Chemical Etching Rate, Schottky Barrier Height, and Specific Contact Resistance Dependence on Crystal Face in n-Type 6H-SiC

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Abstract

We investigated how the crystallographic face polarity in n-type 6H-SiC affects the chemical etching rates, Schottky barrier heights, and specific contact resistance. A solution of $HF:HNO_3$ (1:1) chemically attacked only the (0001) Si-faced material after exposure to an artificial quartz lump. The etching was diffusion limited and the etched depth increased in proportion to the square root of the etching time. The Ni Schottky barrier heights were larger for the (0001) Si-face than for the $(000\bar{1})$ C-face. The specific contact resistance values of the Ni/6H-SiC(n-type) ohmic contacts formed on (0001) Si-faced and $(000\bar{1})$ C-faced materials were $5\sim9 \times 10^{-4}$ $\Omega\cdot cm^2$ and $7\sim10 \times 10^{-5}$ $\Omega\cdot cm^2$, respectively. Severe oxygen contamination was observed in the Ni/ (0001) Si-face ohmic contacts, whereas oxygen was detected only on the uppermost metal surface of the Ni/$(000\bar{1})$ C-face ohmic contacts. We presumed that oxygen played an important role in forming Schottky barrier and the ohmic contacts.

Introduction

Interest in the use of silicon carbide (SiC) in high power and high frequency devices is increasing because of its excellent electrical and physical properties. Silicon carbide exists in cubic, hexagonal, and rhombohedral polytypes. The 6H polytype of hexagonal SiC (6H-SiC) has two different crystallographic faces: (0001) Si and $(000\bar{1})$ C. It is believed that the

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crystallographic polarity greatly affects the chemical etching, metallization, oxidation, and epitaxial growth processes during fabrication of SiC devices.

Chemical etching of monocrystalline SiC has been studied by a number of researchers. However, the etching of SiC requires high temperatures and/or ion bombardment processes because of SiC's excellent chemical and thermal stabilities originating from the large binding energy of its Si-C bonds. Some methods reported so far are molten salt[1], molten metal, reactive ion[2,3], and electrolytic[4] etches, and the features of these methods have been discussed and summarized in the literature[5]. To our knowledge there is no chemical etchant that chemically attacks monocrystalline SiC at room temperature.

A solution of $HF:HNO_3$ (1:1) etches ion implanted amorphous SiC at 318 K with a rate of 100 nm/min[6], but the crystal face dependences are not shown.

Many SiC devices greatly depend on the electrical properties of the metal/semiconductor contacts. The Schottky and the ohmic contacts formed with the use of nickel on monocrystalline SiC have been actively investigated, with a primary focus on the effect the crystal face has on the barrier heights (Φ_b) [7~10]. For the metal/n-type SiC contacts, the Schottky barrier heights were higher on the $(000\bar{1})$ C-face than on the (0001) Si-face for some metals; Ti, Ni, Al, Pd, and Ag [7,8]. However, for the Au/n-type SiC Schottky contacts, A. Itoh et al.[10] have reported higher Φ_b for the $(000\bar{1})$ C-face than for the (0001) Si-face, whereas J. R. Waldrop et al.[7] have obtained higher Φ_b for the (0001) Si-face.

Nickel has been used as an ohmic contact metal with n-type SiC[11], and results of specific contact resistance as small as 5×10^{-6} $\Omega \cdot cm^2$ for n-type 6H-SiC epitaxial material with carrier concentrations of $7\text{-}9 \times 10^{18}$ cm^{-3} have been reported[12]. However, to our knowledge, little has been reported on the dependence of specific contact resistance on the crystal face.

In this study, chemical etching of n-type monocrystalline 6H-SiC was carried out using a solution of $HF:HNO_3$ (1:1) at room temperature after exposure to an artificial quartz lump in order to investigate the crystal face effect on the etching rates. We also investigated the effect of the crystallographic face polarity on the Schottky barrier heights and the specific contact resistance of Ni/n-type SiC.

Experimental Method

The material used in this study was an n-type 6H-SiC with a resistivity of 0.134 $\Omega \cdot cm$; the (0001) Si face was mirror polished and the $(000\bar{1})$ C-face was lapped. The carrier concentration obtained from the C-V measurement was $1.2 \sim 1.5 \times 10^{17}$ cm^{-3}. To clean the surfaces, the sample was serially placed in the following solution: trichloroethylene, acetone, methanol, deionized

water, HF:H_2O (1:8), K_2CO_3:H_2O (1:4) heated at 60 ℃, and HCl:H_2O (1:9), with a final cleaning in an ultrasonic bath of deionized water for 5~10 minutes [13]. Chemical etching was carried out in a solution of HF:HNO_3 (1:1) under exposure to an artificial quartz lump (SOLAX: XC-100ESS, Seric Ltd.); its radiation spectra is shown in Fig. 1. The etched depth was measured by using alpha-step 200 (KLA Tencor Corp.).

A thin film of Ni was used as the metal for both the Schottky and the ohmic contacts. Heat treatment was subsequently carried out for 10 minutes in order to achieve ohmic behavior at 900 ~1000 ℃ for the Ni/(0001) Si-face contacts and at 300~500 ℃ for the Ni/(000$\bar{1}$) C-face contacts. Both evaporation of Ni and subsequent heat treatment were conducted in a vacuum of less than 1 x 10^{-6} Torr. The Ni film was fixed at 1000 Å.

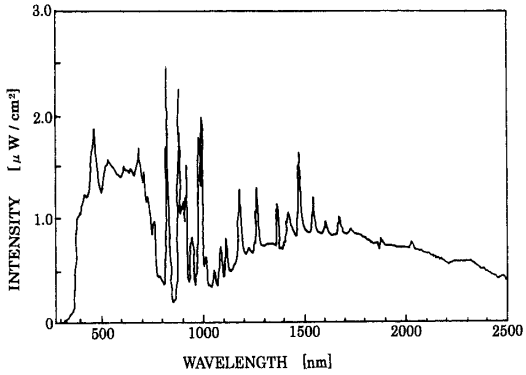

Fig. 1 Radiation energy spectra of an artificial quartz lump.

The current-voltage and the capacitance-voltage characteristics were measured by using an electrometer (610C, Keithley Instrument Ltd.) and a C-meter/C-V plotter (4280A, Hewlett Packard Co.), respectively. The Cox and Strack method[14] was used to measure specific contact resistance. The elemental composition depth profiles were obtained by Auger electron spectroscopy (AES).

Results and Discussion

No chemical attack was observed irrespective of the face polarity under room illumination, when the wafer was soaked in the etchant for 16 hours at 40 ℃. However, on exposure to the artificial quartz lump, etching of the (0001) Si-face was observed, whereas no etching of the (000$\bar{1}$) C-face was observed. The etched depth plotted against the etching time is shown in Fig. 2. The etched depth is proportional to the square root of the etching time, indicating that the etching is

diffusion limited.

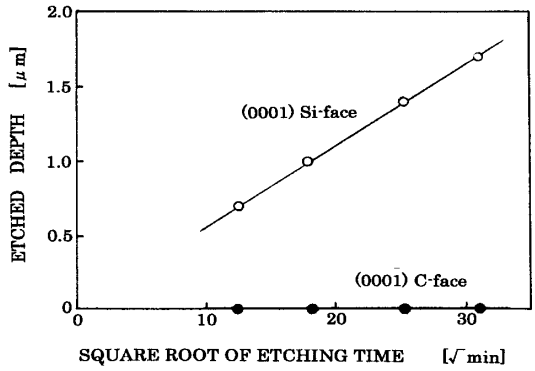

Fig. 2 Etched depth is plotted against square root of etching time for (0001) Si-faced and (000$\bar{1}$) C-faced materials.

The most probable etching mechanism is as follows; For the (0001) Si-face, the Schottky barrier formed at the etching solution- 6H-SiC (n-type) interface, in which the upward surface band-bending was entailed. Under these conditions, electrons and holes generated by the illumination of the artificial quartz lump are swept into the bulk and accumulate on the (0001) Si surface, respectively. The holes were likely dissolved into the etching solution and oxidized the uppermost silicon layer resulting in silicon oxides. Silicon oxides combined with carbon probably formed on the (0001) Si surface and were dissolved into the etching solution.

However, no chemical etching was observed even in response to the artificial quartz lump illumination for the (000$\bar{1}$) C-face. From the AES data obtained in this study, we assume that carbon hardly reacted with oxygen and thus carbon oxides were not produced at room temperature. As shown in Fig. 6, no oxygen was detected at the metal/(000$\bar{1}$) C-faced SiC interface. This sample was annealed at 1000 ℃ for 10 minutes in a vacuum chamber, but severe oxygen contamination was observed in the metal/(0001) Si-faced material. This suggests that the following reactions[15], which have been proposed by J. A. Edmond et al.[6] as the most probable carbon dissociation mechanism, were improbable.

$$C + 2HNO_3 \rightarrow 2HNO_2 + CO_2$$

$$2C + HNO_2 \rightarrow HCN + CO_2$$

Figure 3 shows the surface morphology of the etched (0001) Si-face. Many defect-related striations and etch-pits were observed, and no mirror surface was obtained.

The n-values and barrier heights of the nickel Schottky contacts formed on the (0001) Si-face are plotted against the annealing temperature in Table 1. The barrier height Φ_b was obtained from the following equation[16].

Fig. 3 Surface morphology of etched (0001) Si faced material.

Table. 1 Annealing temperature effect on Ni Schottky barrier height for (0001) Si-faced and (000$\bar{1}$) C-faced materials.

Material	As-deposition	Heat treatment (℃)			
		300	500	700	800
(0001) Si-face	1.08	1.10	1.13	1.63	1.85
(000$\bar{1}$) C-face	1.00	ohmic	ohmic	ohmic	ohmic

$$\Phi_b = -V_i + V_o + 2kT,$$

where V_i is the diffusion potential obtained from the C-V measurement, k is Boltzmann's constant, T is the temperature in K, $V_o = (kT/q)\ln(N_C/N_D)$, N_C is the effective density of states in the conduction band for n-type material, and N_D is the doping concentration determined from the $1/C^2$ versus V plots. If we take a value of $m^* = 0.6\ m_o$[17] for the effective mass of electron in n-type SiC, N_C is calculated to be $1.17 \times 10^{19}\ cm^{-3}$.

The barrier heights of the Schottky contacts were higher for (0001) Si-faced than for (000$\bar{1}$) C-faced materials. This is inconsistent with the results reported with Au, Ni, Ti/4H-SiC (n-type)[10] and Ti, Ni, Al/6H-SiC (n-type)[8] systems, where the barrier heights were higher for (000$\bar{1}$) C-faced than for (0001) Si-faced materials. However, the barrier heights of the Au/ 6H-SiC (n-type), Ag/ 6H-SiC (p-type), and Au/ 6H-SiC (p-type) contacts were larger for (0001) Si-faced than for (000$\bar{1}$) C-faced materials[7]. J. R. Waldrop et al.[7] have suggested that the electronic structure of the metal/6H-SiC interfaces is quite complex and does not conform to a simple pattern or model.

The barrier height for the Schottky contacts formed on the (0001) Si-faced material increased as the annealing temperature increased. Such dependence of Φ_b on the annealing temperature can be observed in the Al / 6H-SiC (p-type)[18] and the Pt / β -SiC (n-type)[19] Schottky contacts.

The results obtained in this study on Schottky contacts suggest that the (000$\bar{1}$) C-faced material is desirable for achieving ohmic contacts with lower specific contact resistance because of its lower

barrier height. High temperature annealing at more than 900 ℃ was essential for the formation of ohmic contacts on the (0001) Si-faced materials, whereas ohmic contacts could be realized at lower temperatures (300～500 ℃) on the Ni/(000$\bar{1}$) C-faced materials. The specific contact resistance values for the Ni/(0001) Si-faced and the Ni/(000$\bar{1}$) C-faced materials were 5～9 x 10^{-4} Ω·cm^2 and 7～10 x 10^{-5} Ω·cm^2, respectively. The resistance values of Ni ohmic contacts formed on the (0001) Si-faced and (000$\bar{1}$) C-faced materials were 2～3 orders of magnitude higher than those that have appeared in the literature[12]. For example, ohmic contacts with reduced specific contact resistance of less than 5 x 10^{-6} Ω·cm^2 have been achieved on n-type epitaxial 6H-SiC with carrier concentrations of 7～9 x 10^{18} cm^{-3}. This variation seems to originate from the difference in the carrier concentrations of the materials used. We used an n-type bulk material with a carrier concentration of 1.2 x 10^{17} cm^{-3}, while J. Croften et al.[12] used an epitaxial material with a carrier concentration of 7～9 x 10^{18} cm^{-3}. The specific contact resistance ρ_c is expressed in the following equation[20].

$$\rho_c \propto \exp(\Phi_b/\sqrt{N}),$$

where Φ_b and N denote the barrier height and the carrier concentrations, respectively. J. Croften et al.[21] have also obtained a specific contact resistance with strong dependence on the carrier concentration for Al-Ti ohmic contacts formed on 6H-SiC (p-type). The same type of dependence is likely in the n-type materials.

Figure 4 shows the depth profiles of Si, C, Ni, and O obtained from AES for the Ni ohmic contact formed on the (0001) Si-face, whose contact was annealed at 1000 ℃ for 10 minutes in a vacuum chamber. Out-diffusions of Si and C were observed. Nickel and oxygen showed severe diffusion into bulk SiC. Figures 5 and 6 show the depth profiles of Si, C, Ni, and O for the ohmic contacts formed on the (000$\bar{1}$) C-face after annealing at 300 ℃ and 1000 ℃, respectively. Although severe inter-diffusions of Si, C, and Ni were observed, oxygen was detected only on the

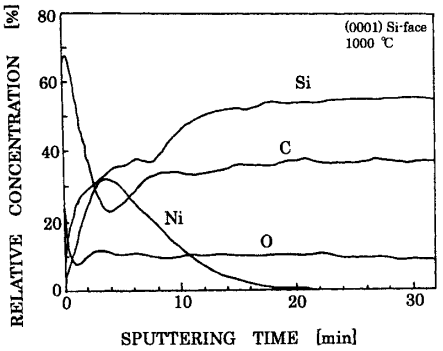

Fig. 4 Depth profiles of Si, C, Ni, and O obtained from AES for Ni/(0001) Si-face ohmic contact annealed at 1000 ℃.

uppermost metal surface, but not in both the metal layer and bulk SiC. The reduced oxygen

presumably produced the reduced barrier height and reduced specific contact resistance for the metal contact onto the (000$\bar{1}$) C-faced materials. The depth profiles shown in Figs. 5 and 6 suggest that the existence of nickel silicides at the metal/6H-SiC(n-type) interface in both samples. C. A. Crider et al.[22] have reported that oxygen as well as carbon dramatically affect silicide formation in the Pt/Si system. It is probable that silicide reduces the barrier height, resulting in the lower specific contact resistances observed in the AuZn/p-type InP[23].

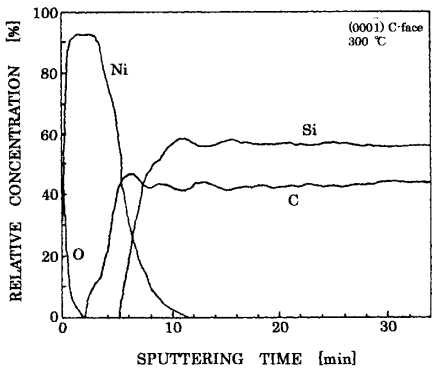

Fig. 5 Depth profiles of Si, C, Ni, and O obtained from AES for Ni/(000$\bar{1}$) C-face ohmic contact annealed at 300 ℃.

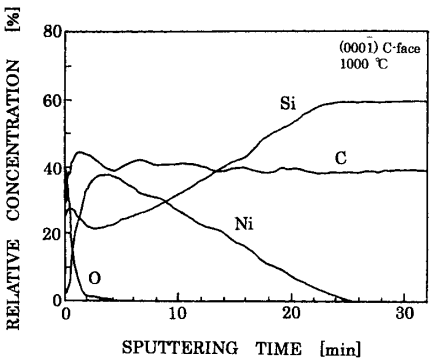

Fig. 6 Depth profiles of Si, C, Ni, and O obtained from AES for Ni/(000$\bar{1}$) C-face ohmic contact annealed at 1000 ℃.

Summary

We studied how the crystallographic face polarity in n-type 6H-SiC affected the chemical etching rates, Schottky barrier heights, and specific contact resistance. No etching was observed for either the (0001) Si-faced or the (000$\bar{1}$) C-faced material under room illumination. Only the (0001) Si-faced material was etched following exposure to an artificial quartz lump. The etched

depth was proportional to the square root of the etching time, indicating that the etching was diffusion limited. Striations and etch-pits apparently caused by defects were revealed and no smooth surface was obtained.

The barrier height of the as-deposited Ni to 6H-SiC was higher for the (0001) Si-faced material than that for the $(000\bar{1})$ C-faced material. The barrier heights for the (0001) Si-faced material increased with increasing annealing temperature.

Ohmic contacts would only form on the Ni/(0001) Si-faced material after high temperature annealing at more than 900 ℃, ohmic contacts on the $(000\bar{1})$ C-faced material could be obtained after annealing at 300～500 ℃. The specific contact resistance values of Ni ohmic contacts formed on the (0001) Si-faced and the $(000\bar{1})$ C-faced materials were 5～9 x 10^{-4} Ω·cm² and 7～10 x 10^{-5} Ω·cm², respectively. Severe inter-diffusion of oxygen, silicon, carbon, and nickel was observed in the Ni/(0001) Si-faced contacts annealed at 1000℃, whereas no oxygen was observed in the metal layer and bulk crystal for the Ni/$(000\bar{1})$ C-faced contacts annealed at 1000℃. The lower Schottky barrier height and lower specific contact resistance are considered to originate from the lower oxygen contamination for the Ni/$(000\bar{1})$ C-faced materials.

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