

# **Solid state reaction and operational stability of ruthenium Schottky contact-on-6H-SiC under argon annealing**

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## **Abstract**

Thin films of ruthenium-on-6-hexagonal silicon carbide (6H-SiC) were analysed by Rutherford backscattering spectroscopy (RBS) at various annealing temperatures. Some thin film samples were also analysed by scanning electron microscope (SEM). RBS analysis indicated minimal element diffusion, and formation of ruthenium oxide after annealing at 500 °C. Large scale diffusion of ruthenium (Ru) was observed to commence at 700 °C. The SEM images indicated that the as-deposited Ru was disorderly and amorphous. Annealing of the thin film improved the grain quality of Ru. The fabricated Ru-6H-SiC Schottky barrier diodes (SBD) with nickel ohmic contacts showed excellent rectifying behaviour and linear capacitance-voltage characteristics up to an annealing temperature of 900 °C. The SBDs degraded after annealing at 1000 °C. The degradation of the SBDs is attributed to the inter-diffusion of Ru and Si at the Schottky-substrate interface.

## **Keywords**

Rutherford backscattering spectroscopy, scanning electron microscope, diffusion, Schottky barrier diodes, ruthenium, ruthenium oxide, 6H-SiC, nickel.

## 1. Introduction

Silicon carbide (SiC), when compared with silicon, has superior qualities of a large band gap, high breakdown electric field, high thermal conductivity, high saturation carrier velocity, and high mechanical strength. It is for these reasons that there is renewed interest among researchers to produce SiC-based diodes and electronic devices that can operate in extreme temperature conditions such as avionics, microwaves, high voltage switching, deep sea wells and space rockets. There are several polytypes of SiC, but the two main polytypes used for semiconductor device fabrication are 4-hexagonal SiC (4H-SiC) and 6-hexagonal SiC (6H-SiC). SiC's properties of a high breakdown electric field ( $2.2 \times 10^6$  V/cm for 4H-SiC,  $2.4 \times 10^6$  V/cm for 6H-SiC) and high thermal conductivity (4.9 W/cmK for 6H and 4H) are ideal for high voltage, high power and high packing density of discrete electronic devices [1]. Ruthenium (Ru) has a high melting point ( $2250^\circ$  C), high chemical stability, low electrical resistance, and high mechanical resistance to abrasion and fatigue [2]. These properties make Ru a good candidate as a Schottky contact for high temperature operating Schottky barrier diodes (SBDs). However there has been limited literature [1,2,3,4,5,6, 7] on the performance of Ru on SiC Schottky diodes, and the limited literature has not delved much into the details of the solid state reaction of Ru with SiC during the annealing process.

In this experiment the Ru-6H-SiC SBDs with nickel back ohmic contacts were annealed in argon at various temperatures. The data on variation of SBH, ideality factor, reverse-saturation current and series resistance with annealing temperature were obtained from the current-voltage (IV) and capacitance-voltage (CV) characteristics of the diode. For microstructure characterisation of the Schottky contact, a thin film of Ru on 6H-SiC was analysed with Rutherford Backscattering Spectrometry (RBS) and scanning electron microscope (SEM) at various annealing temperatures.

## 2. Experimental Method

The preparation of metal-SiC interfaces has a critical effect on the physical, chemical and electrical behaviour of the contact, and on its reliability. Experiments have shown that the electrical performances of Schottky contacts on SiC, in addition to physical and chemical properties are strongly dependent on the quality of the metal–semiconductor interface and the surface preparation prior to metallization [8].

The n-type 6H-SiC from Cree Research was prepared for metallization by degreasing, using an ultra-sonic bath for a period of 5 min for each step, in trichloroethylene, acetone, methanol, and deoxidizing 10% HF. The

sample was finally rinsed in deionised water and then dried with nitrogen before being loaded into the vacuum chamber where 200nm of nickel (Ni) was deposited by vacuum resistive evaporation. The sample was then annealed in a nitrogen atmosphere at a temperature of 1000°C for 1 min to make the contact ohmic. The annealed sample was chemically cleaned again in trichloroethylene, acetone and methanol, and deionised water before a 50 nm thick of Ru was deposited by e-beam through a metal contact mask at  $10^{-6}$  mbar pressure. The Ru film thickness was monitored by Infincon meter until the required thickness was obtained. A number of Schottky contacts of 0.6mm in diameter were fabricated. The SBDs produced were then annealed in argon.

The sample for microstructure characterisation was made by depositing a 50 nm film of Ru on 6H-SiC. Before deposition of the Ru film, the 6H-SiC sample was cleaned through the steps mentioned in the paragraph immediately above.

The Ru-6H-SiC Schottky diodes were annealed in argon for a period of 15 min at temperatures ranging from 100°C to 1000°C. Full IV and CV characterisation of the diodes was performed at an ambient temperature of 24°C after each annealing process, using a 4140B PA meter /DC voltage source by Hewlett Packard, which was interfaced to a LabVIEW-operated computer. The CV measurements were done at a frequency of 1MHz. Both the IV and CV measurement data were automatically saved on the computer by LabVIEW.

The sample for microstructure characterisation was also annealed in argon at various temperatures, and RBS analysis was performed at room temperature after each annealing process. SEM images of the as-deposited thin film of Ru-6H-SiC and the one annealed at 500 °C were also taken.

### **3. Experimental Results and Discussion**

RBS analysis of as-deposited Ru-6H-SiC thin film shows a pure film of Ru on the SiC (Fig. 1). The RBS spectra for samples annealed up to 400 °C (not shown) are similar to the as-deposited spectrum. Oxidation of Ru is observed at an annealing temperature of 500 °C (Fig. 2) as evidenced by a pronounced oxygen peak at channel 182. Diffusion of Ru into the SiC layer is seen to commence at 700 °C (Fig. 3), as indicated by the widening of the base width of the Ru signal. There is increased oxidation of Ru at this temperature as demonstrated by a

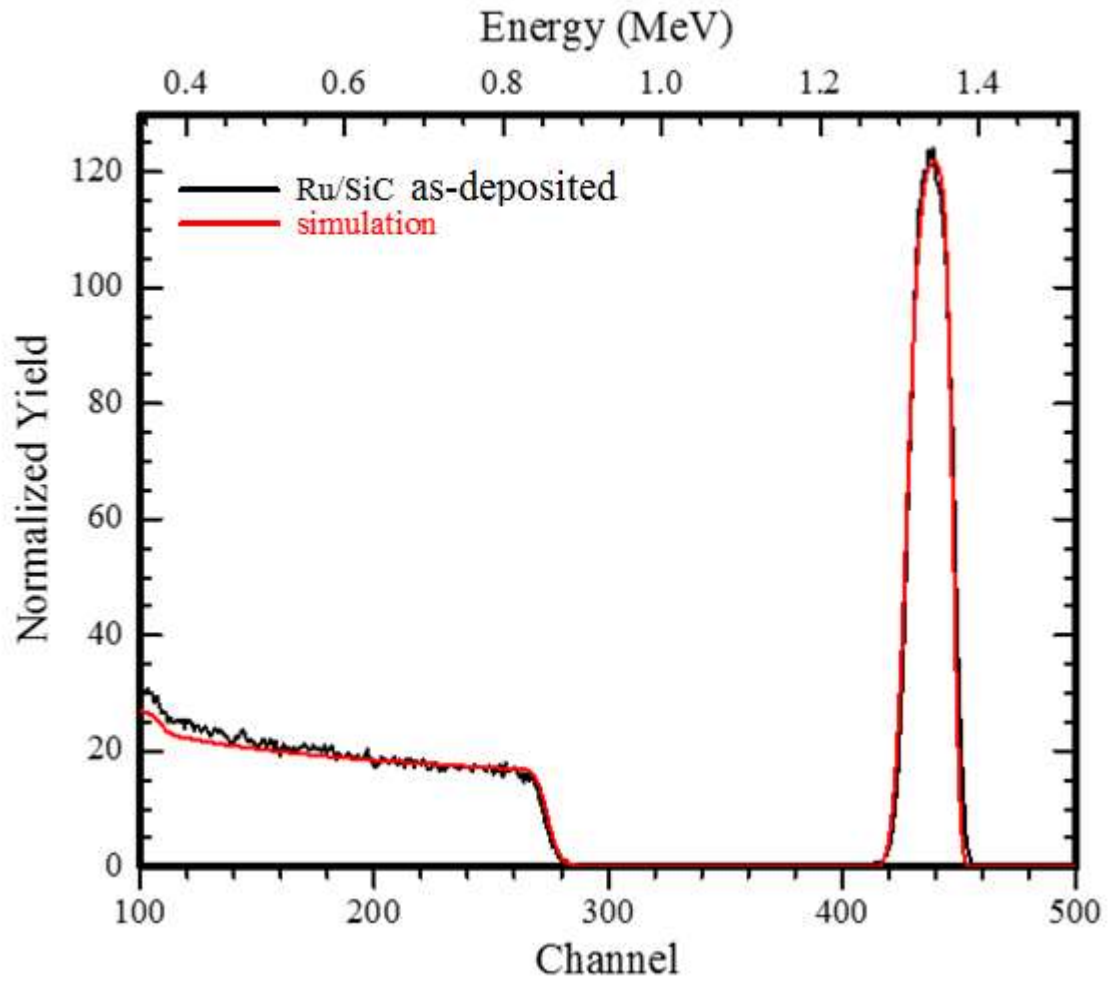


Fig. 1. RBS spectrum of thin film of as-deposited Ru-6H-SiC obtained by using 1.6 MeV helium ions.

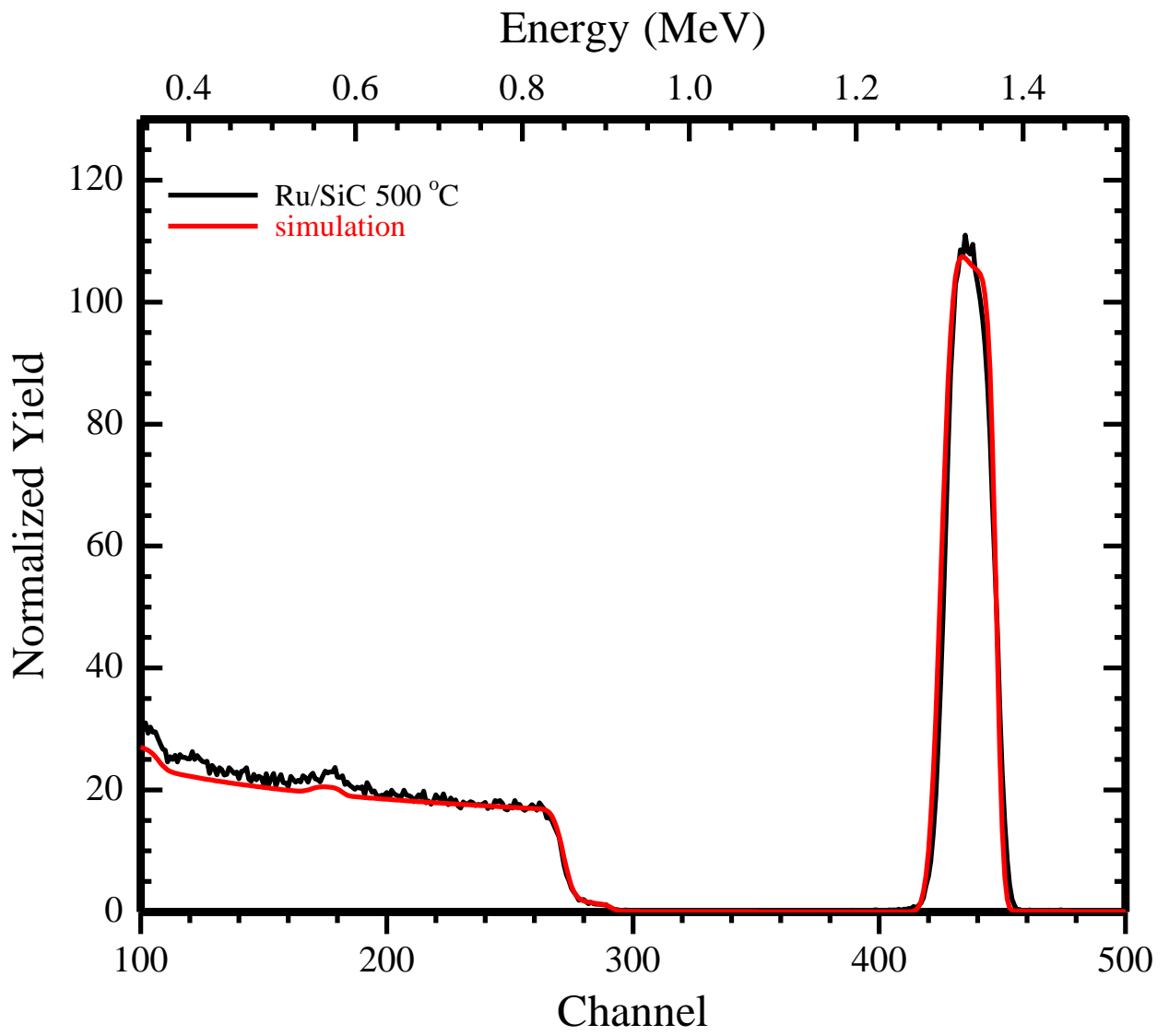


Fig. 2. RBS spectrum of thin film of Ru-6H-SiC annealed in argon at 500 °C obtained by using 1.6 MeV helium ions.

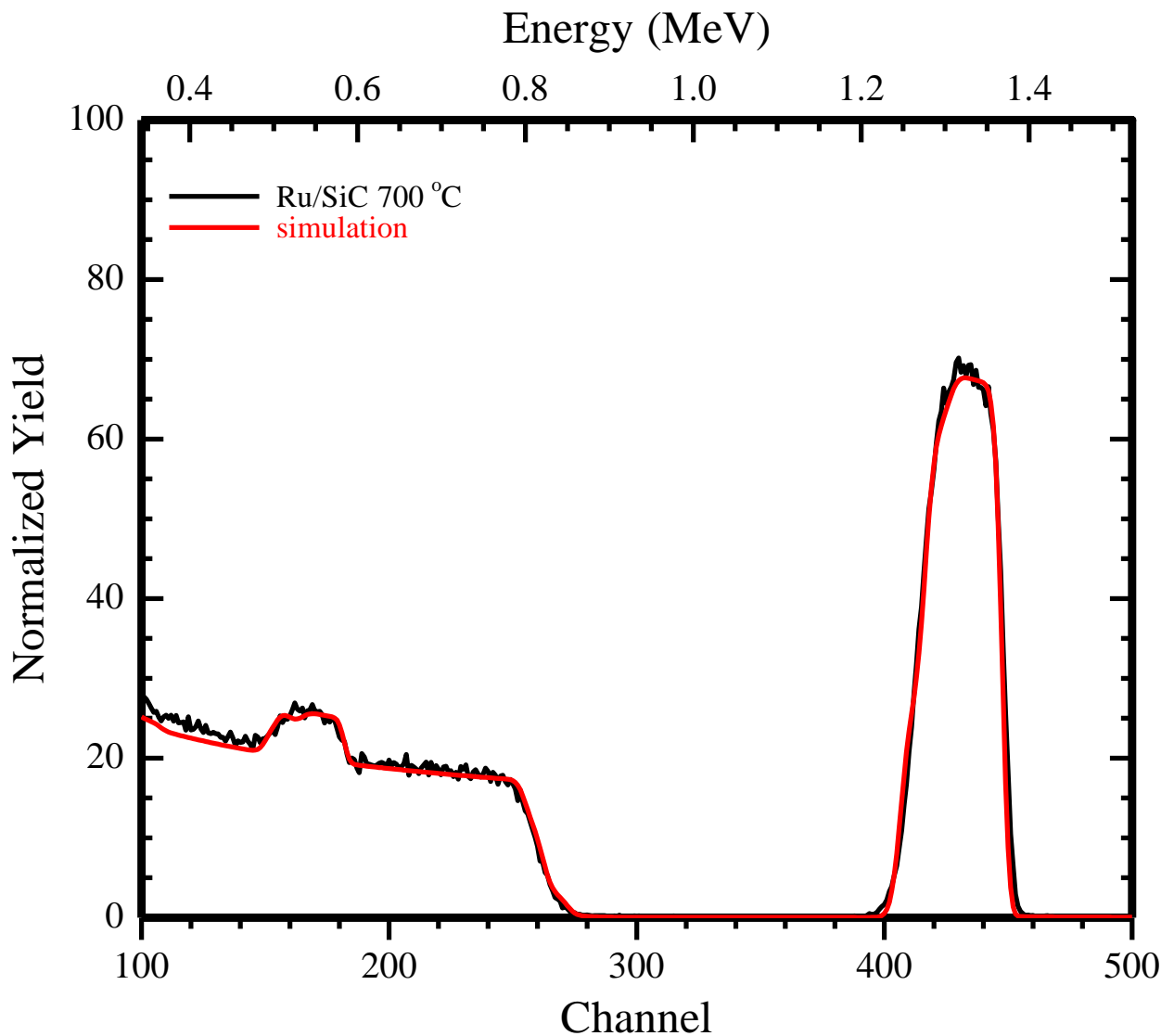


Fig. 3. RBS spectrum of thin film of Ru-6H-SiC annealed in argon at 700 °C obtained by using 1.6 MeV helium ions.

larger oxygen peak. At 1000 °C, it is observed that the interdiffusion of Ru and Si is very deep as indicated by the wide base of the Ru signal and the appearance of the Si at its surface energy position (Fig. 4).

The RBS spectra were simulated using the iterative software RUMP. The simulated spectra have been included together with raw RBS spectra (Fig1-Fig 3). The RBS charging current exhibited some instability during the analysis of the sample annealed at 1000 °C, and therefore its spectrum was not simulated. The simulations were performed by varying the composition of Ru, Si, C and O in a layer-by-layer manner to obtain a good fit. From these simulated spectra, the composition profiles were obtained. It can be observed that the simulated spectra fit well with the raw spectra which indicates that the simulations are a good representation of

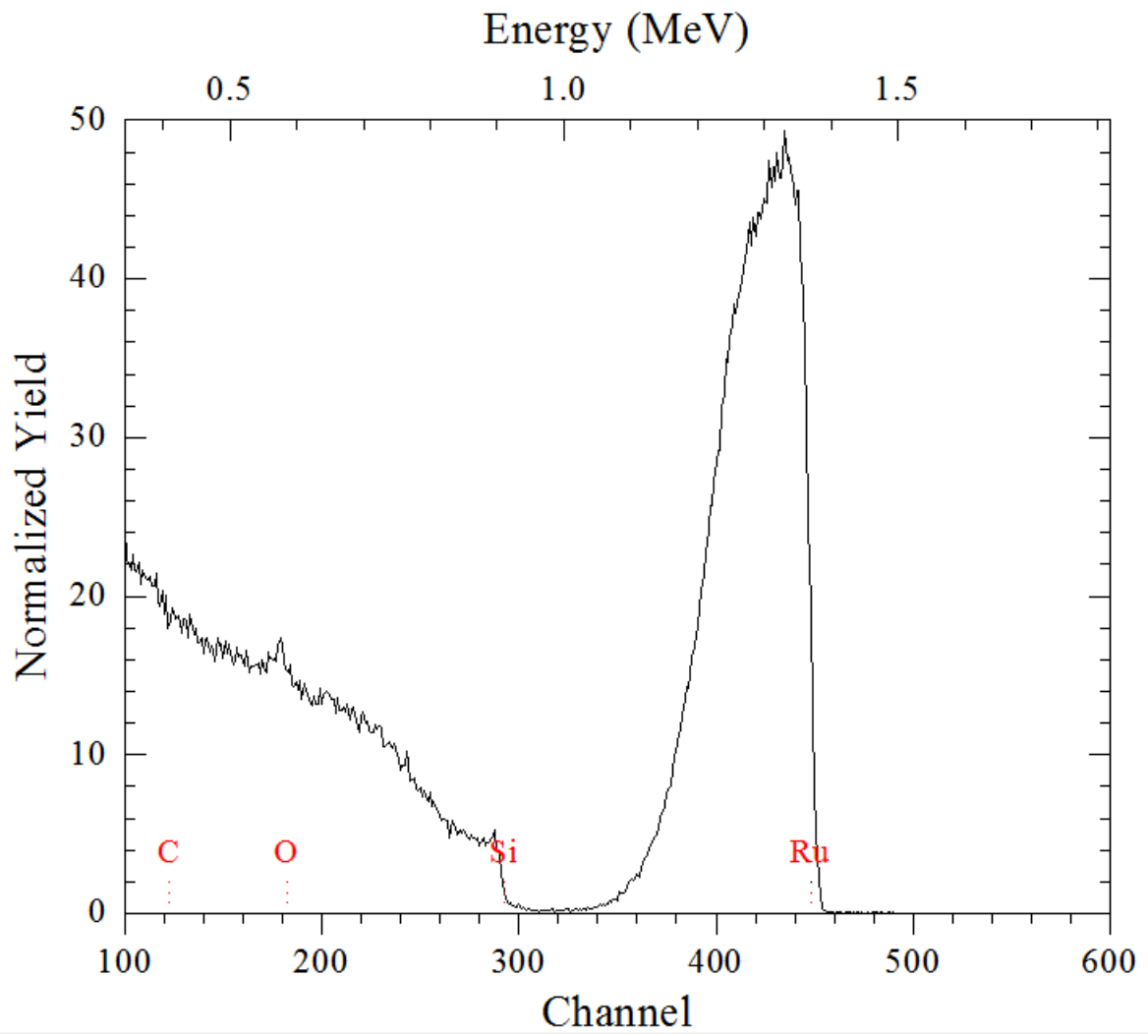


Fig. 4. RBS spectrum of thin film of Ru-6H-SiC annealed in argon at 1000 °C obtained by using 1.6 MeV helium ions.

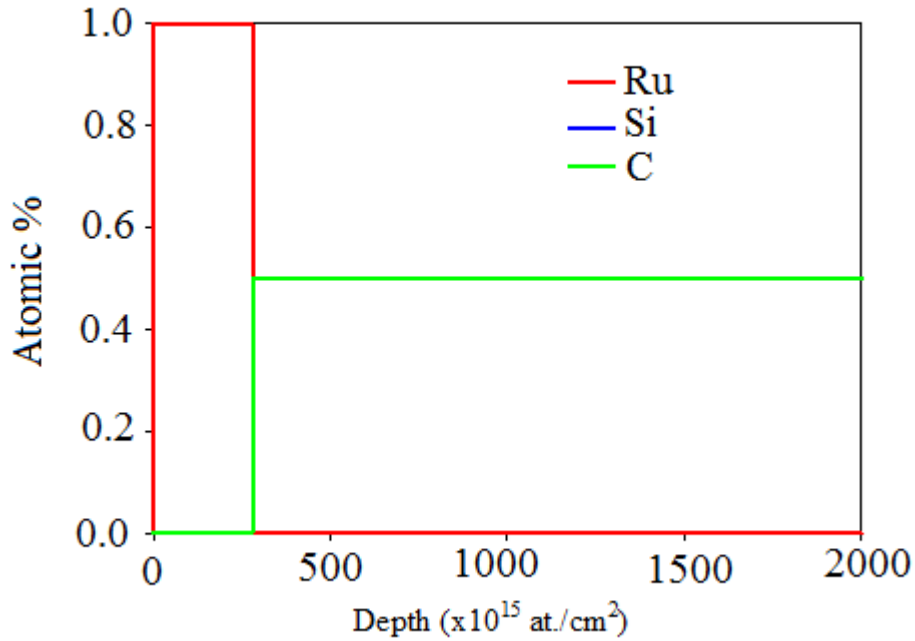


Fig. 5. Depth profile of as-deposited Ru-6H-SiC

the raw RBS spectra. These simulations show that the as-deposited Ru-6H-SiC interface is located at  $280 \times 10^{15}$  at./cm<sup>2</sup> (Fig. 5). Oxidation and minimal Ru, Si and C interdiffusion begin at an annealing temperature of 500 °C (Fig. 6). Oxidation and elements interdiffusion are observed to increase with annealing temperature (Fig. 7 and Fig. 8), such that Ru is found at a depth of  $1100 \times 10^{15}$  at./cm<sup>2</sup> and  $1380 \times 10^{15}$  at./cm<sup>2</sup> at annealing temperatures of 700 °C and 900 °C respectively.

SEM was used to analyse the as-deposited thin film sample and the sample annealed at 500 °C to identify structural changes that took place during the annealing process. From the SEM images one can clearly see that the as-deposited thin film (Fig. 9) of Ru is rough, disorderly and therefore amorphous, while the sample annealed at 500 °C (Fig. 10) is smooth which is an indication of the improvement in the grain quality of Ru or the microcrystalline nature of the ruthenium oxide (RuO<sub>2</sub>) formed during the annealing process.



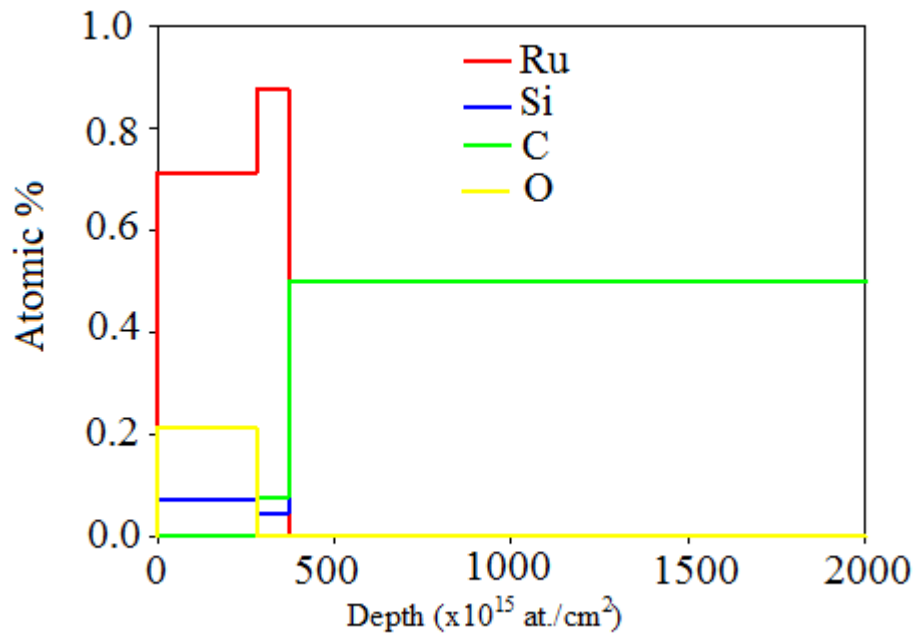


Fig.6. Depth profile of Ru-6H-SiC annealed in argon at 500 °C

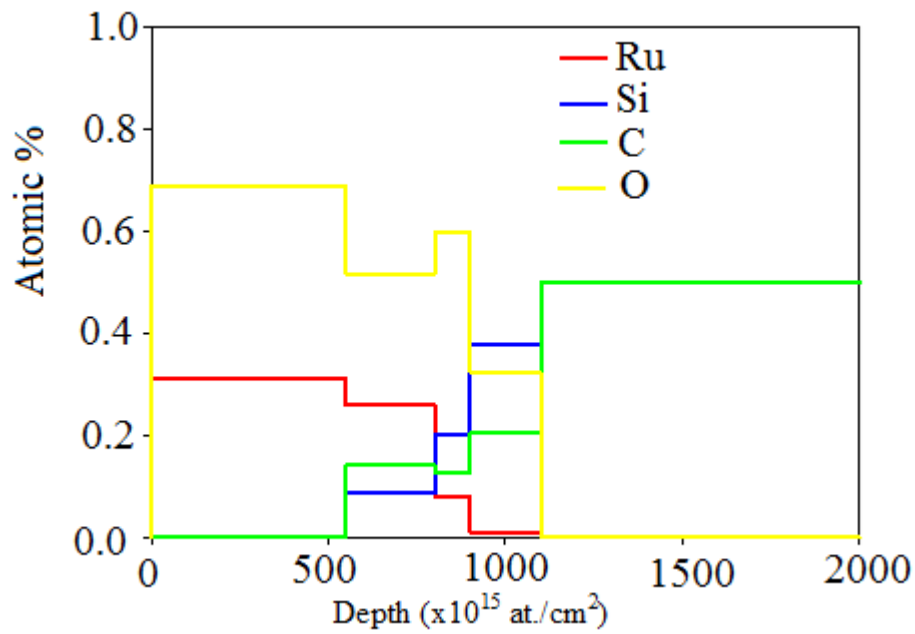


Fig.7. Depth profile of Ru-6H-SiC annealed in argon at 700 °C

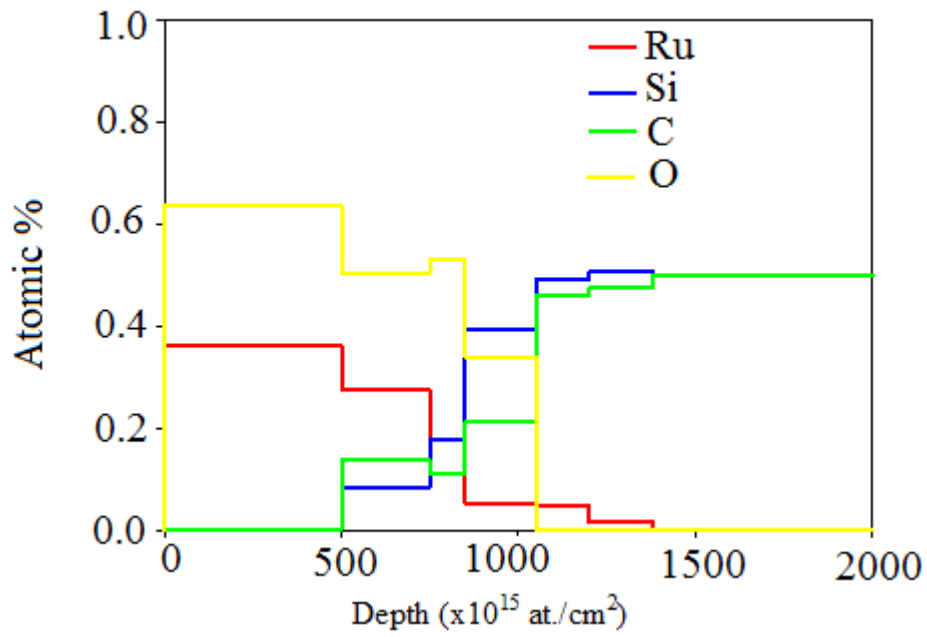


Fig.8. Depth profile of Ru-6H-SiC annealed in argon at 900 °C

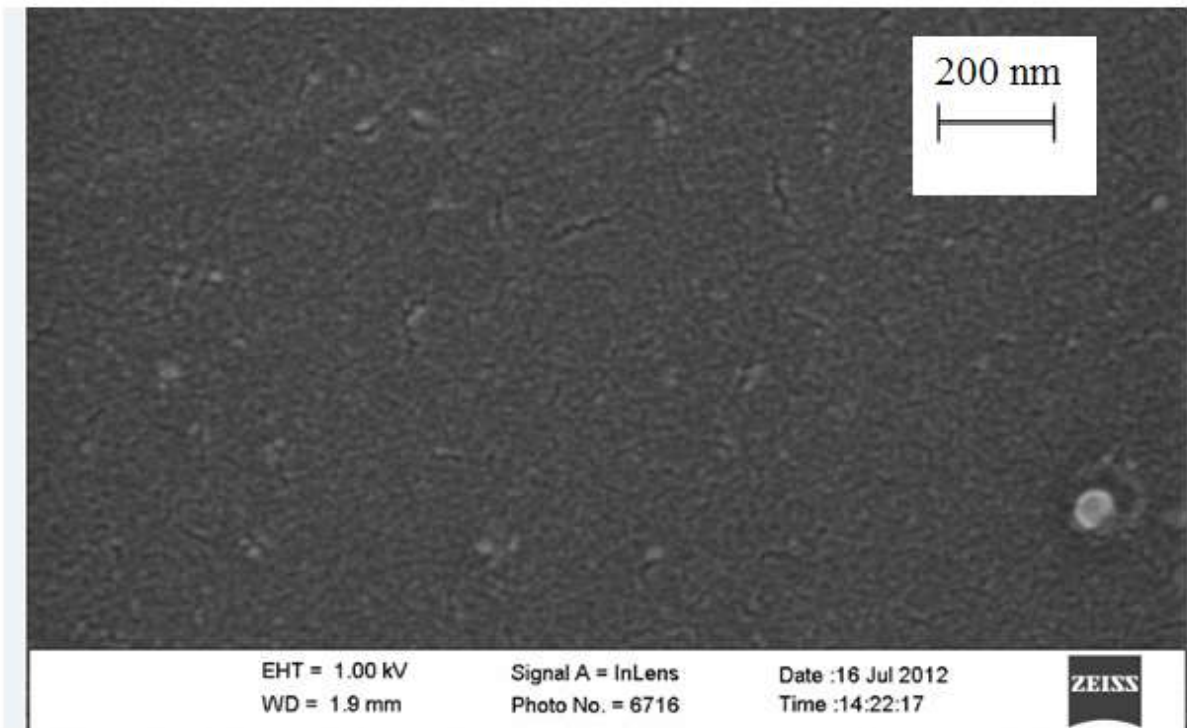


Fig. 9. SEM image of as-deposited thin film of Ru-6H-SiC

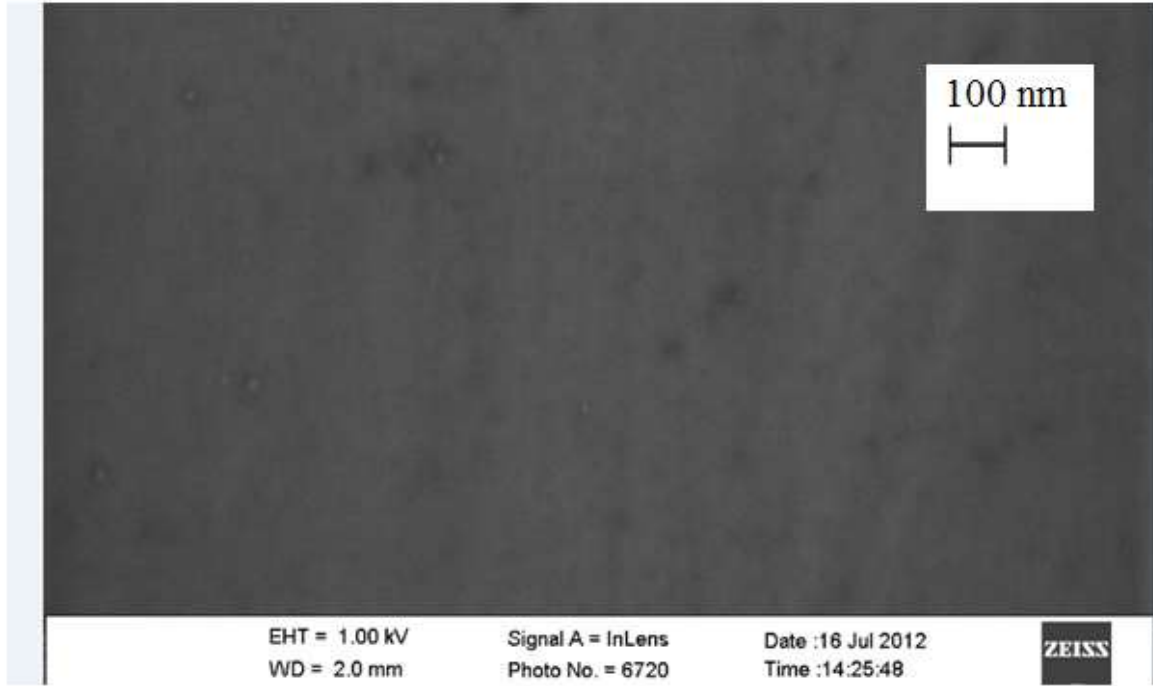


Fig. 10. SEM image of thin film of ruthenium on 6H-SiC annealed in argon at 500 °C.

The Ru-6H-SiC Schottky diodes were evaluated using IV and CV characteristics. The Schottky barrier height (SBH),  $\phi_{Bn}$ , ideality factor,  $\eta$ , and reverse saturation current  $I_s$  were obtained from IV characteristics by assuming that the Schottky diode obeys the thermionic emission model [9] given by equation (1) below.

$$J = J_s (e^{\frac{qV}{\eta kT}} - 1) \quad (1)$$

where

$$J_s = A^* T^2 e^{-\frac{q\phi_{Bn}}{kT}} \quad (2)$$

where  $J_s$  is the reverse saturation current density,  $T$  is absolute temperature in Kelvin,  $k$  is the Boltzmann constant,  $q$  is the absolute amount of charge on an electron, and  $A^*$  is the Richardson constant which is equal to  $72 \text{ Acm}^{-2}\text{K}^{-2}$  for 6H-SiC.

Series resistance  $R_s$  is the resistance of the bulk material of the semiconductor plus that of the back ohmic contact. To account for the series resistance equation (1) is modified to the following equation

$$J = J_s \left[ e^{\frac{q(V-IR_S)}{\eta kT}} - 1 \right] \quad (3)$$

The parameters from CV characteristics are obtained from the junction capacitance of the SBD [9] given by

$$C = \sqrt{\frac{q\epsilon_s N_D}{2(V_{bi}-V)}} \quad (4)$$

$$\frac{1}{C^2} = \frac{2(V_{bi}-V)}{q\epsilon_s N_D} (Fcm^{-2})^{-2} \quad (5)$$

A plot of  $\frac{1}{C^2}$  versus V will give a straight line, and a donor doping density  $N_D$  can be extracted from the graph. The SBH is determined from the voltage intercept by the following equation

$$\phi_{Bn} = V_i + V_o \quad (6)$$

where  $V_i$  is the voltage intercept, and

$$V_o = \frac{kT}{q} \ln \left( \frac{N_C}{N_D} \right) \quad (7)$$

where  $N_C$  is the effective density of states in the conduction band of 6H-SiC.  $N_C$  is equal to  $8.9 \times 10^{19} \text{ cm}^{-3}$  for 6H-SiC at 300K [10].

Table I shows the parameters that were extracted after annealing the Ru-6H-SiC diodes in argon.

According to Table I, that the ideality factor and SBH (obtained from IV characteristics) show very small variation with increasing annealing temperature. The fact that the ideality factor is slightly higher than the ideal value may be attributed to current flow not being by thermionic emission only, some tunnelling effects and recombination currents might be involved as well.

The SBHs obtained from CV characteristics were slightly higher than those from IV characteristics. Normally SBH obtained from CV measurements are slightly higher than those obtained from IV characteristics because there might be an additional capacitance at the metal-semiconductor interface due to the presence of a thin oxide, which develops as a result of surface preparation [10]. The variation of SBH as observed in the table may be attributed to the presence of an inhomogeneous barrier at the metal semiconductor interface. According to Osvald *et al* [11], SBH inhomogeneity may be due to the fact that there are different crystallographic

**Table I. Parameters of Ru-6H-SiC schottky diodes at various annealing temperature**

<b>Annealing temperature</b>	<b>Ideality factor (<math>\eta</math>)</b>	<b>SBH from <math>I</math>-<math>V</math> (eV)</b>	<b>SBH from <math>C</math>-<math>V</math> (eV)</b>	<b>Series resistance <math>R_s</math> (<math>\Omega</math>)</b>	<b>Saturation current <math>I_S</math> (A)</b>	<b>Donor density <math>N_D</math> (<math>\text{cm}^{-3}</math>)</b>
As dep	2.77	0.807	0.629	187.93	$7.39 \times 10^{-10}$	$1.62 \times 10^{18}$
100°C	2.165	0.784	0.582	174.87	$1.8 \times 10^{-9}$	$2.24 \times 10^{18}$
200°C	1.876	0.746	0.808	410.23	$8.1 \times 10^{-9}$	$2.85 \times 10^{18}$
300°C	1.995	0.775	0.986	461.79	$2.55 \times 10^{-9}$	$2.45 \times 10^{18}$
400°C	1.83	0.718	0.823	291.76	$2.39 \times 10^{-8}$	$2.73 \times 10^{18}$
500°C	1.655	0.757	0.94	461.79	$5.11 \times 10^{-9}$	$1.97 \times 10^{18}$
600°C	1.949	0.734	0.544	47.18	$1.29 \times 10^{-8}$	$2.79 \times 10^{18}$
700°C	1.616	0.847	0.639	113.63	$1.53 \times 10^{-10}$	$2.47 \times 10^{18}$
800°C	1.576	0.948	0.957	666.77	$3.02 \times 10^{-12}$	$2.35 \times 10^{18}$
900°C	2.05	1.167	1.827	578.58	$5.78 \times 10^{-16}$	$1.86 \times 10^{18}$

orientations of the grains in the polycrystalline structure of the metallic layer and there is also a possibility that the phase composition of the interface materials may change after annealing. Both arguments are highly applicable to this investigation as there is evidence, from RBS analysis, of formation of RuO<sub>2</sub> and Ru and Si interdiffusion at the interface at higher annealing temperatures as explained above. From the SEM images there is evidence of a change in the crystallinity of the Ru at higher annealing temperatures.

The series resistance exhibited some randomness in value after each annealing temperature. This randomness in the value of series resistance is supported by investigations of Chand [12], who in his research paper found that there is a random variation of series resistance of elementary diodes in inhomogeneous Schottky diodes. At 600 °C, the series resistance is observed to decrease to a low value of 47 Ω. RBS analysis of the thin Ru-6H-SiC film has indicated the formation of RuO<sub>2</sub> at this temperature. The SBH of RuO<sub>2</sub> on SiC of 0.88eV [1] does not explain this change in resistance. A comparison of the electrical resistivities of Ru and RuO<sub>2</sub>, which are 7.4 μΩcm (polycrystalline) and 35.2 μΩcm respectively, does not offer a plausible explanation of the decrease of series resistance as well. Jelenkovic *et al* [13] similarly observed the reduction of resistivity of Ru deposited on silicon after annealing at 400 °C in nitrogen, and they attributed the drop in resistivity to the improvement in grain quality of Ru films. The decrease in series resistance can be attributed to the improvement in the grain quality of Ru or the microcrystalline nature of the RuO<sub>2</sub> formed during the annealing process, as evidenced by the SEM images.

One can also note that there was little variation in SBH even after the formation of RuO<sub>2</sub>. One possible explanation of the small change in SBH variation is that the SBH of RuO<sub>2</sub> on SiC of 0.88 eV [14] is very close to the SBH of Ru on SiC.

A plot of  $\frac{1}{C^2}$  vs reverse voltage (Fig. 11) exhibits excellent linearity from the as-deposited diodes to the diodes annealed at the final annealing temperature of 900 °C. The linearity indicates the operational stability of the Schottky diodes at extremely high annealing temperatures. The doping density N<sub>D</sub> extracted from CV characteristics shows a slight variation at different annealing temperatures. This variation might be due to the variation in series resistance. According to Frojdh *et al* [15] a resistance in series with a capacitor makes the

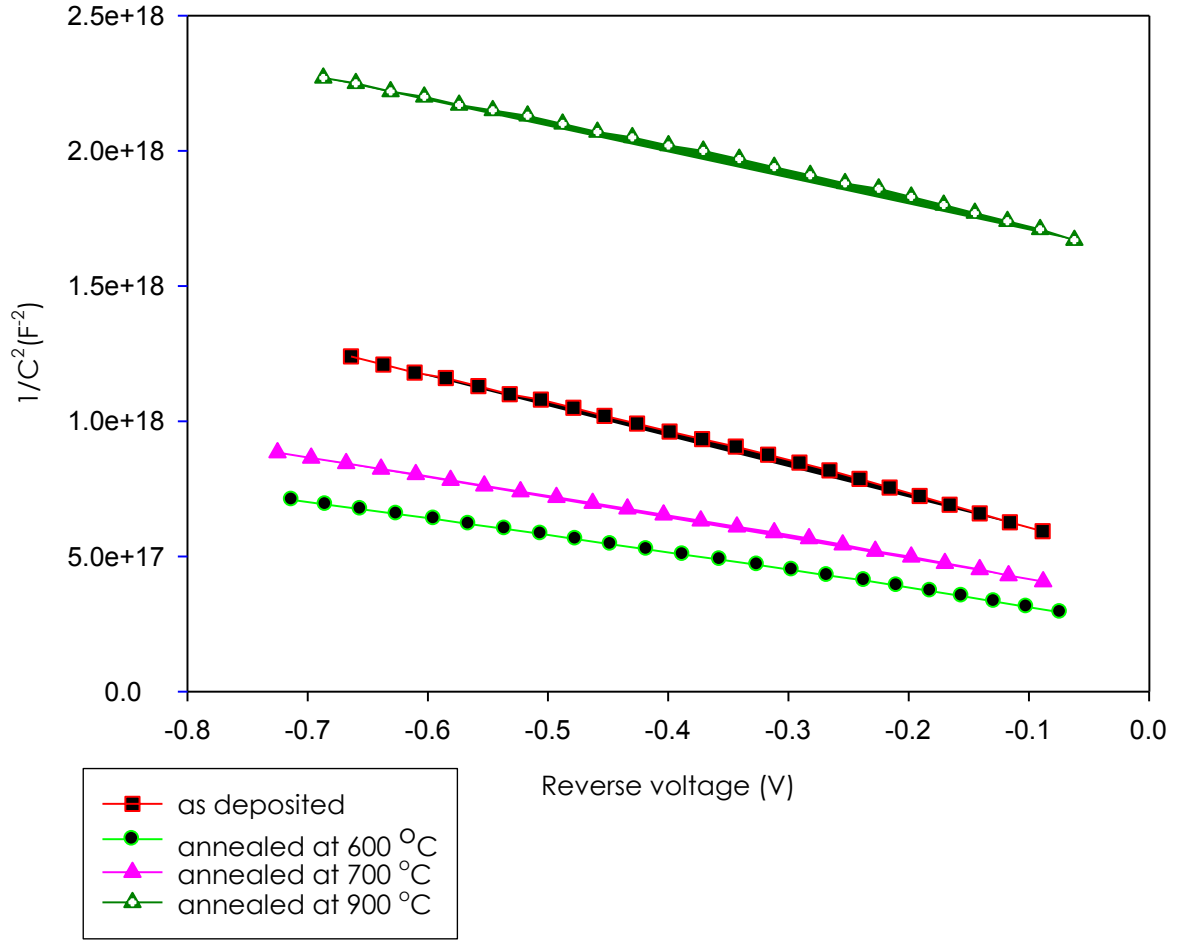


Fig. 11. A plot of  $1/C^2$  vs reverse voltage for Ru-6H-SiC SBDs annealed at various temperatures in argon

measured value of capacitance to decrease. From this assertion, an increase in series resistance will lead to a decrease in the capacitance measured. In this investigation the series resistance showed some randomness in its values which led to the variation of the capacitance which in turn led to the variation in the donor density extracted from the CV curves. Using equation (4) one gets

$$N_D = \frac{2(V_{bi}-V)C^2}{q\epsilon_s} \quad (8)$$

When comparing the values of series resistance and donor density in Table I, and then linking the values with equation (8), one should observe that for high values of resistance, the capacitance measured will be low and therefore  $N_D$  values extracted from the equation should be low as well. The data in Table I largely agrees with this view.

Furthermore the plot of  $1/C^2$  vs reverse voltage will give the space charge density in the depletion layer corresponding to the dopants that are electrically active. If the dopants are not electrically active (i.e have not ionised) then this method will not correctly find the dopant density [15]. The factory specification of  $N_D$  for the 6H-SiC wafer that was used in this investigation is  $9 \times 10^{14} - 1 \times 10^{19} \text{ cm}^{-3}$ . The results of  $N_D$  obtained in the investigation are well within the range of the specification.

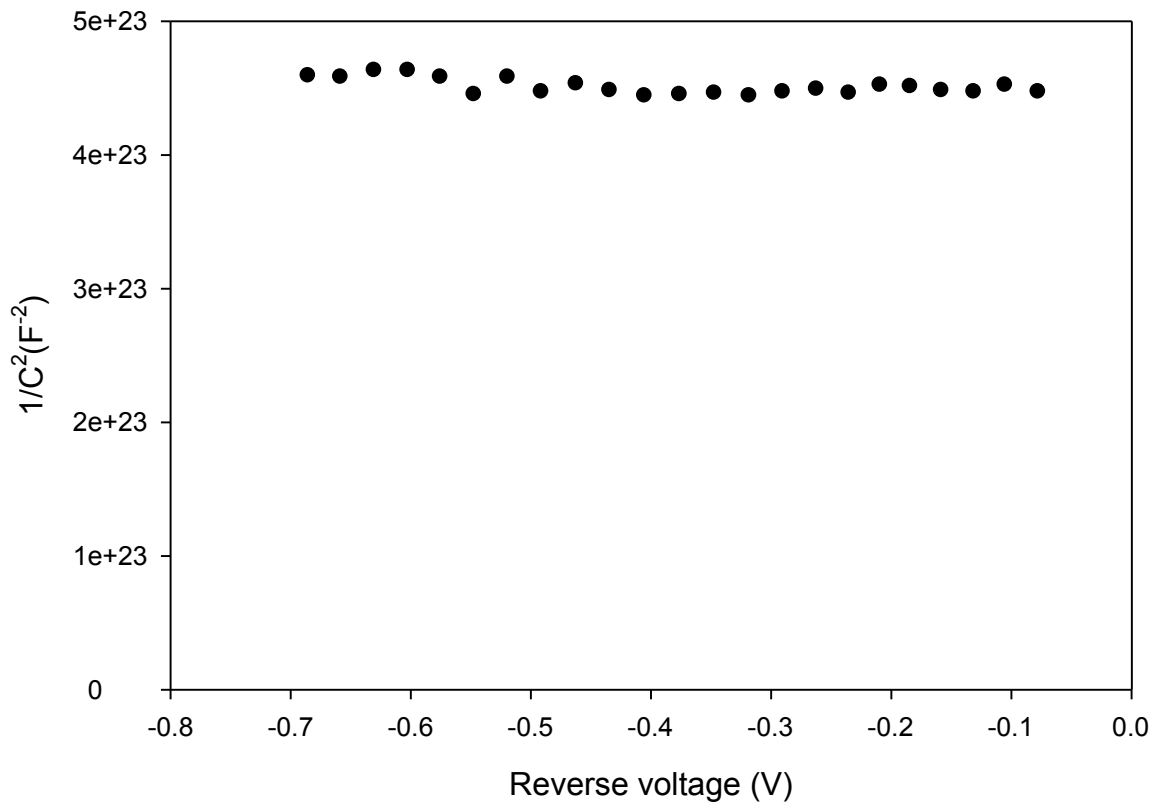


Fig. 12. A plot of  $1/C^2$  vs reverse voltage for Ru-6H-SiC SBDs annealed in argon at 1000 °C

The forward IV characteristic for the Schottky diodes (Fig. 13) showed good rectification behaviour. The Ru-6H-SiC schottky diodes degraded when they were annealed at 1000 °C as evidenced by a non-linear CV graph (Fig 12). Fig 12 was plotted separately from Fig 11 because the inverse square values of capacitance were very much larger at 1000 °C than at other annealing temperatures. The degradation of the Schottky diode can be attributed to the deterioration of the Ru Schottky contact due to the inter-diffusion of Ru and Si at the Ru-6H-SiC interface as indicated by RBS analysis of the sample (Fig. 4) at 1000 °C.



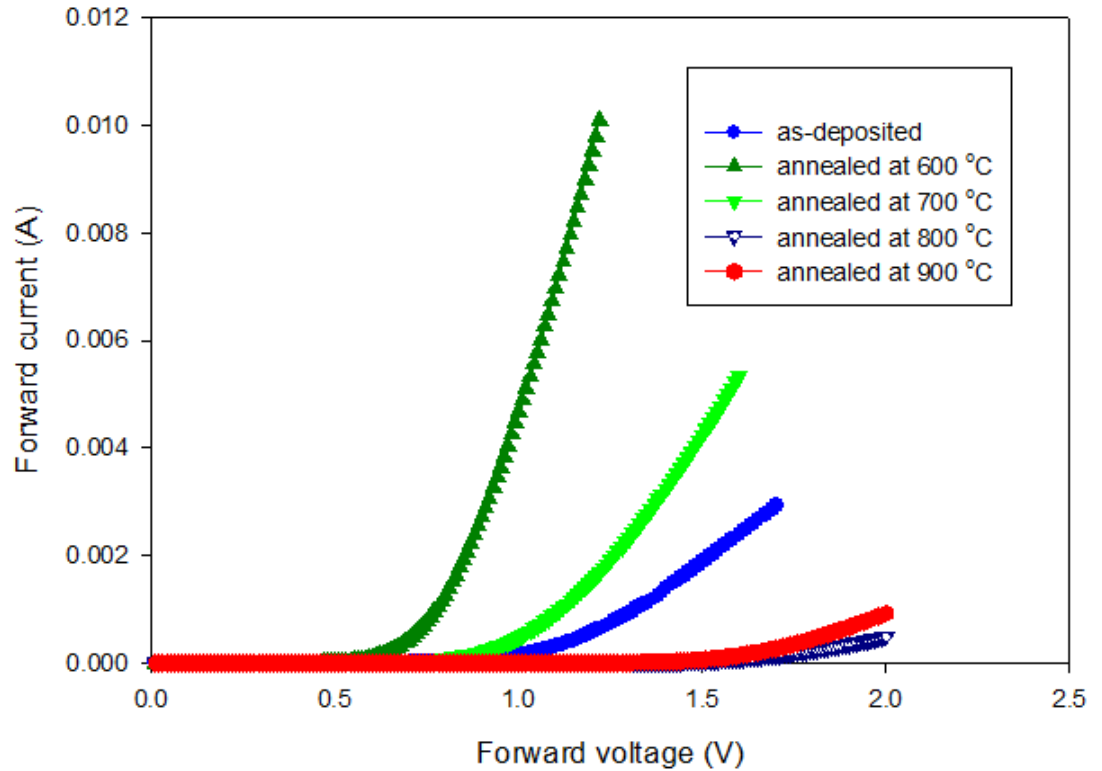


Fig. 13. Graph of forward IV characteristics for Ru-6H-SiC SBDs annealed in argon at various temperatures

#### 4. Conclusion

The Ru-6H-SiC Schottky diodes that were fabricated showed excellent rectifying behaviour by exhibiting linear CV characteristics and exponential IV characteristics up to the final annealing temperature of 900 °C. From the data obtained in this investigation, annealing the SBDs in argon at a temperature of 600 °C gives the lowest series resistance of the SBDs. The investigation has shown that 6H-SiC without an epilayer is able to produce excellent Schottky diodes which can operate at extremely high temperatures. The degradation mechanism of the Schottky diodes has been shown to be the inter-diffusion of Ru and Si at the Ru-SiC interface.

#### 5. References

- [1] L. Stuchlikova, D. Buc, L. Harmatha, U. Helmersson, W. H. Chang, I. Bello, *Appl. Phys. Lett.* **88**, 153509 (2006)
- [2] D. Buc, L. Stuchlikova, U. Helmersson, W.H. Chang, I. Bello, *Chem. Phys. Lett.* **429**, 617–621 (2006)

- [3] D. Buc, L. Stuchlikova, L. Harmatha, I. Hotovy, *J Mater Sci: Mater Electron.* **19**:783–787 (2008)
- [4] S. Roy , C. Jacob , M.Zhang , S. Wang , A.K. Tyagi , S. Basu , *Appl. Surf. Sci.* **211** 300–307 (2003)
- [5] A. Venter , M.E.Samiji , A.W.R.Leitch , *phys. stat. sol. (c)* **1**, No. 9, 2264– 2268 (2004)
- [6] A. Venter, M.E. Samiji, A.W.R. Leitch, *Diamond Relat. Mater.* **13** (2004) 1166–1170 (2004)
- [7] K.V. Munthali, C. Theron, F.D. Auret, S.M.M. Coelho, E. Njoroge, L. Prinsloo, *Mater. Sci. Eng.*, B181, 9–15 (2014)
- [8] F. La Via , F. Roccaforte , A. Makhtari , V. Raineri , P. Musumeci , L. Calcagno, *Microelectron. Eng.* **60**, 269–282 (2002)
- [9] S.M. Sze, *Semiconductor Devices Physics Technology*, 2nd edn. , (John Wiley & Sons, New York, 2002) pp.90-114
- [10] Ioffe Institute, *New Semiconductor Materials-Characteristics and Properties*, <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/SiC/bandstr.html>, accessed 25 April 2013
- [11] J. Osvaldy, E. Dobrockaz, *Semicond. Sci. Technol.* 1198-1202 (1996)
- [12] S. Chand, *Physica B* **373** 284-290 (2005)
- [13] E.V. Jelenkovic, K .Y. Tong, W. Y. Cheung, S. P. Wong, *Semicond. Sci. Technol.* **18** 454-459 (2003)
- [14] E. Stuchlikova, L. Harmatha, D. Buic, J. Benkovska, B. Hlinka, G. G. Siu, *IEEE*. (2006)
- [15] C. Frojdh, G.Thungstrom, H.E. Nilsson, C.S. Petersson, *Phys. Scr.* **Vol. T79**, pp. 297-302, (1999)