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Characteristics of Ni/SiC Schottky Diodes Grown by ICP-CVD

Tae-Hyun Gil*, Han-Soo Kim and Yong-Sang Kim***

Abstract - The Ni/SiC Schottky diode was fabricated with the α-SiC thin film grown by the ICP-CVD method on a (111) Si wafer. α-SiC film has been grown on a carbonized Si layer in which the Si surface was chemically converted to a very thin SiC layer achieved using an ICP-CVD method at 700°C. To reduce defects between the Si and α-SiC, the surface of the Si wafer was slightly carbonized. The film characteristics of α-SiC were investigated by employing TEM (Transmission Electron Microscopy) and FT-IR (Fourier Transform Infrared Spectroscopy). Sputterd Ni thin film was used as the anode metal. The boundary status of the Ni/SiC contact was investigated by AES (Auger Electron Spectroscopy) as a function of the annealing temperature. It is shown that the ohmic contact could be acquired beyond a 1000°C annealing temperature. The forward voltage drop at 100A/cm^2 was 1.0V. The breakdown voltage of the Ni/α-SiC Schottky diode was 545 V, which is five times larger than the ideal breakdown voltage of the silicon device. As well, the dependence of barrier height on temperature was observed. The barrier height from C-V characteristics was higher than those from I-V.

Keywords: Breakdown Voltage, Chemical Vapor Deposition (CVD), Inductively Coupled Plasma (ICP), Schottky Barrier Height, Silicone Carbide (SiC).

1. Introduction

Silicon carbide (SiC) has been recognized as a semiconductor material with outstanding physical and chemical characteristics. Silicon carbide exhibits a larger bandgap, a higher breakdown field, a higher thermal conductivity and a higher saturation velocity, compared to other more widely used types of silicon. These properties make SiC very attractive for high temperature, high power and high frequency electronic devices. In addition, its favorable mechanical properties such as high elastic modulus and toughness, in combination with its large bandgap, make this conductor an excellent material for the micro-sensors that can operate at temperatures higher than 600°C. Such high temperature applications include pressure sensors for internal combustion and jet engines [1]. Furthermore, SiC can be doped both p-type and n-type while the diamond cannot.

SiC power MOSFET's and rectifiers would operate under high voltage, high temperature, and high frequency ranges and also have nearly 20 times smaller die size than that of the correspondingly rated silicon-based devices. Kimoto *et al.* recently demonstrated high voltage (500-1000V) 4H-SiC Schottky rectifiers whose specific-on-resistances are nearly 100 times smaller than the theoretical minimum on resistances attainable in silicon Schottky diodes [2]. SiC's relatively immature crystal growth and device fabrication technologies are not yet sufficiently developed to the degree required for reliable incorporation into electronic systems.

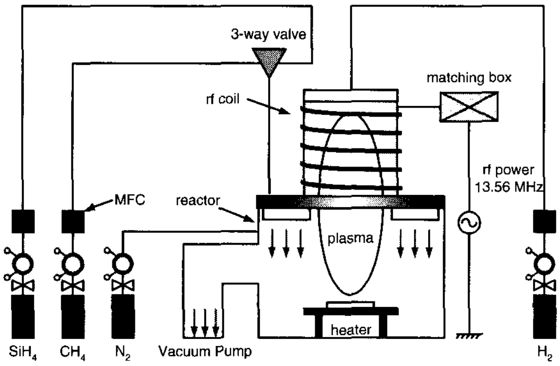

Fig. 1 Schematic of ICP-CVD

There have been numerous methods on heteroepitaxial growth of SiC films on Si substrates. We achieved α-SiC film on Si successfully by the ICP-CVD (Inductively Coupled Plasma Chemical Vapor Deposition) method. A schematic of the ICP-CVD system is shown in Fig. 1. In this paper, we deposited α-SiC epilayer on Si substrate and fabricated a high breakdown voltage SiC Schottky diode using Ni metal thin film, which could operate at elevated temperatures. In addition, we investigated electrical characteristics of the SiC Schottky diode. The nature of the rectifying-ohmic transformation of the Ni-SiC contact

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* Department of Electrical Engineering, Myongji University, Yongin 449-728, Kyunggi-do, Korea(kys@mju.ac.kr)

** Department of Electrical Engineering, Doowon Technical College, 678 Ansung, Kyunggi-do, Korea(hansoo@doowon.ac.kr)

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system is also discussed.

2. α-SiC Film Growth

α-SiC film was deposited by the ICP-CVD (Inductively Coupled Plasma Chemical Vapor Deposition) system shown in Fig. 1. Plasma was generated by the conventional ICP system mounted on top of the process chamber, and it consists of a quartz tube and spiral copper coil. RF (frequency of 13.56 MHz) power was applied to this coil and vertical magnetic fields were generated by currents from the coil. H_2 gas was used for carrier gas to transfer reactive gases and help dissociation of hydride gases. We used SiH_4 and CH_4 gases for source gas and the gas flow rate was controlled by MFC (Mass Flow Controller). H_2 gas was inserted from the top of the ICP-CVD system, generating plasma by RF power. SiH_4 and CH_4 source gases were inserted into the process chamber through nozzles and directly dissociated to reactive radicals by hydrogen plasma parallel to the substrate. Si substrates were set on the heating chuck located below the ICP source. The substrate temperature was monitored with the compensated value from the thermocouple attached to the heater. Heteroepitaxial growth of SiC on Si is a complicated technology because of larger lattice (~20%) and thermal (~8%) mismatches. The breakthrough in material quality was achieved by the development of a buffer layer technology. The key process for the heteroepitaxial growth of SiC on Si was the carbonization of the Si substrate, providing a thin SiC buffer layer [3, 4].

Si wafers [(111)-oriented n^+-type (10^{+17} cm^{-3}), resistivity ≤ 20 Ω·cm] of about 30×30 mm were used as substrates. Si substrates were sequentially cleaned by the conventional RCA method. In order to reduce defects from lattice mismatch between Si and SiC, the carbonization process was employed prior to SiC film growth. The wafer surface was carbonized by heating the substrate to 1100°C for 10 min under a stable flow of hydrogen and methane. The flow rate of hydrogen and methane was 1 slm and 100 sccm, respectively. H_2 gas was used as the carrier and SiH_4 and CH_4 gases were used as source gases. The gas flow rate was controlled by MFC (Mass Flow Controller). SiC film growth was performed at 760 Torr of H_2, SiH_4, and CH_4. The substrate temperature was 700°C and the flow rate of H_2, SiH_4, and CH_4 was 3 slm, 10 sccm, and 20 sccm, respectively.

To investigate the microstructure of the carbonized Si surface, a JEOL JEM-2010 cross-sectional TEM (Transmission Electron Microscopy) was used. Plan-view specimens were prepared by polishing and ion milling from the back side of the substrate to a thickness under 20 μm. The cross-sectional diffraction pattern indicates in Fig. 2 that the carbonized Si surface has both crystallinity and amorphous phase from regularly aligned spots and rings, respectively.

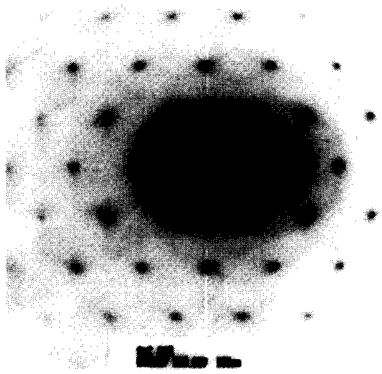

Fig. 2 Bright-field TEM image of carbonized Si surface.

The plasma chemistry of SiH_4/H_2 has been studied by Shieh *et al.*, and that of CH_4/H_2 by Hsu and Mitomo *et al.* Shieh *et al.* suggested that SiH_4 decomposes in the plasma to produce H_2 and the more reactive precursor species SiH_x (x=0, 2, 3), and further that the major radicals for the deposition of silicon should be SiH_x (x=0, 2, 3). Besides, Hsu studied the microwave plasma chemistry of CH_4/H_2 by molecular beam mass spectroscopy (MBMS) and found that CH_4 can react with the hydrogen atom to form CH_3, which can be subsequently converted into C_2H_2 in the excess H-atom. Mitomo *et al.* used Fourier transform infrared (FT-IR) spectroscopy to study the effect of various carbon feed gases. Their reports also confirm the result of Hsu on the formation of C_2H_2 [5].

For SiC growth by CVD, a mechanism has been proposed by Hong *et al.* and is described as follows. Si_2H_6 decomposes in the gas phase to form SiH_4 which then reacts with C_2H_2 in two paths, (i) a reaction of the gaseous SiH_2 with C_2H_2 adsorbed on the surface and (ii) a gas-phase reaction between gaseous SiH_2 and gaseous C_2H_2 to form another intermediate product, most plausibly, $SiH_3{\equiv}CH$ [6].

With the mechanism proposed above, the various types of film formation at different CH_4/SiH_4 flow ratios can be explained as follows. The bond energies of Si-H and C-H are about 320 and 410 kJ/mol, respectively. This suggests that most likely the SiH_4 has a higher dissociation efficiency than CH_4. Since the concentration of CH_4 is too low at CH_4/SiH_4 flow ratios below 2, the decomposition of SiH_4 should dominate and result in many SiH_x radicals. The SiH_x radicals adsorb onto the Si surface where they decompose and poly-crystalline silicon is deposited [7]. Relatively larger amounts of CH_4 must be added into the system at about a CH_4/SiH_4 flow ratio of 2.

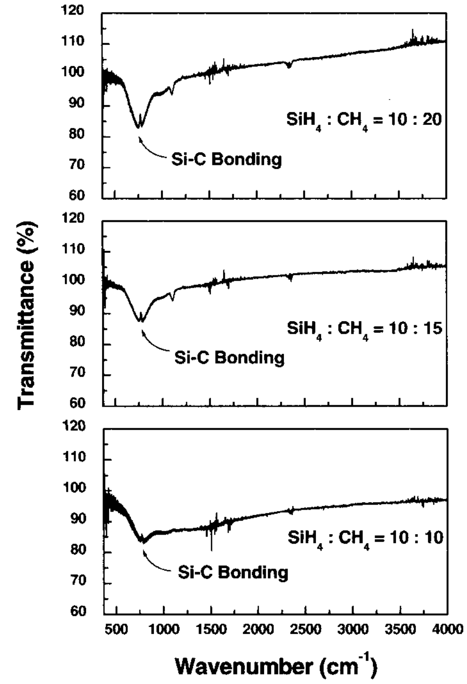

Fig. 3 FT-IR spectroscopy of SiC thin film deposited at 700°C

For chemical composition analysis of SiC film, we utilized FT-IR (Fourier Transform Infrared) spectroscopy. In general, the Si-C vibration band is observed between wavelengths of 740~820 cm^{-1}. We could obtain the results that the spectrum at around 750 cm^{-1} indicates stronger SiC bonding as CH_4/SiH_4 flow ratio becomes higher. In Fig. 3 (a) we could observe the strongest spectrum showing the Si-C band at around 750 cm^{-1}.

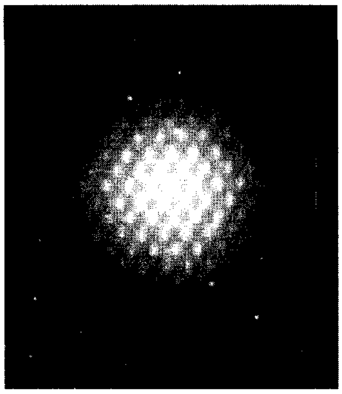

Fig. 4 Dark-field TEM image of grown SiC film at 700°C

The microstructure of the grown SiC film was also analyzed by TEM. Fig. 4 illustrates the crystal structure of the SiC film. The dark-field TEM image indicates that the grown SiC film has an almost amourphous phase from the broad rings surrounding it. We consider that it is due to the relatively low substrate heating temperature of 700°C compared to the carbonization process temperature of 1100°C.

3. Fabrication of SiC Schottky Diodes

The SiC Schottky diode was fabricated with a α-SiC film grown on a Si substrate. The schematic cross-sectional view of the Ni/SiC Schottky diode is represented in Fig. 5. After removing a native oxide of the SiC surface, 3000Å-thick SiO_2 film was deposited with a PECVD (Plasma Enhanced Chemical Vapor Deposition) system at 300°C. The deposition conditions of PECVD oxide were as follows: the flow rates of 5% SiH_4/N_2 gas, N_2 gas, and N_2O gas were 160 sccm, 240 sccm, and 1500 sccm, respectively, 550 mTorr of operating pressure, and 350 Å/min of deposition rate. Blanket Ni-SiC ohmic metallization was accomplished on the backside of the the SiC substrate through the formation of Ni-silicide by a 1 hour anneal at 1000°C in Ar ambient. An additional 2500Å-thick oxide layer was then deposited on the grown thin oxide on the SiC layer, bringing the field oxide to a total thickness of 3000Å.

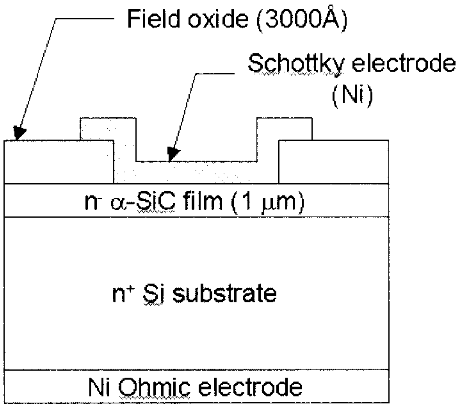

Fig. 5 Schematic of the SiC Schottky diode

The active rectifying electrode was formed by RF magnetron sputter deposition of Ni thin film of 4000Å through a contact window etched in the oxidized SiC epi layer. The Schottky metal deposition was performed with a hot sample stage at a temperature of 130°C. The rectifying electrode was patterned by chemical etching. The edge of the electrode was overlapped with the field oxide.

We have investigated the diffusion of Ni atoms into the SiC layer after thermal annealing. Fig. 6 shows the chemical depth profiles determined using AES for Ni/SiC interface before and after thermal annealing. It indicates that the depth profiles of atomic composition near the Ni/SiC interface after 600°C thermal annealing were almost identical to those before annealing. This may mean that the interface is not attacked under these conditions and the stability of the Ni/SiC contact is preserved. However, the interaction between Ni and SiC is observed and Ni silicide may be formed after 1000 °C annealing for 30 min.

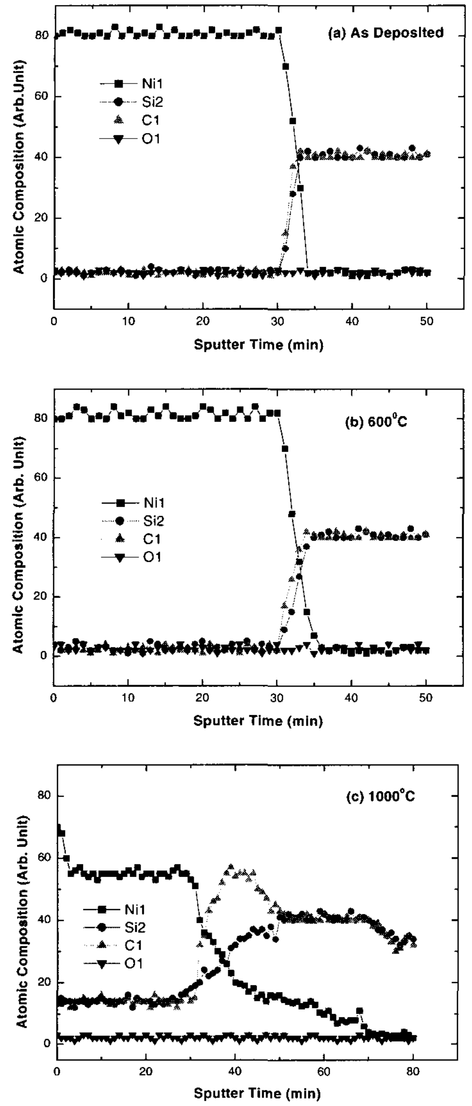

Fig. 6 Auger depth profiles of Ni/SiC interface for (a) as-deposited Ni-SiC structure; (b) annealed at 600 °C for 30 min in Ar; (c) annealed at 1000 °C for 30 min in Ar.

4. Electrical Characteristics of Ni/SiC Schottky Diodes

The electrical properties of SiC schottky diodes have been characterized by means of the I-V curve. I-V characteristics of the Ni/SiC Schottky diodes were measured by Keithley 2361. In order to obtain the temperature effect on the electrical properties of the Schottky diodes, a study on the I-V characteristics as a function of temperature has been performed. Under forward bias conditions, the low current conduction mechanism follows the thermionic emission theory. However, at higher current density levels, a large series resistance was observed and this contributes to an additional voltage drop across the diodes. It is important to note that the log (I)-V characteristics for these diodes were perfectly linear in at least six current decades and thus the ideality factor is bias independents. The ideality factor η calculated in the fitting process is depicted as a function of temperature. The typical current-voltage (I-V) characteristics of Schottky diodes at various temperatures are shown in Fig. 7.

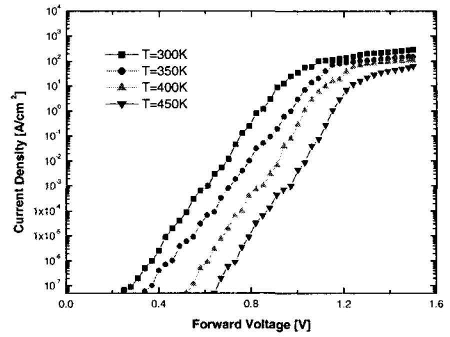

Fig. 7 Forward I-V characteristics of Ni/SiC Schottky diodes at room temperature.

The ideality factor of 1.07 at room temperature was obtained from the slope of characteristics at low current density ($<10^{-2}$ A/cm^2). Thus, the ideal thermionic emission theory can be applied for the analysis of these Schottky contacts.

The forward voltage drop at 100A/cm^2 was about 1.0V and it increased with an increase in temperature due to series resistance. The breakdown voltage was obtained from the I-V characteristic in Fig. 8. The breakdown voltage was 545V while the ideal BV of the silicon at the same condition was 100V.

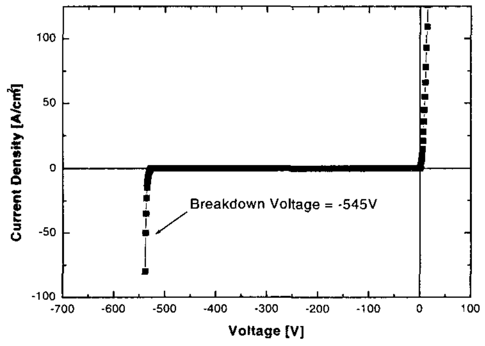

Fig. 8 I-V characteristics of Ni/SiCSchottky diodes with breakdown voltage.

The barrier height was most commonly calculated from the current I_S, determined by an extrapolation of the log (I) versus V curve to V=0[V]. The barrier height ϕ_B was calculated from I_s in Eq. 1 according to

$$\Phi_B = \frac{kT}{q}\ln\left(\frac{AA^*T^2}{I_s}\right) \quad (1)$$

The barrier height ϕ_B of Ni/SiC Schottky contact was 1.63eV. The variation of Schottky barrier height and ideality factor as a function of temperature were shown in Table 1. As the temperature increases, the ideality factor and barrier height were decreased.

Table 1 Variation of Schottky barrier height and ideality factor as a function of temperature.

Temp.(K)	Schottky barrier height ϕ_B (eV)	Ideality factor η
300	1.05	1.06
350	0.93	1.05
400	0.74	1.02
450	0.61	1.01

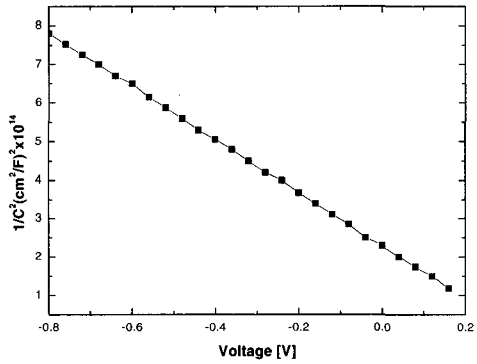

Fig. 9 C-V characteristics of Ni/SiC Schottky diodes at room temperature.

Fig. 9 is the plot of $1/C^2$/V. The intercept in the plot at $1/C^2=0[F^{-2}]$ corresponds to the built-in potential V_{bi}. The plot of $1/C^2$ versus V is a straight line, which implies that the donor concentration is constant throughout the depletion region. The calculated N_D, ϕ_B for metal contact is also listed in Table 2. The $1/C^2$-V plot demonstrates good linearity, and the Schottky barrier height ϕ_B was 2.37eV. Relatively low $\phi_B^{I\text{-}V}$ (about 1.63eV), as well as no correlation between ϕ_M and $\phi_B^{C\text{-}V}$, suggests that the ϕ_B value was determined by the surface condition in our experiments. The difference between $\phi_B^{I\text{-}V}$ and $\phi_B^{C\text{-}V}$ can be explained by the presence of interfacial layers.

Table 2 Schottky diode parameters of Ni on SiC.

	N_D(cm^{-3})	Ideality factor (η)	SBH($\phi_B^{I\text{-}V}$) (eV)	SBH($\phi_B^{C\text{-}V}$) (eV)
Ni	2.3×10^{16}	1.07	1.63	2.37

5. Conclusions

We fabricated vertical Ni/SiC Schottky diodes on SiC thin films grown on Si substrates. We deposited amorphous SiC on Si(111) substrates by ICP-CVD at 700°C using $SiH_4/CH_4/H_2$ gas mixture. We performed TEM analysis on carbonized thin films and deposited SiC thin films. This showed that the film was almost amorphous and had a small amount of polycrystalline phase. We utilized FT-IR as a chemical analysis method for the SiC bonding peak (740~820 cm^{-1}) of deposited SiC thin films as different flow ratios of SiH_4 and CH_4. The interface between the Ni layer and the SiC substrate after a 600°C thermal annealing remained identical to that prior to annealing. This indicated that the interface is not attacked under these conditions and, therefore, the stability of the Ni/SiC contact is preserved. After 1000 °C annealing, the interaction between Ni and SiC was evident.

The barrier heights and ideality factor in Ni/SiC Schottky structures were measured by current-voltage and capacitance-voltage characteristics. At room temperature, the barrier height was 1.63eV(I-V curve) and 2.37(C-V curve) and the ideality factor was 1.07. The barrier height difference can be explained by the presence of interfacial layers. Current-voltage measurements have been performed in the temperature range of 300K to 450K. As the temperature increases, the Schottky barrier height and ideality factor decreases.

The forward voltage drop at 100A/cm^2 was 1.0V and the reverse breakdown voltage of the Schottky diodes was 545V. We can find that thin α-SiC deposition on the Si layer could sustain the high BV without loss of the forward voltage drop.

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Tae-Hyun Gil

He received his M.S. degree in Electrical Engineering from Myongji University in 2000. Currently, he is an Engineer for Sunic System. His area of interest includes Semiconductor Processing Instrument.

Han-Soo Kim

He received his M.S. and Ph.D. degrees in Electrical Engineering from Seoul National University in 1990 and 1995, respectively. Currently, he is an Assistant Professor at Doowon Technical College. His area of interest includes Power Semiconductor Devices.

Tel: 81-31-670-7169

Yong-Sang Kim

He recieved his M.S. and Ph.D. degrees in Electrical Engineering from Seoul National University in 1990 and 1994, respectively. Currently, he is an Associate Professor at Myongji University. His research area includes Bio MEMS, Bio Sensors and Si nano crystal.

Tel: 81-31-330-6365