## Deep energy levels in RuO<sub>2</sub>/4H-SiC Schottky barrier structures

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RuO<sub>2</sub>/4H–SiC Schottky diode structures based on n-type 4H–SiC  $(7 \times 10^{17} \, \mathrm{cm}^{-3})$  with stoichiometric RuO<sub>2</sub> Schottky contacts were characterized by electrical capacitance-voltage and current voltage methods and deep-level transient spectroscopy in order to determine their unique semiconducting and electronic properties. The RuO<sub>2</sub> films exhibited electrical conductivity of  $60 \, \mu\Omega$  cm for Schottky barrier heights of approximately 0.88 eV. These Schottky structures revealed two deep energy levels with thermal activation energies of 0.56 and 0.85 eV with reference to the conduction band. ©  $2006 \, American \, Institute \, of \, Physics$ . [DOI: 10.1063/1.2195775]

Silicon carbide (SiC) is a wide-band-gap semiconductor crystallizing in many polytypes with cubic, hexagonal, and rhombohedral lattice symmetry and different sequential stacking of atomic planes. Both the epitaxial growth and doping of 6H-SiC and 4H-SiC (Ref. 1) have been developed on a consistent level. Each crystal structure however possesses unique electrical, electronic, and optical properties.<sup>2</sup> The SiC wide-band gap (3.26 eV for 4H–SiC and 3.03 eV for 6H-SiC) enables the fabrication of devices operating at extreme temperatures and irradiative environments without inducing intrinsic conduction. The same property permits the emission and detection of short-wavelength light. The SiC breakdown electric field (2.2×10<sup>6</sup> V/cm— 4H-SiC,  $2.4 \times 10^6$  V/cm—6H-SiC), approximately eight times greater than that for silicon, allows high-voltage<sup>3,4</sup> and high-power device applications and high-packing density of high-voltage discrete elements.<sup>5</sup> The high thermal conductivity up to  $\sim$ 450 W m<sup>-1</sup> K<sup>-1</sup> allows effective heat dissipation and device operation at high powers. Relatively, electron mobility ( $\sim 1000 \text{ cm}^2/\text{V s}$  and donor density  $10^{14}$ – $5 \times 10^{16}$  cm<sup>-3</sup>) (Ref. 6) also enables operation of power devices at high switching frequencies. Conventional silicon and GaAs devices do not allow operation at these conditions. For example, Si recovery diodes limits the performance of many insulated gate bipolar transistors operating at high switching frequencies (>10 kHz) with high voltage and high current. Alternative solutions include SiC Schottky diodes.8 The reproducibility of metal Schottky contacts is not well controlled because of the reaction between the metal and the SiC. The reaction could be suppressed or eliminated with the selection of stable contact materials. RuO2 is extensively explored as a contact material. 10 The low electrical resistivity at room temperature, and thermodynamic stability, are certainly interesting properties of RuO<sub>2</sub>. These properties suit it for applications where high resistance to abrasion, oxi-

dation, fatigue, e.g., and formation of RuO2 contact electrodes in PZT thin-film capacitors<sup>11</sup> are required. The chemical stability, low resistance, and electronic properties of RuO<sub>2</sub> films are suitable for construction of Schottky contacts. On SiC, Carbal et al. 12 found that the thermal stability of RuO<sub>2</sub> gate electrodes deposited on the SiO<sub>2</sub> dielectric of a field effect transistor in hydrogen forming gas is fairly low. Despite many works devoted to metal-semiconductor devices, SiC Schottky barrier diodes with stoichiometric RuO<sub>2</sub> Schottky contacts have not been prepared, and therefore have not been investigated, for electronic properties—particularly deep energy levels (DELs). Very few papers discuss the use of ruthenium oxide as a gate electrode in metal-oxidesemiconductor structures on dioxide, and the formation of ruthenium oxide Schottky diodes based on semiconductors such as AlGaN/GaN heterostructure. 13

In this work, we report on the preparation of RuO<sub>2</sub>/4H-SiC Schottky barrier diodes (SBDs) and their characterization by electrical methods and standard deep-level transient spectroscopy (DLTS).

SiC Schottky barrier diodes were produced on n-type 4H-SiC substrates fabricated at Linköping University. 14 The Schottky contacts provided RuO<sub>2</sub> thin films (400 nm) deposited via a contact metal mask to yield contact areas with a diameter of 0.8 mm. The RuO2 films were prepared by reactive unbalanced magnetron sputtering using a planar ruthenium target with a 50 mm diameter. The axis target-substrate geometry was fixed at a distance of 60 mm. The films were deposited at 500 °C using a constant voltage mode and power of 100 W. The dynamic operating pressure of the  $O_2(16\%)$ /Ar gas mixture was 0.5 Pa. The radio-frequencyinduced self-bias of the substrate was -60 V. 15 The prepared structures were examined by current-voltage (I-V) measurements, and then analyzed by capacitance-voltage (C-V) and standard DLTS. 16 High frequency C-V measurements were carried out using a 1 MHz C meter/C-V Plotter-type 4280 Hewlett-Packard system. Parametric data extraction, analysis, and visualization were done by a personal computer.

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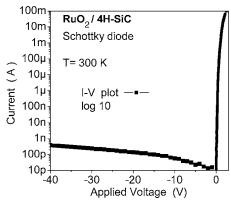


FIG. 1. Measured I-V characteristics.

DLTS measurements were performed using a Polaron DLT Spectrometer 4900 equipped with a boxcar detection system.

The electric resistivity of the deposited RuO<sub>2</sub> films is 60  $\mu\Omega$  cm, as measured by a four-point probe method, while the I-V measurements of the RuO<sub>2</sub>/4H-SiC structure display an asymmetric rectifying characteristic (Fig. 1) with a fairly low reverse leakage current of 10<sup>-10</sup> A at the bias of -10 V. The ideality factor  $n = \sim 1.28$  is comparable with values from 1.2 to 1.3 for RuO2/4H-SiC annealed in air at 450 °C for 20 h. 18 A relatively higher value of n for our Schottky diodes is also affected by a 16-times larger contact area than reported in Ref. 18. Both the saturation current,  $I_S$  and Schottky barrier height are found to be 10 pA and 0.88 eV, respectively. Unlike the Ru/6H-SiC system, the zero-bias current offset is not observed for the RuO<sub>2</sub>/4H-SiC Schottky structure. The value of the reverse leakage current is lower by two orders of magnitude, and the reverse characteristic is not as distorted at least with pure Ru metal. 19 Han and Lee 18 prepared similar Schottky structures. However, they compared presumed RuO2 was made by Ru evaporation, and subsequently annealed it in oxygen at 300 °C. Since diffusion at this temperature is fairly limited, the semiconductor interface is metallic Ru rather than oxide, which is also suggested with their x-ray diffraction analysis. Annealing changed the Schottky barrier from 1.74 to 1.84 eV, which is approximately twice as high as that (0.88 eV) reported herein. The difference has to be in (ruthenium and ruthenium oxide) contact at the semiconductor interfaces. We prepared RuO<sub>2</sub> films on SiC by advantageously using a single-step process yielding stoichiometric RuO<sub>2</sub>.<sup>1</sup>

Figure 2 shows the measured C-V and conductance-voltage (C-V) curves and the calculated C-V curve of

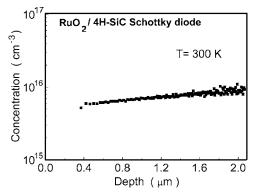
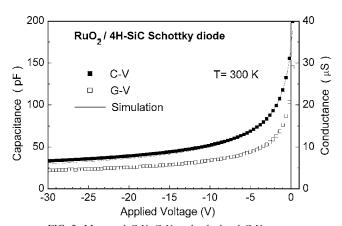


FIG. 3. C-V concentration profile.

RuO<sub>2</sub>/4H–SiC Schottky barrier diodes. The calculated C-V curve includes a correction for the conduction effect at the capacitance measurements. The differences between the measured and calculated C-V data are negligible. The doping concentration of the SiC epitaxial layer determined by C-V measurements is  $7 \times 10^{15}$  cm<sup>-3</sup> (Fig. 3). The representative measured  $1/C^2$ -V plot of the RuO<sub>2</sub>/4H–SiC SBDs is shown in Fig. 4. This plot reveals a built-in voltage of 0.97 V when extrapolated.

The measured DLTS spectra of the  $RuO_2/4H-SiC$  SBDs rather deviate from an exponential dependence which could be caused by the presence of several mutually influenced DELs. A wide range of reverse voltage biases (from -6.9 to 0.2 V), temperatures (from 85 to 450 K), and times of the filling pulse bias (from 0.5 to 3 ms) were used as initial conditions.

The DLTS measurements were performed at the edge of sensitivity of the DLTS instrument which is unexpected because of the presence of intrinsic and extrinsic defect centers in SiC crystals, such as dislocations, micro- and nanopipes (pinholes), oxides, metallic overlayers, impurities, etc. These deep levels may act either as trapping centers for electrons/ holes or recombination centers.<sup>20</sup> These affect the lifetime and diffusion length of minority charge carriers, the efficiency of light-emitting diodes and photodetectors, the gain of transistors, and the breakdown voltage of p-n junctions. Hence, the electronic and electrical properties of these deep levels are of major interest for the design of electronic devices. The best characteristic DLTS spectra of the RuO<sub>2</sub>/4H-SiC Schottky barrier diodes for rate windows of 2 and 0.8 s<sup>-1</sup> were obtained at reverse voltage  $U_R$ =-1.59 V, filling pulse bias  $U_F$ =0.1 V, and filling pulse time  $t_F$ =1.5 ms (Fig. 5). Two deep levels, DL1 and DL2, are



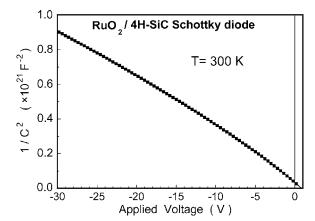


FIG. 2. Measured C-V, G-V, and calculated C-V curves.

FIG. 4.  $1/C^2$  vs voltage plot.

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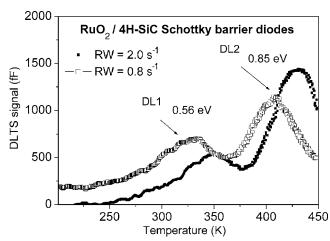


FIG. 5. Typical DLTS spectra of the  ${\rm RuO_2/4H-SiC}$  Schottky barrier diodes.

identified in the spectra. These DLs are the traps of majority charge carriers (electrons). The DLs' parameters were determined by regression of the experimental data set. The values for electron deep level activation enthalpy,  $\Delta E_T$  and capture cross section,  $\sigma_T$  were calculated from an Arrhenius diagram using the equation: <sup>16</sup>

$$\ln\left(\frac{e_n}{T^2}\right) = \ln(\sigma_n K_n) - \left(\frac{\Delta E_T}{k_B T}\right),$$

where  $e_n$  is the emission rate,  $K_n$  is a material constant, T is the absolute temperature, and  $k_B$  is the Boltzmann constant.

DEL DL1 has the activation energy of 0.563 eV and a capture cross section of  $2 \times 10^{-15}$  cm<sup>2</sup>. DL2 has the activation energy of 0.845 eV and capture cross section of  $2 \times 10^{-16}$  cm<sup>2</sup>. No straightforward explanation of the DL1 and DL2 peaks however is available because the DL1 is detected in vicinity of the known deep level  $Z_1$  with a corresponding ionization energy of 0.63–0.68 eV and capture cross section of  $3 \times 10^{-15}$ – $2 \times 10^{-14}$  cm<sup>2</sup>. Dalibor *et al.*<sup>21</sup> reported that the  $Z_1$  level is not only the result of residual defects detectable in as-grown n-type layers, but also due to acceptor-like states which can be generated by either He<sup>+</sup> or H<sup>+</sup> implantation. This center is thermally stable, at least up to temperatures 2015 °C. It is, therefore, assumed that the  $Z_1$  defect is caused by the same intrinsic defect complex, and it is suggested that it might consist of a nonaxial C-Si nearest-neighbor divacancy. <sup>22</sup> These defects may be induced at the ion-assisted deposition of RuO2. DL2 at 0.85 eV was detected in vicinity of the RD<sub>1/2</sub>, with an activation energy of 0.89 to 0.97 eV and capture cross section of  $7 \times 10^{-16} - 5 \times 10^{-15}$  cm<sup>2</sup> which is usually attributed to an implantation-induced center. The reasons for this emerging energy level are still unclear. It could be induced by impurities, more likely Ru, that might be incorporated into the interfacial region of the semiconductor. However, evidence based on chemical and defect analysis is needed to ascertain the origin of the energy levels.

In summary, we fabricated  $RuO_2/4H-SiC$  Schottky barrier diodes and studied those using DLTS measurements. The DLTS analysis revealed two DELs; DL1/DL2 in these structures. The thermal activation energy of DL1 at 0.56 eV is in good agreement with the values reported for the defect  $Z_1$  which may consist of a nonaxial C-Si nearest-neighbor divacancy. However, the thermal activation energy DL2 with a value of 0.85 eV, though similar to that of an unexplained deep level  $RD_{1/2}$ ,  $^{23,24}$  could be associated with incorporated Ru impurities in a 4H-SiC film.

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<sup>1</sup>H. Fujiwara, K. Danno, T. Kimoto, T. Tojo, and H. Matsunami, J. Cryst. Growth **281**, 370 (2005).

<sup>2</sup>J. A. Powell, P. Pirouz, and W. J. Choyke, in *Semiconductor Interfaces, Microstructures, and Devices: Properties and Applications*, edited by Z. C. Feng (IOP, Bristol, 1993), p. 257.

<sup>3</sup>R. Singh, J. A. Cooper, Jr., M. R. Melloch, T. P. Chow, and J. W. Palmour, IEEE Trans. Electron Devices **49**, 665 (2002).

<sup>4</sup>H. Tsuchida, I. Kamata, T. Jikimoto, and K. Izumi, J. Cryst. Growth 237, 1206 (2002).

<sup>5</sup>R. Ahuja, A. Ferreira da Silva, C. Persson, J. M. Osorio-Guillen, K. Jarrendalh, O. P. Linquist, N. V. Edwards, Q. Wahab, and B. Johnson, J. Appl. Phys. **91**, 2099 (2002).

<sup>6</sup>A. Itoh and H. Matsunami, Phys. Status Solidi A 162, 389 (1997).

<sup>7</sup>R. J. Trew, Phys. Status Solidi A **162**, 409 (1997).

<sup>8</sup>C. M. Johnson, M. Rahimo, N. G. Wright, D. A. Hinchley, A. B. Horsfall, and A. Knights, in *Proceedings of the Power Electronics and Variable Speed Drives*, 18–19 September 2000 (IEEE, New York, 2000), Conference No. 475.

<sup>9</sup>F. La Via, F. Roccaforte, V. Raineri, M. Maceri, A. Ruggiero, P. Musumeci, L. Calcagno, A. Castaldini, and A. Cavallini, Microelectron. Eng. 70, 519 (2003).

<sup>10</sup>S. Desgreniers and K. Lagarec, Phys. Rev. B **59**, 8467 (1999).

<sup>11</sup>C. W. Law, K. Y. Tong, J. H. Li, and K. Li, Solid-State Electron. 44, 1569 (2000)

<sup>12</sup>C. Carbal, Jr., C. Lavoie, A. S. Ozcan, R. S. Amos, V. Narayanan, E. P. Gusev, J. L. Jordan-Sweet, and J. M. E. Harper, J. Electrochem. Soc. 151, F283 (2004).

<sup>13</sup>Ch. M. Jeon and J. L. Lee, J. Appl. Phys. **95**, 698 (2004).

<sup>14</sup>M. Tuominen, R. Yakimova, E. Prieur, A. Ellison, T. Tuomi, A. Vehanen, and E. Janzén, Diamond Relat. Mater. 6, 1272 (1997).

<sup>15</sup>D. Búc, D. Music, and U. Helmersson, *Proceedings of the ASDAM'* 2000 Conference, Smolenice, Slovakia (IEEE, Piscataway, NJ, 2000), p. 465.

<sup>16</sup>D. V. Lang, J. Appl. Phys. **45**, 3014 (1974).

<sup>17</sup>M. Tapajna and L. Harmatha, Solid-State Electron. **48**, 2339 (2004).

<sup>18</sup>S. Y. Han and J. L. Lee, J. Appl. Phys. **94**, 6159 (2003).

<sup>19</sup>A. Venter, M. E. Samiji, and A. W. R. Leitch, Diamond Relat. Mater. 13, 1166 (2004).

<sup>20</sup>A. A. Lebedev, in *Silicon Carbide: Materials and Processing*, edited by Z. C. Feng and J. H. Zhao (Taylor Francis, New York, 2004), p. 121.

<sup>21</sup>T. Dalibor, G. Pensl, H. Matsunami, T. Kimoto, W. J. Choyke, A. Shöner, and N. Nördell, Phys. Status Solidi A **162**, 199 (1997).

<sup>22</sup>L. Patrick and W. J. Choyke, Phys. Rev. B **5**, 3253 (1972).

<sup>23</sup>A. Castaldini, A. Cavallini, L. Rigutti, F. Nava, S. Ferrero, and F. J. Giorgis, J. Appl. Phys. 98, 053706 (2005).

<sup>24</sup>A. Kawasuso, M. Weidner, F. Redmann, T. Frank, R. Krause-Rehberg, G. Pensl, P. Sperr, W. Triftshäuser, and H. Itoh, in *Materials Science Forum*, *Silicon Carbide and Related Materials 2001*, edited by S. Yoshida, S. Nishino, H. Harima, and T. Kimoto (Trans. Tech., Uetikon-Zuerich, 2002), Vol. 389-393, p. 489.