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Interface behaviour and electrical performance of ruthenium Schottky contact on 4H-SiC after argon annealing

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Abstract. **Rutherford backscattering spectrometry (RBS) analysis, carried out at various annealing temperatures, of a thin film of ruthenium on n-type four-hexagonal silicon carbide (4H-SiC) showed the evidence of ruthenium oxidation, ruthenium silicide formation and diffusion of ruthenium into silicon carbide starting from an annealing temperature of 400°C. Ruthenium oxidation was more pronounced, and ruthenium and silicon interdiffusion was very deep after annealing at 800°C. Raman analysis of some samples also showed ruthenium silicide formation and oxidation. The Schottky barrier diodes showed very good linear capacitance–voltage characteristics and excellent forward current–voltage characteristics, despite the occurrence of the chemical reactions and interdiffusion of ruthenium and silicon at ruthenium–silicon–carbide interface, up to an annealing temperature of 800°C.**

Keywords. **Rutherford backscattering spectrometry; Raman spectroscopy; oxidation; silicide; Schottky barrier diodes; ruthenium; 4H-SiC.**

1. Introduction

There is renewed interest by researchers in silicon carbide (SiC), owing to the fact that it has superior properties of a large band gap, a high breakdown electric field, high thermal conductivity, high saturation carrier velocity and high mechanical strength when compared with silicon. These properties make SiC an ideal material for the fabrication of electronic devices which can operate in extreme environments. Four-hexagonal silicon carbide (4H-SiC) and six-hexagonal silicon carbide (6H-SiC) have very similar physical, chemical and electrical properties, however, 4H-SiC exhibits a higher electron mobility on the *c*-axis when compared with 6H-SiC.[1] Due to this high electron mobility, 4H-SiC-based power devices can operate at high frequency.[2]

In this study ruthenium (Ru) has been used as a Schottky contact, and nickel as an ohmic contact in the fabrication of Schottky barrier diodes (SBDs). Ru properties of high melting point (2250°C), high chemical stability, low electrical resistance and high mechanical resistance to abrasion and fatigue[3] make it ideal as a Schottky contact for high-temperature operating SBDs. However at such extreme operating temperatures, chemical reaction and diffusion of elements at the interface of the Schottky contact and SiC are bound to happen. The occurrence of these processes may lead to the electrical-performance degradation of the device. However, there has been a dearth of literature on the linkage among chemical reactions, diffusion and the electrical performance of Ru–4H-SiC Schottky devices. In this study the chemical reactions and diffusions at Ru–4H-SiC interface are probed and their linkages with the electrical performance and failure mechanism of the Ru–4H-SiC SBDs are established.

The investigation involved annealing of Ru–4H-SiC SBDs and Ru–4H-SiC thin films in argon at various temperatures. The chemical reactions and diffusion at Ru–4H-SiC interface were analysed at room temperature by Rutherford backscattering spectrometry (RBS) and Raman spectroscopy. Electrical performance of the SBDs was gauged from parameters such as SBH, ideality factor, reverse-saturation current and series resistance of the SBDs which were extracted from current–voltage (I–V) and capacitance–voltage (C–V) characteristics of the diode.

2. Experimental

The electrical performance of Schottky contacts on SiC, in addition to physical and chemical properties, is strongly dependent on the quality of the metal–semiconductor interface and the surface preparation prior to metallization.[4] The n-type 4H-SiC wafer from Cree Research Inc. with a thickness of 368 μm, resistivity of 0.021 Ω cm with an epilayer of donor concentration of 1.16×10^{16} cm^{-3} and thickness of 6 μm, was prepared for metallization by degreasing, using an ultra-sonic bath for a period of 5 min for each step, in trichloroethylene, acetone and methanol, followed by rinsing in deionized water. The sample was then deoxidized in 10% hydrofluoric acid. The sample was finally rinsed in deionized

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water and then dried with nitrogen gas before being loaded into the vacuum chamber, where 200 nm of nickel (Ni) was deposited on the rough side by vacuum resistive evaporation. The sample was then annealed in an argon atmosphere at a temperature of 1000°C for 1 min to make the nickel contact ohmic. The annealed sample was then chemically cleaned again in trichloroethylene, acetone and methanol and deionized water before a 50-nm-thick layer of Ru was deposited on the polished side (Si-terminated face) by an electron-beam deposition technique 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 diameter 0.6 mm were fabricated.

The sample for solid-state reaction and diffusion investigation was made by depositing a 50 nm film of Ru on the polished side of n-type 4H-SiC. Nickel was not deposited on the rough side of this sample. Before deposition of the Ru film, the n-type 4H-SiC was cleaned through the steps mentioned in the paragraph immediately above.

The Ru–4H-SiC SBDs and thin films were both annealed in an argon (of purity 99.998%) atmosphere using a Lindberg Heviduty furnace for a period of 15 min at temperatures ranging from 400 to 900°C. The Ru–4H-SiC thin films were analysed at room temperature after each annealing step by RBS using helium ions with energy of 1.4 MeV. Some samples were analysed by Raman spectroscopy with excitation laser of wavelength 514.6 nm. Full *I–V* and *C–V* characterization of the diodes were 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 *C–V* measurements were done at a frequency of 1 MHz. Both the *I–V* and *C–V* measurement data were automatically saved on the computer by LabVIEW.

3. Results and discussion

RBS analysis of as-deposited Ru−4H-SiC thin film (figure 1) shows a pure Ru signal. Ru silicide (Ru_2Si_3) formation as indicated by a step on the high energy edge of Si, Ru oxide (RuO_2) formation as evidenced by oxygen peak at channel 279 and Ru and Si diffusion as shown by increasing base widths of both signals all appear to commence after annealing at 400°C (figure 2). At 800°C, the Ru and Si interdiffusion is very deep, and Ru oxidation is very high as exhibited by a pronounced oxygen peak (figure 3).

The Raman spectrum of as-deposed Ru–4H-SiC (figure 4) shows a broad peak near position 1600 cm^{-1}, in addition to a small peak near 1400 cm^{-1}, that can be attributed to second-order Raman processes of 4H-SiC which appear in the same spectral region as the second-order Raman lines of 3C-SiC.[5,6]

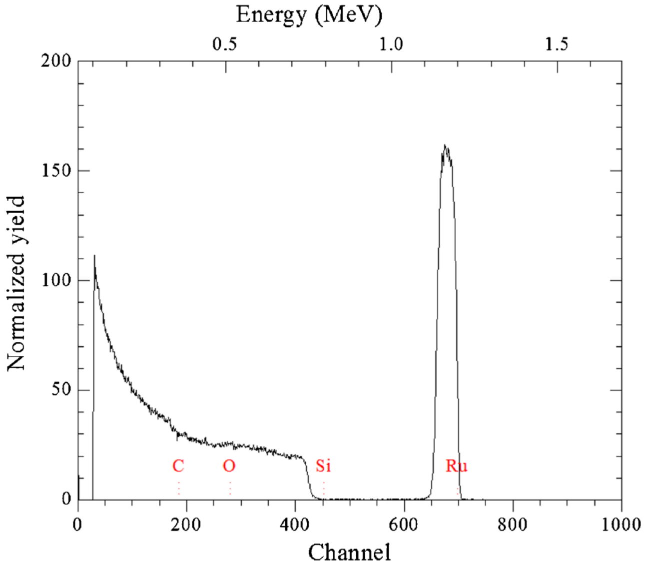

Figure 1. RBS spectrum of as-deposited Ru–4H-SiC obtained by using 1.4 MeV helium ions.

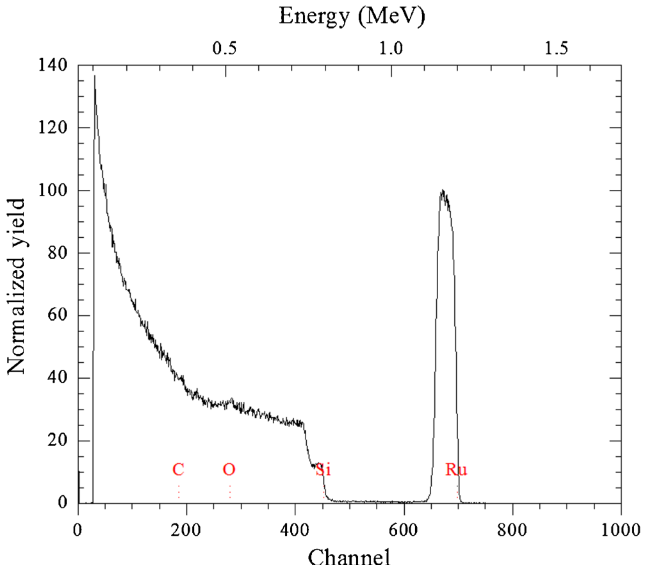

Figure 2. RBS spectrum of Ru–4H-SiC annealed in argon at 400°C obtained by using 1.4 MeV helium ions.

For the Raman spectrum of the sample annealed at 900°C (figure 5), there are clear Ru_2Si_3 and RuO_2 peaks at positions 203 and 610.1 cm^{-1}, respectively,[7,8] and typical three main phonon bands of 4H-SiC with A1, and E2 symmetries.[9] The planar E2, transverse optic E1 and the longitudinal optic A1 modes are at positions 776.4, 797 and 975.6 cm^{-1}, respectively. These findings closely agree with those of Munthali *et al*[10] for the Ru–4H-SiC annealed in air at 600°C.

The SBH, ϕ_{Bn}, ideality factor, η, and reverse saturation current, I_s, were obtained from *I–V* characteristics by assuming that the Schottky diodes obey the thermionic emission current transport model[12] given by equation $J = J_s(e^{(qv/\eta kT)} - 1)$, where $J_s = A^*T^2 e^{-(q\phi Bn/kT)}$.

J_s is the reverse saturation current density, T is the absolute temperature in Kelvin, k the Boltzmann constant, q the absolute amount of charge on an electron and A^* the Richardson constant which is equal to 146 A cm^{-2} K^{-2} for 4H-SiC.[11]

Series resistance R_s is the resistance of the bulk material of the semiconductor plus that of the back ohmic contact, and to account for the series resistance, the current equation is modified[12] to become

$$J = J_s[\mathrm{e}^{q(V-IR_s)/\eta kT} - 1].$$

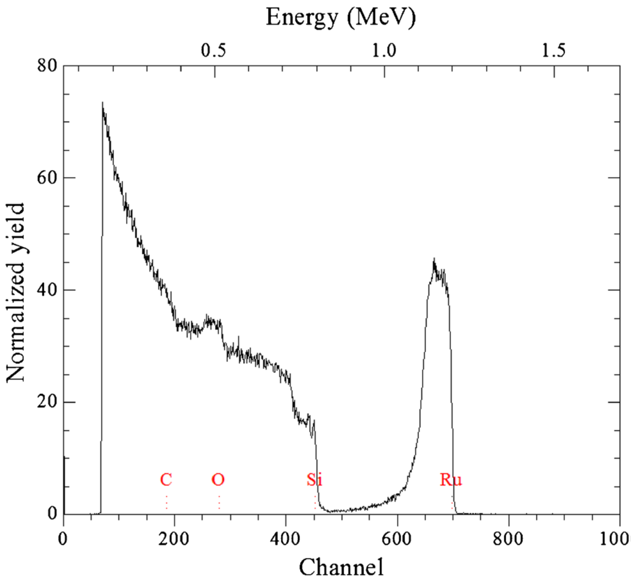

Figure 3. RBS spectrum of Ru–4H-SiC annealed in argon at 800°C obtained by using 1.4 MeV helium ions.

The parameters from C–V characteristics are obtained from the junction capacitance of the SBD[11] given by

$$C = \sqrt{\frac{q\varepsilon_s N_D}{2(V_{bi} - V)}}.$$

Re-arranging this equation gives

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{q\varepsilon_s N_D}(\mathrm{F\ cm}^{-2})^{-2}.$$

A plot of $1/C^2$ *vs.* 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[12] by the equation $\phi_{Bn} = V_i + V_o$, where V_i is the voltage intercept and

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

N_C is the effective density of states in the conduction band of 6H-SiC. N_C is equal to 1.7×10^{19} cm^{-3} for 4H-SiC at 300 K.

Table 1 displays the important parameters which were extracted from both I–V and C–V characteristics of the SBDs .

From the table, ideality factor is observed to generally decrease with annealing temperature. The SBH obtained from C–V characteristics is observed to be higher than the

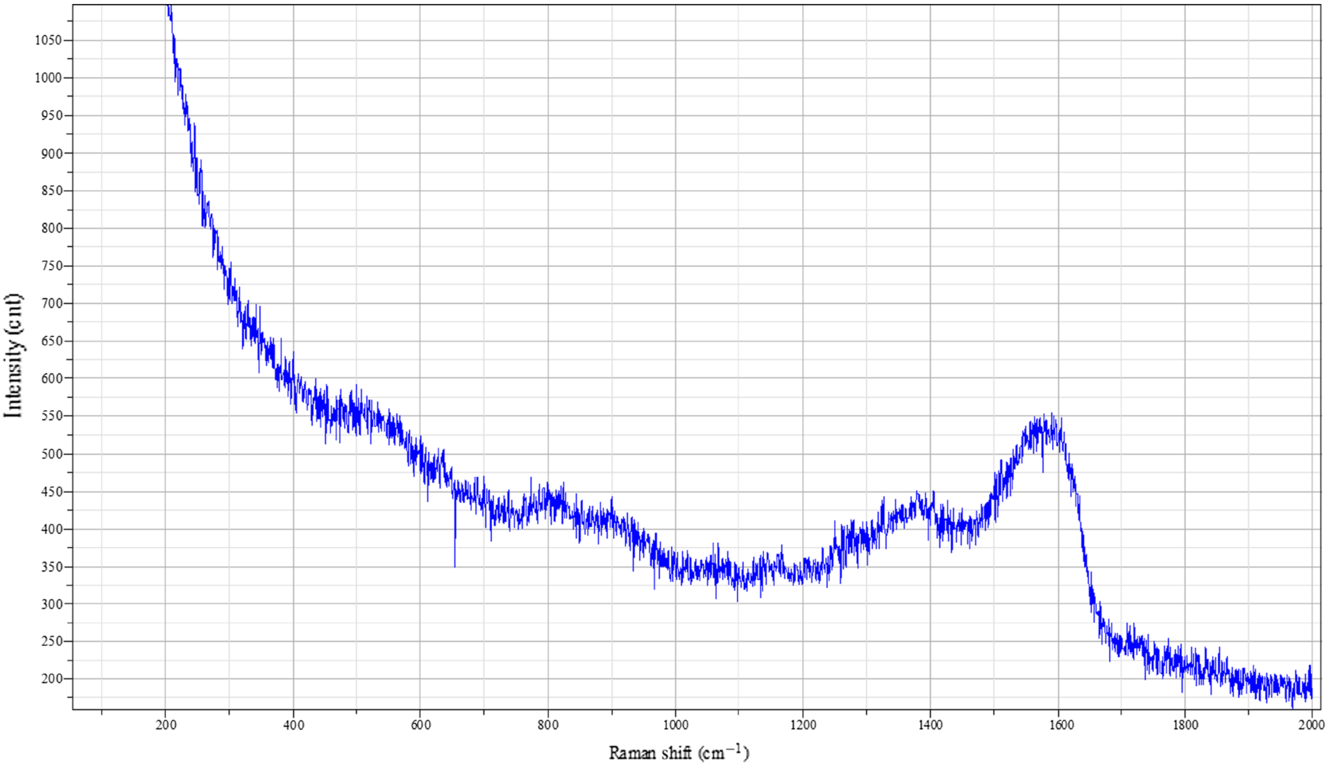

Figure 4. Raman spectrum of as-deposited Ru–4H-SiC.

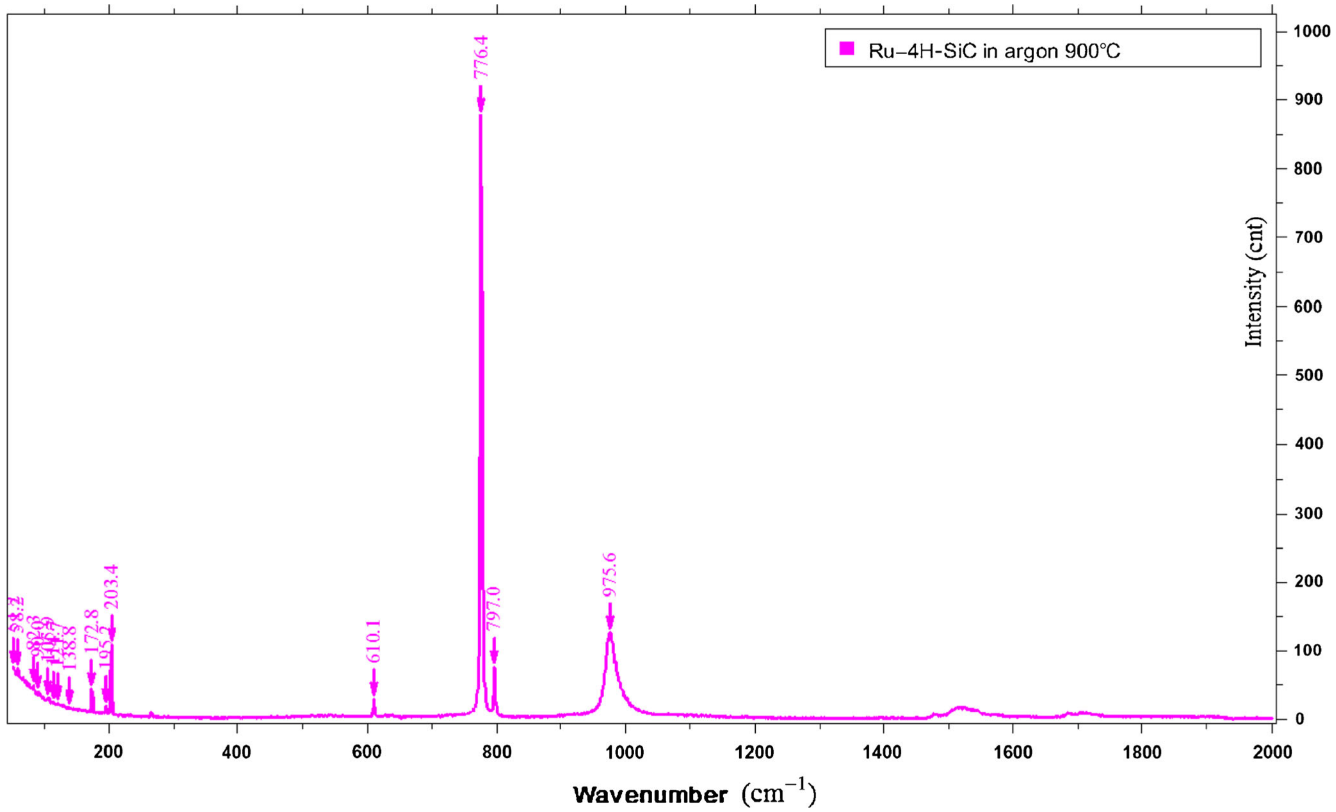

Figure 5. Raman spectrum of Ru–4H-SiC annealed in argon at 900°C.

Table 1. Parameters of Ru–4H-SiC Schottky diodes at various annealing temperatures.

Annealing temp. (°C)	Ideality factor, η	SBH from I–V (eV)	SBH from C–V (eV)	Series resistance, R_s (Ω)	Saturation current, I_s (A)	Donor density, N_D (cm^{-3})
As dep	2.636	0.945	2.377	20.306	2.089E−12	9.681E+15
400	1.008	1.078	2.072	20.488	1.847E−14	1.001E+16
500	1.191	1.417	3.132	952.417	3.333E−20	7.624E+15
600	1.692	1.453	2.256	34.171	8.202E−21	8.86E+15
700	1.660	1.416	2.242	175.898	1.68E−20	1.12E+16
800	1.259	1.666	1.956	138.365	1.96E−24	1.10E+16
900	[a]		48			

[a] Non-exponential I–V graph.

SBH from I–V characteristics. Normally the SBHs that are obtained from C–V measurements are slightly higher than those from I–V characteristics, as there is a possibility of the existence of an additional capacitance at the metal–semiconductor interface due to the presence of a thin oxide layer which comes as a result of surface preparation.[13] Another explanation for the differences may be the existence of inhomogeneous interfaces, which result in non-uniform Schottky contacts where current can flow via two pathways (i.e., over a lower barrier or a higher barrier).[14] The formation of Ru_2Si_3, RuO_2 and the interdiffusion of Ru and Si at the Ru–4H-SiC interface as observed by RBS analysis and Raman spectroscopy did not lead to dramatic changes in SBH below annealing temperature of 900°C. One possible explanation of the small variation of SBH after the formation of RuO_2 is that the SBHs of Ru and RuO_2 on SiC are nearly equal to each other.[15] Furthermore, Ru_2Si_3 is semiconducting and has a barrier height close to that of Ru on SiC. The SBH of Ru_2Si_3 on silicon (which one can conjecture to be close to that on SiC) of 0.76 eV[16] is very close to the SBH of Ru on SiC.

The donor density obtained from the C–V characteristics closely agree with the carrier density of the wafer of 1.16×10^{16} cm^{-3} specified by Cree Research Inc.

The SBDs exhibit excellent I–V and C–V characteristics (figures 6 and 7, respectively) up to an annealing temperature of 800°C despite the occurrence of chemical reactions and Ru and Si diffusions at the Ru–4H-SiC interface.

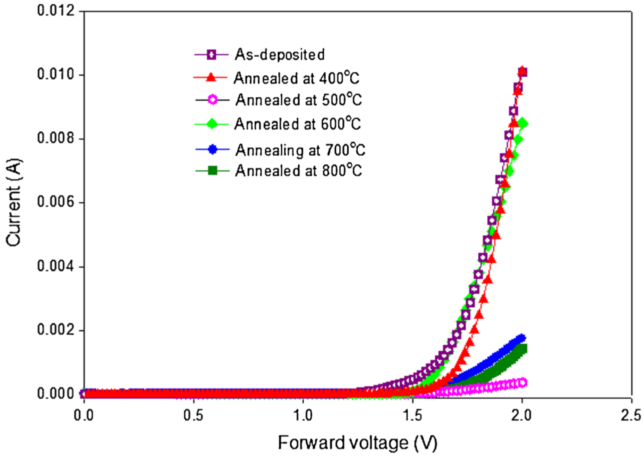

Figure 6. Forward *I*–*V* characteristics of Ru–4H-SiC SBDs annealed in argon.

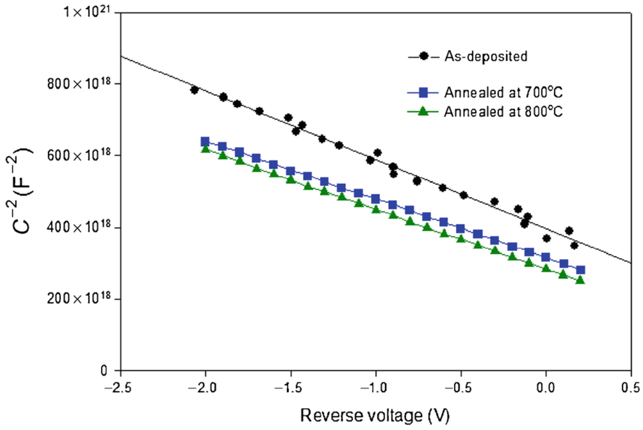

Figure 7. *C*–*V* characteristics of Ru–4H-SiC SBDs annealed in argon.

The best fit line was drawn for the as-deposited *C*–*V* plot as the measuring instrument exhibited some instability during the measurement process. The Schottky diode degraded and became unusable after annealing at 900°C as indicated by the non-exponential *I*–*V* characteristics and awkward value of SBH obtained from *C*–*V* characteristics. The device failure is attributed to the deep interdiffusion of Ru and Si at the Ru−4H-SiC interface as indicated by RBS analysis.

4. Conclusion

RBS and Raman analysis of the Ru−4H-SiC thin films have shown that annealing leads to the formation of an oxide and a silicide of Ru, in addition to the interdiffusion of Ru and Si at the Ru−4H-SiC interface. The Ru−4H-SiC SBDs exhibit electrical-operational stability up to an annealing temperature of 800°C. The diodes degrade above this temperature, and the device failure is attributed to the deep interdiffusion of Ru and Si at the Ru–4H-SiC interface. The results provide hope that there is a good future for the commercial production of SiC-based devices which can operate at extremely high temperature.

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