pressure of N2 is kept at 0.8 Pa for Sample 4. Ti atoms sputtered out of the target fly through the gas. The distance between the target and the substrate was 50 mm, which is approximately one order of magnitude longer than the mean free path of the atoms. Therefore, Ti atoms collide several times with N2 molecules and react to form TiN during their flight to the
substrate, i.e., most of the Ti atoms have become TiN when they reach the substrate. TiN will not react with GaN. Nitrogen vacancies are not formed in the GaN sub-interface and the contacts are non-ohmic. On the other hand, the pressure for Sample 5 is considered to be very low. Although Ti atoms and N₂ gas are emitted by sputtering of the TiN target, the number of N₂ molecules will be insufficient to increase its partial pressure. Thus, Ti atoms seldom react with N₂ gas, i.e., Ti atoms will reach the substrate as Ti. Ti deposited on GaN reacts immediately with GaN and forms nitrogen vacancies in the GaN sub-interface to attain ohmic conduction. The results shown in Figure 6 indicate that whether the target is Ti or TiN has little effect on the development of ohmic contacts, whereas the partial pressure of N₂ in the sputtering gas has a critical effect on it.

Samples 2, 3 and 5 have ohmic contacts in their as-deposited state, i.e., without annealing. Generally, formation of ohmic contacts requires high-temperature annealing after deposition of metallic layers. However, such a high-temperature process can deteriorate the performance of the devices and other contacts formed before the ohmic contact. Consequently, to form ohmic contacts without annealing is preferred. The key point of the contact formation process employed in the present study will be the deposition of Ti on GaN immediately after the sputter-cleaning of the surfaces of the substrates. 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-cleaning 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 to 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 clarified.
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) The partial pressure of N$_2$ during RF magnetron sputter deposition affects the conduction properties of the contact interface. A low partial pressure of N$_2$ is needed to form low resistance ohmic contacts.

5) 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.

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References
[1] Nakamura S, Mukai T and Senoh M 1991 Jpn. J Appl. Phys. 30 L1998
[2] Akasaki I 2007 J. Cryst. Growth 300 2
[3] Trew R J, Shin M W and Gatto V 1997 Solid-Stat. Electron. 41 1561
[4] Zhang A P, Ren F, Anderson T J, Abernathy C R, Singh R K, Holloway P H, Pearton S J, Palmer D and McGuire G E 2011 Critic. Rev. Solid Stat. Mater. Sci. 27 1
[5] Blaabjerg F, Chen Z and Kjaer S B 2004 IEEE Trans. Power Electron. 19 1184
[6] Luther B P, Mohney S E and Jackson T N 1998 Semicond. Sci. Technol. 13 1322
[7] Mohammad S N 2004 J. Appl. Phys. 95 7940
[8] Fan Z, Mohammad S N, Kim W, Aktas Ö, Botchkarev A E and Morkoç H 1996 Appl. Phys. Lett. 68 1672
[9] Smith L L, Davis R F, Liu R-J, Kim M J and Carpenter R W 1999 J. Mater. Res. 14 1032
[10] Maeda M, Matsumoto N, Hatakawa H and Takahashi Y 2009 Quart. J. Jpn. Weld. Soc. 27 204s
[11] 1996 Binary Alloy Phase Diagrams 2nd edition plus updates on CD-ROM ed Massalski T B, Okamoto H, Subramanian P R and Kacprzak L (Materials Park, OH: ASM International)
[12] Metin E and Inal O T 1989 Metall. Trans. A 20A 1819
[13] Maeda M, Matsumoto N and Takahashi Y 2010 Materials Science and Technology (MS&T’10) Conf. Proc. CD-ROM (Houston, TX, 17-21 October 2010) (Warrendale, PA: The Minerals, Metals & Materials Society) pp 2732–2742
[14] Mohney S E, Luther B P and Jackson T N 1996 Mater. Res. Soc. Symp. Proc. 395 843
[15] Lin Y-J, Chen Y-M, Cheng T-J and Ker Q 2004 J. Appl. Phys. 95 571
[16] Powder Diffraction Files (Newtown Square, PA: ICDD) 38-1420
[17] Powder Diffraction Files (Newtown Square, PA: ICDD) 50-0792
[18] Powder Diffraction Files (Newtown Square, PA: ICDD) 44-1294
[19] Koyama Y, Hashizume T and Hasegawa H 1999 Solid-Stat. Electron. 43 1483
[20] Jang J-S, Park S-J and Seong T-Y 2002 Phys. Stat. Sol. A 194 576
[21] Eibler R 1993 J. Phys.: Condens. Matter 5 5261