1. Introduction

Wide band-gap compound semiconductors, such as silicon carbide (SiC) and gallium nitride (GaN), are expected to improve the energy efficiency of power electronic devices. Many researchers are actively studying to develop the devices. One of the issues preventing the development is the formation of low-resistance metallic electrode on the semiconductors.

Each material has its characteristic Fermi level, which is determined by the composition and chemical bond states of the constituent atoms. If two different materials come into contact to each other, some of the constituent electrons move from the material with higher Fermi level to the other. In the case of the contact of semiconductors to metals, the transfer of electrons forms a Schottky barrier at the interface. The barrier hinders the current of charge carriers across the interface, i.e., it is a kind of resistance. Thus, electric conduction through the interface generates Joule heat. The heat corresponds to the energy loss at the interface and lowers the energy efficiency of the devices. Even worse, the local heating at the interface deteriorates the bond strength of the interface and shortens the service life of the devices. Consequently, the reduction of the contact resistance is inevitable issue for the development of the next-generation high-efficiency power electronic devices.

The contact resistance can be reduced by lowering the Schottky barrier height and by thinning the Schottky barrier width. The barrier height can be suppressed by forming a contact electrode made of an appropriate material. In most cases, precursor films are deposited one after another on the semiconductor substrate and then annealed. The heat treatment in-
duces the interlayer reaction which forms aligned interface between the contact phase and the semiconductor substrate. On the other hand, the barrier thickness can be decreased by increasing the local carrier density of the semiconductor in the vicinity of the electrode by heavy-doping of donor or acceptor elements.

For n-type SiC, NiSi is known as an excellent material for lowering the Schottky barrier\(^9\). It is commonly formed by deposition of Ni on SiC and subsequent annealing at temperatures higher than 1173 K\(^3,9,10\). The interfacial reaction during the heat treatment forms NiSi adjacent to SiC. However, NiSi is not the only one phase produced by the reaction. The most fatal product of the reaction is the free carbon, consisting of graphite and/or amorphous carbon. The free carbon deteriorates the mechanical properties of the electrode. To suppress the formation of the free carbon, an element X of which affinity with carbon is high should be added in the deposited layer to absorb carbon atoms by forming X-carbide instead of the free carbon. A candidate of such element X is Ti, since it is a strong carbide former\(^11\). Furthermore, TiC has a low work function\(^12\), which is favorable for lowering the Schottky barrier on n-type SiC. Although several papers report Ni-Ti electrode on SiC, the mechanical properties are scarcely discussed\(^13\). The present study reports the mechanical properties of Ni-Ti contacts on n-type 4H-SiC in relation with electrical properties. TiC contact on SiC is also examined.

Difficulty in the formation of low-resistance electrode on p-type GaN arises from the following two points. One is that no conductive material can lower the Schottky barrier to a sufficient level, since the Fermi level of p-type GaN is very deep (7.49 eV under the vacuum level)\(^8\). The other point is that only Mg can be used as the acceptor dopant for GaN. Mg can be doped up to \(2 \times 10^{25} \text{ m}^{-3}\) in GaN, and further doping deteriorates the crystal stability of GaN. Generally, the doping concentration is sufficient for thinning the Schottky barrier. However, the most of doped Mg is inactivated by hydrogen atoms inevitably entrapped during the MO-CVD crystal growth process of GaN. Most of the research papers, however, report the results of material seeking and their formation process\(^6\) \(i.e.,\) the approach from the former point of the difficulty. On the other hand, almost no approach is made from the latter point. In the present study, a method to evacuate hydrogen by applying voltage during annealing is demonstrated. Since the inactivation of Mg acceptors occurs by electron transfer from hydrogen to Mg, hydrogen is ionized to plus. Therefore, hydrogen can be evacuated by applying voltage between the electrodes on GaN. Furthermore, the evacuation will be enhanced by increased mobility of atoms at high temperatures. In this way, the electrode annealing process is combined with voltage application.

2. Improvement of mechanical properties of NiSi electrode formed on n-type SiC

2.1 Strategy for control of interfacial reaction among SiC, Ni, and Ti

The interfacial reaction between SiC and Ni is considered based on the Ni-Si-C ternary phase diagram. Fig. 1 shows the isotherm at 1173 K\(^14\). SiC and Ni cannot coexist in equilibrium. Therefore, the interfacial reaction proceeds during annealing to establish local equilibrium. Since Ni does not form any stable carbides nor dissolves carbon, the interfacial reaction produces Ni-Si compounds and the free carbon. Therefore, the formation of the free carbon is inevitable when only Ni reacts with SiC. Addition of Ti overcomes this problem. Formation of TiC proceeds spontaneously, since the formation reduces the chemical potential of carbon in the system significantly. However, it has to be reminded that Ti can react also with Si.

Naka et al. reported that the reaction between SiC and pure Ti forms \(\text{Ti}_5\text{Si}_3\text{C}_x\) and \(\text{Ti}_2\text{SiC}_2\) at the interface\(^15\). To avoid the formation of these products, the chemical potential of Ti at the reaction interface has to be lowered to a sufficient level. The chemical potential can be reduced by forming compound phases and/or by diluting Ti at the reaction interface. Thermo-dynamic calculations suggests that the formation of NiTi and Ni$_3$Ti intermetallic compounds lowers down the chemical potential of Ti to an appropriate level\(^16\). On the other hand, it is effective to dilute Ti by placing a Ti-source at a portion distant

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![Fig. 1 Isothermal section of Ni-Si-C ternary phase diagram](image-url)

The broken line indicates the phase sequence reported by Gülpen et al.\(^7\).
from the reaction interface, suppressing the diffusion flux of Ti through the phase adjacent to SiC. The Ni layer should be thick for this purpose, since the thickness of the Ni layer determines the chemical potential gradient and diffusion flux of Ti. Consequently, the Ti layer is formed on the Ni layer in the present study in order to make Ti form Ni-Ti intermetallic compounds and to supply Ti to the interface by diffusion of Ti through the intermetallic compound. The thickness was set to 100 nm.

The phase diagram shown in Fig. 1 presents another concern. Gülpen et al. reported that the interfacial phase sequence of a SiC/ Ni diffusion pair becomes SiC/ (Ni$_2$Si + C)/ (Ni$_3$Si$_2$ + C)/ Ni$_3$Si/ Ni$^{17}$). The sequence corresponds to the diffusion path indicated on Fig. 1 with a broken line. The diffusion path implies that NiSi cannot be formed while Ni exists as the end-member of the diffusion pair. Two methods to overcome this problem are considered. One is to change the annealing temperature at which SiC, NiSi and C coexist in equilibrium. However, the three-phase equilibrium cannot be achieved at temperatures below the eutectic of Ni and Ni$_3$Si at 1416 K. The other method to form NiSi adjacent to SiC is to make Ni$_2$Si react with SiC by reducing the chemical potential of carbon. Addition of Ti in the film reduces the chemical potential by forming TiC. Fig. 2 shows the original and modified diffusion path on the Ni-Si-C ternary chemical potential diagram at 1173 K$^{19}$. It is clearly understood that the diffusion path reported in the literature goes through a high chemical potential of carbon. Due to this, NiSi is kept away from formation. By preventing the formation of the free carbon, the diffusion pair is allowed to take a direct path with monotonous chemical potential gradients of all constituent elements. In addition, the formation of Ni-Ti intermetallic compound reduces the chemical potential of Ni at one of the end-member, which magnifies the driving force to establish a diffusion path through a low chemical potential of C.

Therefore, the key point of the electrode formation process proposed in the present study is to control the interfacial reaction behavior of Ti, i.e., to facilitate the TiC formation preventing the formation of other Ti-Si-C byproducts.

2.2 Experimental procedure

SiC substrates used in the present study were nitrogen-doped n-type 4H-SiC substrates cut to a size of 5.0 mm square from a 360-μm-thick wafer 50.8 mm in diameter of which surface correspond to (0001) crystallographic plane. Only the (0001) Si-face of the SiC substrates was used. Ni and Ti were deposited consecutively on the substrates by radio-frequency magnetron sputtering. The thickness of the Ni layer was kept constant at 100 nm, whereas that of the Ti layer was varied from 0 to 640 nm. The samples were then heated up to 1273 K in vacuum of 3×10$^{-3}$ Pa and immediately cooled down after reaching the temperature (hereinafter described as the annealing time of 0 s). For comparison, TiC electrode was formed on some SiC substrates by deposition of C/Ti bilayer and subsequent annealing at 1273 K for 0 s in vacuum. Since this process can form TiC on the substrate without an interfacial reaction between the deposited film and the substrate, Ti-Si-C byproducts will not be formed at the interface.

The interfacial structures were analyzed by X-ray diffraction (XRD). The electrical properties were measured by direct-current conduction test. The mechanical properties were evaluated by constant-load scratch test. A Rockwell-C indenter was plunged into the electrode with a force of 5.0 N and swept along the surface of the electrode. The depth of the trench formed by the scratch was measured by atomic force microscopy at a position 1.0 mm distant from the start point of the scratch test. The reciprocal value of the trench depth was used as the strength index of the contact layer.

2.3 Results and discussion

Fig. 3 shows the XRD patterns of the samples with various thickness of Ti layer after annealing. The initial thicknesses of the Ti layer for the patterns (a), (b), (c) and (d) are 0, 16, 80 and 640 nm, respectively. The pattern (a) consists of the peaks of SiC and Ni$_3$Si. The peaks of NiSi and the free carbon do
not appear in the pattern. Failure of detection of the NiSi layer indicates that the layer is very thin, which agrees with the previous reports\(^9\). On the other hand, the free carbon will not appear if it is amorphous. Also the pattern (b) consists of the peaks of SiC and Ni\(_2\)Si, being similar to the pattern (a). The initial thicknesses of the Ni and Ti layers of this sample are 100 and 16 nm, respectively, which corresponds approximately to the composition of Ni-10 mol\%Ti. Therefore, the peaks of NiSi, TiC and Ni\(_3\)Ti are expected to appear in addition to those present in the pattern. It is likely that the Ti layer is consumed by the interlayer reaction before the Ni adjacent to SiC changes to Ni\(_3\)Ti. SiC starts to react with this unchanged Ni. In this way, the XRD pattern of the sample becomes almost the same with the pattern (a).

In the pattern (c) of Fig. 3, a peak of TiC appears at the diffraction angle of 41.8°, indicating that a considerable amount of TiC is successfully formed at the interface and thus the formation of the free carbon is suppressed. Even in this pattern, however, the peaks of Ni-Ti intermetallic compounds are not found. It is hardly expected that the film of which total thickness is 180 nm is completely consumed by the reaction with SiC. A further analysis is needed to clarify the interfacial phenomena during annealing and the resultant structure.

The interfacial reaction fails to form Ni-Si compounds and TiC when the Ti layer is very thick. In the pattern (d) of Fig. 3, Ti\(_3\)Si\(_3\) and Ti\(_5\)SiC\(_2\) are detected instead of TiC. Furthermore, the film after annealing is easily peeled off the substrate even under a careful handling. Therefore, the electrical and mechanical properties of this sample could not be measured.

The results shown in Fig. 3 suggest that there is an optimum thickness of the Ti layer to facilitate the TiC formation. Among the samples shown in Fig. 3, the sample with a 100-nm-thick Ni layer and a 80-nm-thick Ti layer seems to be the closest to the optimum condition. The composition of the film corresponds approximately to Ni-33 mol\%Ti. The Ni-Ti binary phase diagram suggests that Ni\(_3\)Ti and NiTi are stable at the composition\(^8\), i.e., the results agree with the thermodynamic consideration described in the former section.

Fig. 4 shows the electrical current–voltage profiles of the SiC/Ni, SiC/Ni/Ti (16 nm), SiC/Ni/Ti (80 nm), and SiC/C/Ti samples after annealing at 1273 K for 0 s. The plots of each sample lie on a first-order least-square line in good agreement, indicating that all samples show Ohmic conduction. Among the samples, the highest electrical conductance is obtained with the SiC/Ni/Ti (80 nm) and SiC/Ni samples. On the other hand, the lowest electrical conductance is obtained with the SiC/C/Ti samples. Although it is proven that TiC is an ohmic contact former for n-type SiC, NiSi contacts exhibit higher electrical conductance. Nevertheless, TiC is an indispensable phase for improving both the electrical and mechanical properties of the electrode by eliminating the free carbon phase. The electrical conductance of SiC/Ni/Ti (16 nm) appears lower than that of the SiC/Ni samples.

Fig. 5 shows the mechanical indices of the samples against their electrical conductance. The highest mechanical index is obtained with the SiC/C/Ti samples. This result evinces the successful formation of TiC at the interface, i.e., it is likely that the high hardness of TiC made the trench shallow. In addition, the adhesion between the contact electrode and the substrate is strong and ductile enough to endure the scratch test. The SiC/Ni/Ti (80 nm) sample also endures the scratch test. Although its mechanical index appears lower than those of the SiC/C/Ti samples, it achieves high electrical conductance and mechanical strength simultaneously. On the other hand, the mechanical indices of the SiC/Ni and SiC/Ni/Ti (16 nm)
nm) samples are almost one order of magnitude lower than those of the other two samples. The contact films on these samples are completely removed by scratching. It should be noted that an inappropriate combination of thicknesses of the Ti and Ni layers deteriorates both the mechanical and electrical properties. The interfacial phenomena during the formation process and the resultant performance of the contact film are very sensitive to the thicknesses of the Ti and Ni layers.

2.4 Short summary

The present paper proposed and demonstrated the improvement of the mechanical properties of a Ni-based electrode for n-type SiC by the addition of a Ti layer. The following points became clear.

(1) SiC/Ni samples achieve low-resistance Ohmic contact after annealing at 1273 K for a short time. However, the mechanical properties are significantly deteriorated by the annealing.

(2) SiC/C/Ti samples become Ohmic after annealing at 1273 K for a short time. The electrodes perform high mechanical properties. However, the electrical conductance is lower than that of annealed SiC/Ni electrodes.

(3) SiC/Ni/Ti samples also become Ohmic after annealing at 1273 K for a short time. Appropriate thicknesses of the Ti and Ni layers significantly improve the mechanical properties, retaining high electrical conductivity.

3. A new electrode formation process which activates acceptors in p-type GaN

3.1 Strategy for thinning the Schottky barrier at the metal/GaN interface

The commonly known process for contact electrode forma-

tion on p-type GaN consists of two steps: deposition of four-layered precursor film on GaN and subsequent annealing at approximately 900 K\(^\circ\). The first layer of the precursor, being adjacent to GaN, is, in most cases, Ni\(^\circ\). Ni has a work function as large as 5.15 eV, which is effective for lowering the Schottky barrier\(^\circ\). In addition, Ni does not react with nitrogen. This character in the reactivity of Ni is important for electrodes on p-type GaN, since the consumption of nitrogen by the interfacial reaction forms nitrogen vacancies, which act as donor dopants, in GaN in the vicinity of the interface. On the other hand, Ni does not permeate hydrogen. Hydrogen ions will accumulate at the negative electrode by the voltage applied during annealing. However, further evacuation is difficult as far as the electrode does not allow hydrogen go through the electrode.

Consequently, Pd is selected as the second candidate for the electrode material in this study. Pd shows the highest hydrogen permeability among all metals\(^\circ\), a large work function being 5.12 eV, and sufficient nobleness against nitrogen.

3.2 Experimental procedure

The p-type GaN used in the present study was a 2.0-µm-thick epitaxial film grown by MO-CVD process on the (0001) plane of sapphire wafer with a 2.4-µm-thick undoped GaN buffer layer. The surface orientation and the Mg-doping concentration were (0001) Ga-face and 3.0×10\(^{22}\) m\(^{-3}\), respectively.

The GaN substrates were cut to 4.0-mm square size in the directions of [101\(-\)0] and [1\(-\)21\(-\)0] of the GaN. After ultrasonic cleaning of the GaN substrates with acetone, the electrode films of Ni or Pd were deposited on the substrates by radio-frequency magnetron sputtering. The gray areas in Fig. 6(a) show the size and layout of the electrodes on a GaN substrate. The electrodes were connected to a direct-current power supply as schematically shown in Fig. 6(b) and installed in a tubular furnace. The heat treatment was implemented in a flow of high-purity (99.999%) nitrogen atmosphere at 673 K for 3.6 ks, applying 30 V along the [1\(-\)21\(-\)0] direction of GaN. The effect of voltage application was investigated by comparing the samples annealed with and without the voltage application. The major carrier-type after the heat treatment was measured by the van der Pauw method. The interfacial microstructure after the heat treatment was analyzed by transmission electron microscopy (TEM).

3.3 Results and discussion

Fig. 7 compares three types of the electric conduction profiles between two Ni electrodes arranged along the [12\,10] direction of GaN. The line connecting black circles is the profile
of as-deposited electrodes. Almost no conduction occurs with this electrode. This result indicates that both GaN/Ni interfac- es are rectifying interconnections. The line connecting hollow circles is the profile of electrodes after annealing at 673 K for 3.6 ks without voltage application. The conductivity at high voltage is improved, whereas it is still poor at low voltages. Such a non-linear electric conduction profile indicates that a high Schottky barrier is still existing at the GaN/Ni interface and suppressing the conduction at low voltages. The line connecting black squares is the profile of electrodes after anneal- ing at 673 K for 3.6 ks applying voltage. Although the profile is still non-linear, it shows that the conduction at low voltages is improved by the annealing applying voltage.

Fig. 8 shows a TEM bright field image and corresponding selected-area electron diffraction pattern taken from a cross-section of a GaN/Ni interface after annealing at 673 K for 3.6 ks applying voltage. From the bright field image shown in Fig. 8(a), Ni is directly connected to GaN. This result indicates that no Ga-Ni intermetallic compound is formed by any of possible interfacial reactions. The diffraction pattern shown in Fig. 8(b) consists of arrayed spots corresponding to $[12\bar{1}0]$ zone-axis of GaN sin-
gle crystal and continuous rings of fine Ni polycrystalline film. Diffraction spots or rings corresponding to intermetallic compounds do not appear on the pattern.

By combining the results shown in Figs. 7 and 8, it can be mentioned that the improvement in electric conductivity is achieved without changing the material adjacent to GaN, i.e., without lowering the Schottky barrier height. The improvement is brought by thinning of the Schottky barrier. The heat treatment at 673 K increases the apparent carrier concentration in GaN beneath the Ni electrodes and the application of voltage enhances the increase. The van der Pauw measurement revealed that holes are the major carrier after annealing. Therefore, the results shown above lead to an answer: the heat treatment at 673 K applying 30 V between the electrodes activates the acceptor dopants in GaN by evacuating the hydrogen atoms.

Although acceptor dopants can be activated without voltage application, it takes a long time to achieve a certain conductivity. This fact indicates that the heat evaporates hydrogen through GaN surface. The voltage application enhances the evacuation by the following steps. First, the voltage accumulates hydrogen in a narrow zone beneath an electrode. Then, the diffusion flux of hydrogen through the electrode becomes larger, since the flux is determined by the diffusion coefficient and the gradient of hydrogen composition. Therefore, the hydrogen permeability of the electrode material is important.

**Fig. 9** compares three types of the electric conduction profiles between two Pd electrodes formed on GaN. Comparison of Fig. 9 with Fig. 7 reveals the following two points. One is that the as deposited electrodes of Pd is conductive at high voltage. Another point is that the conductivity is improved by heat treatment and can be enhanced by application of voltage. The last point is that the conductivity of Pd electrode is lower than Ni, except the high voltage zone of as deposited state.

**Fig. 10** illustrates schematically the difference in the hydrogen evacuation behavior between Ni and Pd. Ni electrodes does scarcely dissolve hydrogen. The hydrogen accumulated in the vicinity of the cathode by heat treatment applying voltage must be evacuated to the atmosphere through the GaN/Ni interface, as shown in Fig. 10(a). On the other hand, Pd electrodes allow evacuation through both the Pd film interior and the GaN/Pd interface, as shown in Fig. 10(b1). In addition, Pd electrodes can store a considerable amount of hydrogen. The hydrogen atoms stored in the Pd electrodes can return back into GaN, as shown in Fig. 10(b2). Low conductivity of Pd electrodes can be caused by those back-diffused hydrogen, since the inactivation of acceptor dopants by the mechanism will be more significant in the volumes closer to the GaN/Pd interface.

### 3.4 Short summary

The present paper proposed and demonstrated a new method to improve the conductivity of an metallic electrode on p-type GaN. The following points became clear.

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**Fig. 9** Differences in I-V characteristics among three GaN/Pd electrodes with or without heat treatment and voltage application.

**Fig. 10** Schematic illustration of the difference in hydrogen evacuation behavior between Ni and Pd.
Both as-deposited Ni and Pd electrodes show poor conductivity.

Heat treatment at 673 K for 3.6 ks improves the conductivity at high voltage. The conductivity is improved further by application of 30 V between the electrodes during the heat treatment.

Ni electrodes achieve higher conductivity than Pd electrodes.

4. Conclusions

The present study proposed and demonstrated strategies for designing low-contact-resistance electrodes on two representative wide bandgap compound semiconductors, SiC and GaN, both of which are required in the next generation power electronics. The strategies and methods were newly proposed, based on firm materials science. The points to control the materials behavior and to lead the materials to the preferred state are presented.

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広禁制帯幅半導体と電極の界面微細構造の制御

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概 要
次世代パワーエレクトロニクス材料として優れた特性を有する広禁制帯幅化合物半導体のコンタクト電極形成に関する諸問題の中から、p型窒化ガリウム（GaN）とn型炭化ケイ素（SiC）の電極形成プロセスの制御に取り組んだ。p型GaNにおいては、電極直下のGaN中有效正孔濃度を増加させてショットキー障壁の薄化を図るため、アクセプター元素を不活性化させている原因となっている水素原子を除去する方法として、熱処理中に電極間に電圧を印加する技術を開発した。その結果、電気伝導度の向上に効果があることが実証された。n型SiCではNiを成膜して熱処理した電極が電気伝導特性に優れる一方で脆弱な機械的性質を示す問題に対して、脆弱化の原因となる遊離炭素の生成を抑制する界面反応制御法を考案した。その結果、電気伝導特性を維持しながら著しい機械的特性向上を実現できることを実証した。

キーワード：炭化ケイ素、窒化ガリウム、コンタクト電極、界面反応制御法
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