RESEARCH ON PROPERTIES AND INTERFACE CHEMISTRY IN THE Ti/3C-SiC SYSTEM

Cristiana VOICAN
Electronic College of Bucharest, Romania
E-mail: voicancristiana@yahoo.com

KEYWORDS: Carbides, ohmic contacts, SiC.

ABSTRACT. Characterizations were performed to determine the properties of Ti contacts on 3C - SiC. Both titanium carbides and titanium silicides were studied carefully following heat treatments from 600 to 1000^{0}C.The peak associated with titanium silicides in Auger Si spectrum is identified. Structural and chemical analyses using AES, XPS, and XRD revealed how the electrical properties of the contacts correlate with the interface chemistry. It is found that while the carbide improves the ohmic behavior of the contacts, the cubic structure disilicide C49 $TiSi_2$ formed at the interface at above 700^{0}C is closely related to the lowering in the contact resistance. The barrier height decreases from 0.53 eV for as-deposited films to 0.44 eV due to annealing. The contacts maintained stable electrical characteristics after annealing at 600^{0}C for extended periods of time.

1. NTRODUCTION

It has been known that SiC is superior in hostile environments such as high temperature, high power, and high irradiation. An important requirement for any emerging device technology is the development of electrical contacts with low specific resistivity and high stability [1],[2]. the contacts cannot be improved unless the factors that determine the electrical conduction through the contacts become fully understood. To this end, the chemical bonding and crystallographic structures at the metal/SiC interface must be studied. Despite the increasing works in recent years, only limited information is currently available.

In the present letter, we report on the correlation of the electrical properties with the chemical nature at the Ti/3C-SiC interface resulting from solid-phase reactions upon thermal annealing. The reliability of contacts was also studied.

2. EXPERIMENTAL RESEARCHES

The experiments described here involve Ti films deposited on n-type 3C-SiC layers on Si substrate. The thickness of the layers used was set to 10µm with an electron concentration of $1*10^{16}$ cm^{-3} as determinated by Hall measurements. The surface of the samples was examinated by Nomarski microscope and was mirrorlike.

Prior to the Ti deposition, the surfaces were chemically and sputter cleaned and the Ti target was heated for one minute. The deposition was done by Ar sputtering in a vacuum system with a base pressure of $3*10^{-8}$ Torr. A Ti film of 1000 ? was deposited. Afterwards, the samples were annealed in a vacuum rapid thermal processor. The chamber pressure during annealing was 10^{-5} Torr, and the samples were annealed for 3 min at temperatures ranging from 600 to 1000^{0}C .Since the whole sample surface was exposed to heat and, therefore, there are no temperatures gradients (i.e. ,no convection, the solid-phase

reactions are supposed to rely on diffusion processes alone.

Auger electron spectroscopy (AES) , X-ray induced photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) measurements are employed to inform on the interactions at the Ti/SiC interface and the subsequent formation of compound materials (e.g., carbides ,silicides) upon annealing. Auger analysis was done with the Japan Electronics JAMP-7900 AES scanning microprobe. The 3 keV,24 nA primary electron beam was rastered over a 0.01 mm^2 area. Sputter depth profiling was performed with a 3 keV Ar^+ ion beam rastered over a 2 mm^2 area. The Surface Science Instruments model SSX - 100 XPS spectrometer was used for chemical analysis. The survey and high - resolution spectra were collected using a $A1K_{alpha}$ anode operated at 15 kV and 400 W. Depth profiling was performed using an Ar^+ sputtering gun. XRD analysis was performed in a conventional 2-teta diffractometer (Electric Science model RAD-2) equipped with a CuK_{alpha} source. Using a standard photolithography process and etching,1.0-mm^2 Ti contacts were defined. Current-voltage (I-V) measurements were performed on these contacts at room temperature using a Keithley model 236.The total resistance between two electrodes was measured (R_c).The results were confirmed by interchanging contact pairs.

3. EXPERIMENTAL RESULTS

3.1. CURRENT-VOLTAGE CHARACTERISTICS

Fig.1 shows typical room-temperature current-voltage (I-V) characteristics of the contacts as a function of the annealing temperature where the voltage is varied from -2 to 2 V. The voltage range was not extended to higher voltages to avoid Joule heating of the contacts. Changes in the characteristics can be attributed to changes in the resistance of the contacts (R_c). The values of R_c obtained for the various annealing temperatures are summarized in Table 1.these values represent the average from several runs.

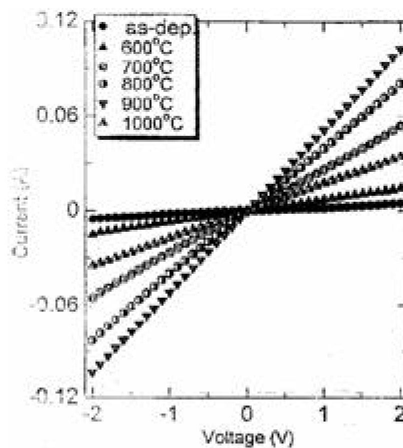

Fig.1 Room-temperature I-V characteristics of Ti contacts on 3C-SiC/Si as a function of the annealing temperature

TABLE.1
VARIATION OF THE INTERCONTACT RESISTANCE ANNEALING TEMPERATURE IN THE Ti/3C-SiC SYSTEM

T (^{0}C)	As-dep	600	700	800	900	1000
R_c(ohm)	476.1	140.9	37.5	24.8	19.4	57.8

Generally, values were reproducible to better than +/- 25%.The as-deposited contracts are nearly ohmic but slightly rectifying. The annealed contacts show ohmic properties with excellent linearity. By annealing at 600^{0}C ,the ohmic characteristics improve yielding a decrease in R_c from 476.1 to 140.9 O as shown in Table 1. At 700^{0}C,R_c decreases steeply down to 37.5 O indicating a major change at the interface. The R_c continues to decrease with temperature up to 900^{0}C where a lowest value of 19.4 O was obtained. However, contacts annealed at 1000^{0}C unexpectedly showed a sudden increase of R_c to 57.8 O.

3.2. AUGER ELECTRON SPECTROSCOPY MEASUREMENTS

Figs.2 - 4 show the depth profiles of AES peak-to-peak intensities of Si_{LMM} (80-100eV), C_{KLL} (260-280eV),Ti $_{LMM}$ (372-392eV),and O_{KLL} (495-515eV) atoms obtained for as-deposited,900^{0}C , and 1000^{0}C anneal, respectively. The shape of the Si and C profiles in the as-deposited sample (fig.2) suggest a Ti-Si and Ti-C reaction limited to a thickness of less than 25 ?. The Auger depth profiles for the samples annealed at 600 and 700^{0}C show that at 600^{0}C , C diffuses into Ti film to a depth of 160? and becomes distributed along the whole Ti film above 700^{0}C.

On the other hand , however, no traceable Si diffusion into Ti film was observed at 600^{0}C.At 700^{0}C ,Si diffusion was estimated to be about 250? and becomes 700? at 900^{0}C (fig.3).At 1000^{0}C,Si diffusion was restricted to only about 200? (fig.4).

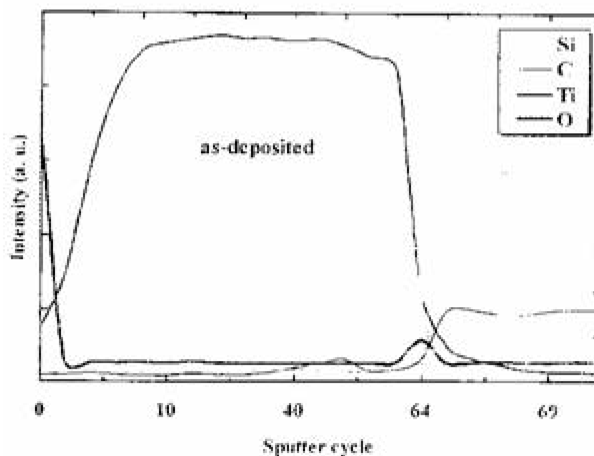

Fig.2 Depht profiles of the AES signals by Si,C,Ti, and atoms for the Ti/3C-SiC/Si as-deposited samples.

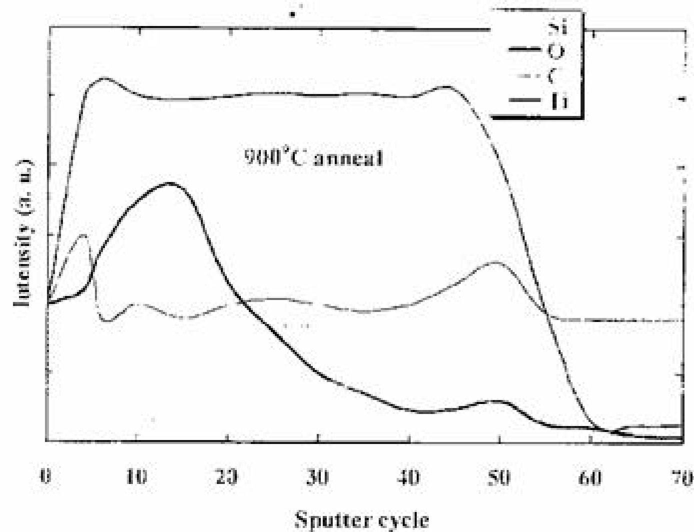

Fig.3. Depht profiles of the AES signals by Si,C,Ti, and O atoms for the Ti/3C-SiC/Si sample annealed at 900^0C.

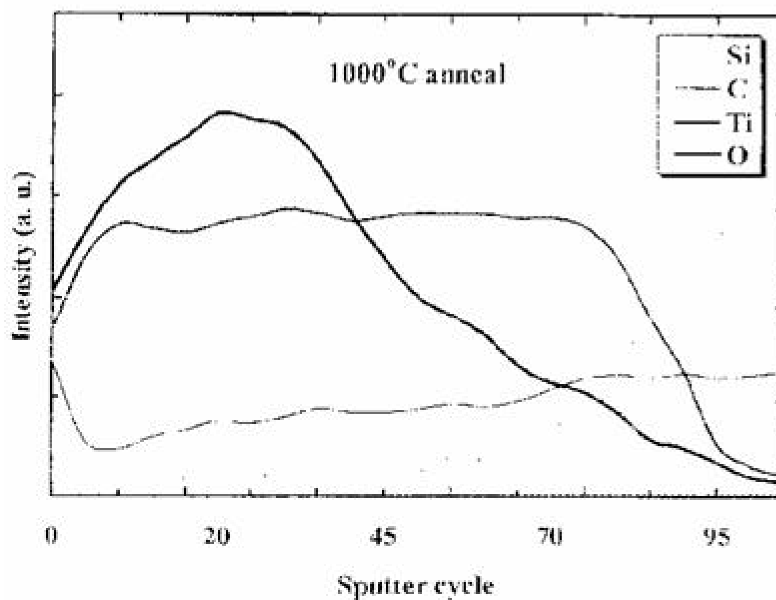

Fig.4. Depht profiles of the AES signals by Si,C,Ti, and O atoms for the Ti/3C-SiC/Si sample annealed at 1000^0C.

Figs.5 and 6 show the AES spectra of C_{KLL} and Si_{LMM}, respectively, at the interfacial region after the various annealing processing steps.Fig.5 shows that there is no observable titanium carbide (TiC) peak (shoulder[3]) for as-deposited samples.

After annealing at 600^0C the spectrum exhibits a noticeable TiC peak. At 700^0C, the peak increases drastically but does not change for anneals at temperatures from 700 to 900^0C.This indicated that there is no further formation of TiC above 700^0C ,as confirmed by XPS measurements.

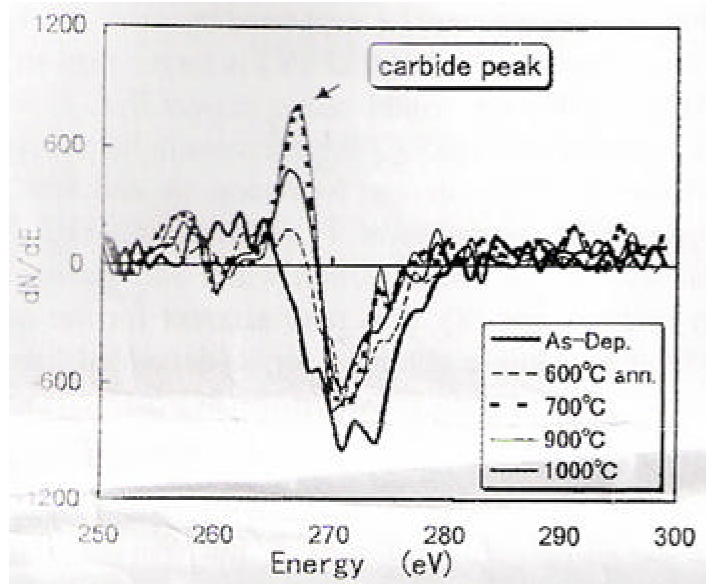

Fig.5. Auger electron spectra of the Ti/3C-SiC/Si system demonstrating the variation in the C 1s spectra at the interface with annealing temperature.

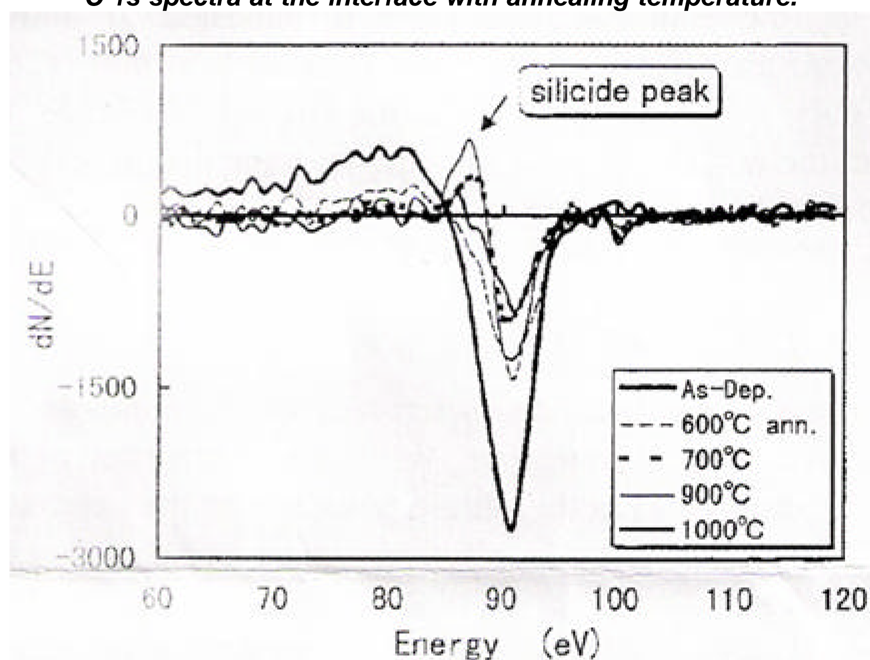

Fig.6. Auger electron spectra of the Ti/3C-SiC/Si system demonstrating the variation in the Si 2p spectra at the interface with annealing temperature

This is also consistent with the uniform distribution of C observed in the Auger depth profile above 700^0C.At 1000^0C, the peak shrinks indicating a decrease in the carbide formation.

According to the Auger depth profile (fig.4), Auger spectra, and XPS data, the decrease in TiC was due to a dramatic oxidation of titanium at 1000^0C.In fact, oxidation of titanium occurred at less than 1000^0C but becomes more significant at 1000^0C as can be understood by comparing figs. 3 and 4.

Fig.6 shows that the titanium silicides peak, assumed as the peak shoulder, is absent at 600^0C which indicates that there are no titanium silicides formed at this temperature. By annealing at 700^0C, the peak of silicides appears very clearly. However, contrary to TiC, the peak intensity of titanium silicides continues to increase with temperature until 900^0C indicating a further increase in silicides. At 1000^0C, the peak shrinks due to Ti oxidation as seen for the TiC. For the TiC peak no significant changes with temperature were observed.

The above results indicate that, first; the change from the rectifying to the ohmic behavior observed in the I-V profile at 600^0C is due to the formation of titanium carbide, the only interfacial change at this temperature. Second, the step decrease in R_c at above 700^0C can be attributed to the nucleation of silicides and not carbide. This is because the presence of titanium carbide throughout the whole upper film at 700^0C, as revealed by Auger depth profile, did not produce the lowest R_c. In contrary, R_c continues to decrease as long as the silicides continue to increase above 700^0C.

3.3. X-RAY DIFFRACTION MEASUREMENTS

The change of the crystallographic structure at the interface due to annealing was studied by XRD experiments. The results obtained for the various annealing temperatures are shown in Fig.7.

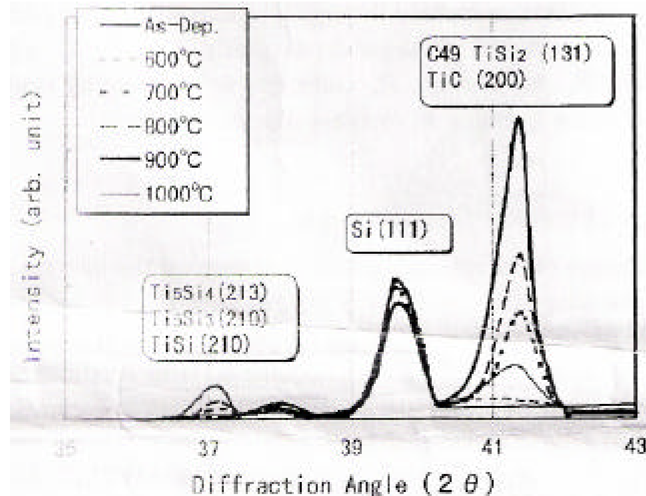

Fig.7. Variation of X-ray diffraction patterns of the Ti/3C-SiC/Si system with annealing temperature.

The disilicide C49 $TiSi_2$ encountered here crystallizes in the cubic structure C49 [4].According to Bragg reflections, the lines of C49 $TiSi_2$ (131) and TiC (200) occurred around the same reflection angle of 41.4^0. The lines of Si (111) and the silicides [Ti_5Si_4 (213), Ti_5Si_3 (210),and TiSi(210)] occurred at 39.7^0 and 37.2^0,respectively.The Si line observed in fig.7 is from the silicon substrate while the other lines are due to the compounds formed upon thermal annealing. At 600^0C,the carbide peak is not clear although the carbide was confirmed from the Auger C_{KLL}, XPS C 1s, and Ti $2p_{3/2}$ spectra. This is because the carbide layer

is not thick enough (<200?) at this temperature as revealed by the Auger depth profile. This indicates that AES is very effective in detecting chemical changes at the interface. A mixture of metastable silicide phases (left hand) such as TiSi, Ti_5-Si_3, and Ti_5Si_4 are detected from 700^0C and continue to grow with temperature up to 900^0C in agreement with the Auger and XPS data. This indicates that the threshold for silicidation in Ti/3C-SiC is 700^0C.

The presence of several compound phases is not surprising in view of the fact that the interfacial concentration prior to annealing ranges from the pure SiC to pure Ti, covering thus the whole phase diagram. The intensity of the main peak (right hand) shows major changes with annealing temperature. This peak can be assigned to either the C49 $TiSi_2$ or TiC [4].However, since AES and XPS data analyses showed that the carbide did not change above 700^0C, we assign the changes above 700^0C to C49 $TiSi_2$. This result is not in line with that obtained in Zr/Si systems where the crystallization of the silicide ($ZrSi_2$) at the interface by high-temperature annealing brought about an increase in the contact resistance [5].For 1000^0C anneal the entire silicide peak intensities decrease in agreement with AES and XPS results. This is associated with the observed increase in R_c.

Fig. 8. compares the variation of the contact resistance and the intensity of the XRD C49 $TiSi_2$ peak with the annealing temperature. It is clear that the contact resistance follows closely the variation in C49 $TiSi_2$ peak intensity. This indicates that the formation of C49 $TiSi_2$ is the step limiting the contact resistance lowering in the Ti/3C-SiC system. Annealing in a better vacuum than 10^{-5} Torr is expected to improve the contact resistance above 900^0C by favoring silicidation and reducing oxidation since Ti has a large affinity to oxygen ($Hf(TiO_2) = -72.0$ kcal/mol < $Hf(TiSi_2) = -10.7$ kcal/mol) [5],[6].

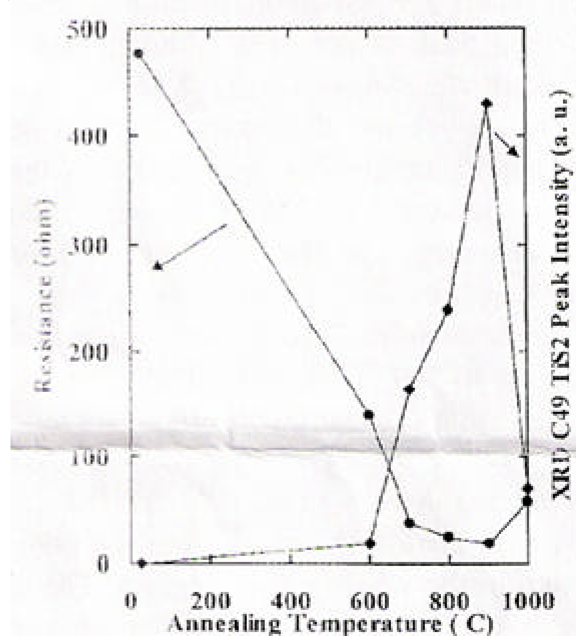

Fig.8. Correlation of the measured intercontact resistance with the XRD peak intensity of interfacial C49 $TiSi_2$ as a function of annealing temperature in the Ti/3C-SiC/Si system.

On the other hand, since the peak shoulder in the Auger Si spectrum (fig.6) follows closely the changes of the XRD peak intensities of the Ti silicides, that shoulder is effectively associated with Ti silicides as assumed before. This indicates that changes of TiC and Ti silicides with annealing temperature can unambiguously be understood from C and Si Auger spectra alone.

3.4. X-RAY PHOTOELECTRON SPECTROSCOPY

The XPS measurements show that chemical shifts of Ti $2p_{3/2}$ and C 1s peaks compared to the bulk in a Ti/SiC system due to carbide formation by annealing at above 600^0C are +1.0 and -3.3 eV, respectively. While the shifts of Ti $2p_{3/2}$ and Si 2p due to silicidation by annealing at above 700^0C are +0.6 and -0.6 eV, respectively. These energy shifts are in good agreement with the reported values [7] - [9] for metal/Si systems. This suggests that the bonding nature in metal/Si is similar to that in the metal/3C-SiC system.

3.5. SCHOTTKY BARRIER MEASUREMENTS

The Schottky barrier height in the Ti/3C-SiC system was also examined. It was found that the effective barrier height measured for the as-deposited contacts is 0.53 +/- 0.01 eV. After annealing at 900^0C, the barrier height decreases to 0.44 +/-
0.01 eV. This decrease cannot be explained by work functions. Since the work function of Ti (4.33 eV) is larger than that of $TiSi_2$ (5.54 eV) [10],we would rather expect that Ti forms ohmic contacts better than $TiSi_2$.The decrease in barrier height can be attributed to the defect formation at and near the SiC surface via the formation of Ti silicides and TiC. Such defects can also narrow the depletion width and increase the probability of tunneling [8].This may account for the nearly linear I-V characteristic obtained for as-deposited samples since their are a lot of defects within the 3C-SiC surface. A closer examination involving high-resolution techniques (e.g., HRTEM) is necessary to investigate the lateral microstructure (e.g., cellular, precipitates) of the interface region.

Thermal aging experiments were carried out to study the stability of the contacts. The contacts annealed at above 700^0C were able to withstand more than 20h at 600^0C in air with only a 15-25% increase in the contact resistance. In particular, the results obtained foe samples annealed at 900^0C are reproducible and showed quite a small scatter.

4. CONCLUSIONS

In summary, electrical characteristics of Ti contacts on 3C-SiC have been investigated. While the formation of titanium carbide improves the ohmic behavior of the contacts, the strong reduction of the contact resistance has been traced back to the formation of crystalline silicide C49 $TiSi_2$.The formation of this silicide occurred by annealing at above 700^0C.The lowest contact resistance was obtained for 900^0C anneal. Annealing at a higher temperature of 1000^0C

unexpectedly increases the contact resistance. This is attributed to a dramatic oxidation of titanium at this temperature. We believe that annealing in a vacuum better than 10^{-5} Torr improves further the contact resistance. The peak associated with the titanium silicides in the Auger Si spectrum was identified. The Schottky barrier height decreases from 0.53 to 0.44 eV upon annealing possibly due to defects at the interface produced via the formation of Ti silicides and Ti carbide. The contacts obtained at above 700^0C are reliable and can withstand more than 20h at 600^0C.

REFERENCES

[1] Int. Workshop Hard Electron. Abstr.,AIST, Tsukuba Research Center, Tsukuba, Japan, Feb. 17-18,1997.
[2] Tech. Dig. Int. Conf. SiC and Rel. Mater. ICSCRM'95,Kyoto,Japan,1995,pp. 140-155 , 377-378.
[3] K.L.Moazed,"Metal/semiconductor interfacial reactions",Metallurgical Trans.A,vol. 23A, pp.1999-2006 ,1992.
[4] I.J.H.M.Raajmakers, A.H.Reader, and P.H.Oasting,"The formation of an amorphous silicide by thermal reaction of sputter-deposited Ti and Si layers", J.appl. Phys.,vol.63,pp. 2790-2795,1998.
[5] T.Yamauchi, S.Zaima, K.Mizuno, H.Kitamura, Y.Koide, and Y.Yasuda,"Solid-phase reactions and crystallographic structures in Zr/Si system.", J.Appl.Phys., vol.69, pp. 7050-7056,1991.
[6] "Solid phase reactions and electrical properties in Zr/Si system.", J.Appl.Phys.Lett., vol.57, pp.1105-1107,1990.
[7] V.Venkatesan, D.M.Malta, and K.Das."Evaluation of ohmic contacts formed by B+ ion implantation and Ti-Au metallization on diamond",J.Appl.,Phys.,vol.74,pp. 1179-1187,1993.