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R. Palmieri,[1,a] C. Radtke,[2] H. Boudinov,[1] and E. F. da Silva, Jr.[3]

[1]*Instituto de Física, UFRGS, 91501-970 Porto Alegre, Rio Grande do Sul, Brazil*
[2]*Instituto de Química, UFRGS, 91501-970 Porto Alegre, Rio Grande do Sul, Brazil*
[3]*Departamento de Física, UFPE, 50670-901 Recife, Pernambuco, Brazil*

The effect of using H$_2$O$_2$ in the thermal growth process of dielectric films on *n*-type 4*H*-SiC substrates has been investigated. In comparison to conventional oxide growth using H$_2$O, we found that the interface trap density is reduced close to the conduction band edge of 4*H*-SiC. This electrical improvement is correlated with the decrease in SiC$_x$O$_y$ compounds at the SiO$_2$/4*H*-SiC interface region as confirmed by two independent methods. These results point to the use of H$_2$O$_2$ as an alternative passivating agent of SiO$_2$/4*H*-SiC interface electrically active defects. © *2009 American Institute of Physics*. [doi:10.1063/1.3231923]

Silicon carbide (SiC) is the material of choice for high-power (>1 kW), high-frequency (>5 GHz), and high-temperature (300–600 °C) device applications. This wide-bandgap material has several of the required properties for these extreme conditions, including high thermal conductivity (4.9 W cm^{-1} K^{-1}), high-breakdown field strength (4 MV cm^{-1}), and high electron saturated drift velocity (2×10^7 cm s^{-1}).[1] Besides, it is the only compound semiconductor on which a dielectric film (SiO$_2$) can be thermally grown in a similar way as on Si. Thus, it is expected that most of the processes used in Si-based metal-oxide-semiconductor (MOS) technology can be adapted to SiC.

Nevertheless, the electrical properties of the resulting SiO$_2$/SiC interface are degraded by large densities of interface states (D_{it}). Different types of electrically active defects were identified, including carbon clusters,[2,3] C dangling bonds,[4] and silicon oxycarbides (SiC$_x$O$_y$).[5] The latter one is considered to be primarily responsible for the observed D_{it} values (mainly near the conduction band edge[6]) and for trapping majority carriers in SiO$_2$/4*H*-SiC structures.[7] Several pre- and postoxidation treatments were already explored in order to reduce these D_{it} values.[8–11] Postoxidation annealing in N-containing atmospheres was shown to be an effective passivation route.[11] Such passivation processes incorporate N mainly at the dielectric/SiC interface region,[12] where Si–N and C–N bonds[13] are formed and a reduction of the amount of carbonaceous compounds was observed.[14] These physicochemical modifications result in improved electrical characteristics of the final structure. In the same sense, preoxidation treatments of SiC with H$_2$ (Ref. 8) help in removing residual carbon and associated SiC$_x$O$_y$ at the interface region.

SiC$_x$O$_y$ are spontaneously formed during exposure of SiC to air[15] and constitute the main oxidation by-product of this semiconductor material.[16] Due to the high chemical inertness of SiC$_x$O$_y$,[17] wet etching chemistries usually employed in the semiconductor industry do not remove such compounds from the SiC surface. In view of this scenario, we used a different oxidizing agent in order to thermally grow a dielectric layer on SiC aiming at reducing the amount of oxidation by-products. Thermal oxidation of SiC is usually accomplished by heating the sample at temperatures above 1000 °C under a flux of oxygen bubbled through de-ionized water. In the present work, we replaced water by hydrogen peroxyde (H$_2$O$_2$), which is a powerful oxidizing agent. The use of such a reagent could oxidize SiC$_x$O$_y$ already formed at the SiC surface and minimize its formation during oxidation. Our results provide direct evidence of improved electrical characteristics of SiO$_2$/4*H*-SiC structures obtained by thermal oxidation using H$_2$O$_2$ instead of H$_2$O, which were correlated with the reduction of SiC$_x$O$_y$ compounds at the SiO$_2$/SiC interface region.

MOS capacitors were fabricated on Si-faced, n/n^+ 4*H*-SiC commercial epitaxial wafers, 8° off the (0001) direction, doped with nitrogen. The wafers contained 4.6 μm thick epitaxial layers with doping concentration of 1.1 $\times 10^{16}$ cm^{-3}. The wafers were cleaned in a H$_2$SO$_4$:H$_2$O$_2$ solution followed by a standard RCA cleaning. Prior to oxidation, wafers were dipped in a 1% HF solution for 30 s aiming at removing the native oxide. Oxide growth was carried out at atmospheric pressure in a horizontal quartz tube furnace at 1000 °C for 2 h. Two oxidation processes were employed, bubbling O$_2$ in (i) de-ionized water or (ii) hydrogen peroxide (H$_2$O$_2$). In both cases, oxidation was followed by annealing in Ar at 1100 °C for 30 min to decrease the quantity of unreacted oxygen in the oxide layer. MOS structures were fabricated in a vacuum system by Al thermal evaporation through a mechanical mask, forming circle capacitors with a diameter of 200 μm. An InGa eutectic was used as back contact. Samples were electrically characterized using a computer-controlled HP4284A Precision *LCR* Meter. 10 kHz to 1 MHz ac conductance measurements (G-ω) (Ref. 18) with an ac amplitude of 20 mV were performed between 30 and 300 °C in order to obtain interface states data deeper in the 4*H*-SiC bandgap.

Figure 1 shows D_{it} data as a function of energy position in the bandgap measured from the 4*H*-SiC valence band (E-E_V) for MOS capacitors built following processes with H$_2$O or H$_2$O$_2$ atmospheres. Comparing these data, we found a reduced interface trap density of the H$_2$O$_2$ sample (in the energy range 2.4–2.6 eV) from 1.6×10^{11} to 6.6×10^{10} eV^{-1} cm^{-2} at 2.6 eV and from 7.8×10^{10} to 7

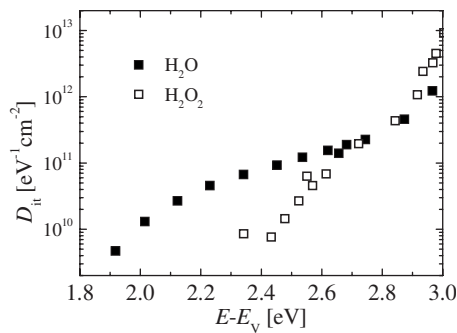a)Electronic mail :palmieri@if.ufrgs.br.

FIG. 1. Interface state density D_{it} as a function of energy for 4H-SiC MOS structures. Energy scale corresponds to the region of bandgap near the bottom of the 4H-SiC conduction band. Measurements were carried out between 30 and 300 °C.

TABLE I. ^{18}O areal densities of samples A, B, and C determined by nuclear reaction analysis. In each case, it is marked the existence of a component related to the SiC substrate in XPS analysis.

Sample	10^{15} ^{18}O cm^{-2}	Evidence of a SiC signal in XPS
A	37.6	No
B	1.4	No
C	0.4	Yes

$\times 10^9$ eV^{-1} cm^{-2} at 2.4 eV. Reduction of D_{it} in the same region of the 4H-SiC bandgap was also observed following: (i) H$_2$ pretreatment of the semiconductor substrate prior to the dielectric growth[8] and (ii) postoxidation annealing in NO.[10] Both procedures were shown to reduce the amount of residual carbon and, consequently, the amount of SiC$_x$O$_y$ at the region close to the SiO$_2$/SiC interface. Thus, the use of H$_2$O$_2$ in the oxidation of 4H-SiC should also reduce the amount of these compounds. The slight increase of D_{it} in the energy range 2.9–3.0 eV could be associated to near-interfacial oxide defects[19] introduced by H$_2$O$_2$.

Aiming at investigating the physicochemical modifications induced by H$_2$O$_2$, a new batch of samples was prepared. More specifically, we developed a strategy to evidence that the use of H$_2$O$_2$ as an oxidizing agent reduces the amount of silicon oxycarbides (SiC$_x$O$_y$) at the SiO$_2$/SiC interface region. 4H-SiC samples underwent a sequence of etching and annealing steps depicted in Fig. 2. 4H-SiC oxidation was performed in a resistively heated quartz tube furnace for 2 h under a static pressure of 100 mbar of O$_2$ enriched to 97% in the isotope of mass 18 (termed ^{18}O$_2$). The use of ^{18}O$_2$ allowed us to quantify oxygen amounts as low as 10^{13} ^{18}O cm^{-2} using nuclear reaction analysis (NRA). We were also able to distinguish oxygen intentionally incorporated by the first thermal oxidation step from other oxygen sources like air exposure, etching procedures, and subsequent annealing steps. The H$_2$O$_2$ annealing was carried out at atmospheric pressure in a horizontal quartz tube furnace at 420 °C for 4 h, bubbling O$_2$ in H$_2$O$_2$. ^{18}O amounts were determined by NRA using the plateau region at 730 keV in the cross section curve of the ^{18}O$(p, \alpha)^{15}$N nuclear reaction,

referenced to a standard Si ^{18}O$_2$ film on Si. X-ray photoelectron spectroscopy (XPS) was performed using an Omicron-SPHERA station with Mg $K\alpha$ radiation (1253.6 eV). Si 2p regions of the spectra were recorded with a 20 eV pass energy. The detection angle of the photoelectrons, with respect to the normal of the sample (emission angle), was fixed at 73°.

The ^{18}O areal density of the sample just after oxidation (sample A in Fig. 2) is 37.6×10^{15} ^{18}O cm^{-2} (Table I). This amount corresponds to an oxide film of 8.5 nm, using the density of thermally grown SiO$_2$ (2.21 g cm^{-3}).[20] In order to evidence the formation of SiC$_x$O$_y$ compounds at the SiO$_2$/SiC interface region, sample A underwent an etching step in an HF aqueous solution (sample B in Fig. 2). SiC$_x$O$_y$ were shown to be resistant to HF wet etching chemistries.[17] Thus, if they are formed at the SiO$_2$/SiC interface region, one should detect ^{18}O reminiscent from the oxidation step after etching. ^{18}O was indeed detected while analyzing sample B. Its concentration was 1.4×10^{15} ^{18}O cm^{-2} (Table I). This amount cannot be attributed to native oxide formation during air exposure between the etching step and NRA analysis.[17] Sample B underwent an H$_2$O$_2$ annealing in the conditions described in Fig. 2. The low temperature (420 °C) employed in this treatment was chosen in order to avoid further SiC substrate oxidation and, consequently, formation of additional SiC$_x$O$_y$. By this way, we could investigate the effect of H$_2$O$_2$ on the existing SiC$_x$O$_y$ layer. After this annealing, the sample underwent an additional HF etching step. The ^{18}O amount of the resulting sample (sample C in Fig. 2) was 0.4×10^{15} ^{18}O cm^{-2} (Table I). A significant reduction of the ^{18}O amount is observed while comparing samples B and C. This fact suggests that H$_2$O$_2$ converts SiC$_x$O$_y$ in SiO$_2$ that is subsequently removed by HF.

One could argue that the lower ^{18}O amount detected from sample C is due to oxygen isotopic exchange from the existing SiC$_x$O$_y$ layer and the O$_2$+H$_2$O$_2$ gas phase. In this case, the reminiscent ^{18}O amount of sample C would not be representative of SiC$_x$O$_y$ removal. An independent result is needed in order to confirm the proposed mechanism. In view of that, we performed XPS analysis of samples B and C to compare the amount of oxidized species remaining at these samples' surfaces. Figure 3 shows Si 2p regions of XPS spectra of samples B and C. Si 2p doublets were simulated by two lines with a branching ratio 2$p_{1/2}$/2$p_{3/2}$ of 0.5 (the statistical ratio) and a spin-orbit splitting of 0.6 eV. The Si 2p region of sample B was fitted with one component with binding energy (BE) of 102.1 eV, attributed to SiC$_x$O$_y$. The absence of a signal from the SiC substrate evidences that photoelectrons generated underneath the oxidized layer are completely attenuated. If this SiC$_x$O$_y$ layer was removed or at least thinned in some extent, one would observe a lower BE signal from the SiC substrate. That is exactly the case of
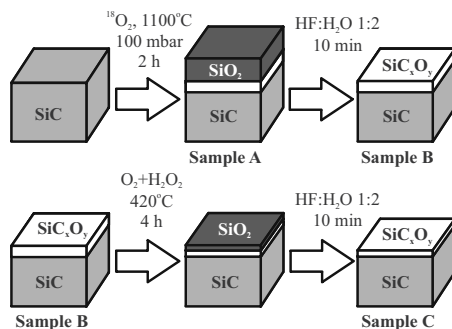

FIG. 2. Sketch of the sample processing route evidencing the annealing and etching conditions used in the experiment. A specific name is assigned to each sample corresponding to its processing history.
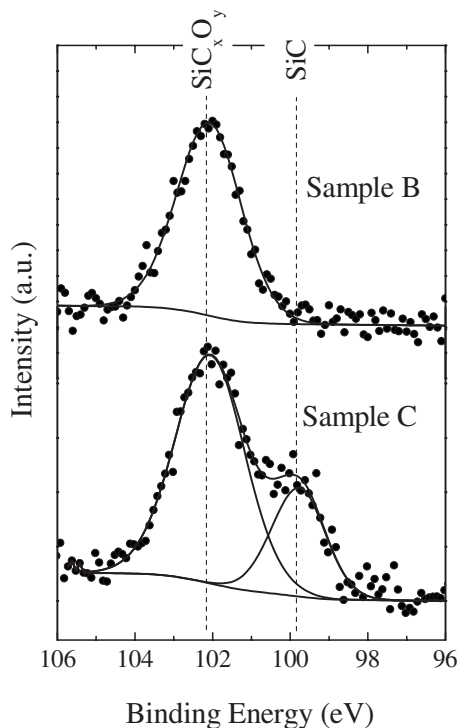
FIG. 3. Si 2*p* regions of XPS spectra corresponding to samples B (upper part) and sample C (bottom part). Points represent experimental data. Solid curves correspond to fitting components, background, and their sum. The energy position of components assigned to silicon oxycarbide and silicon carbide are indicated. a.u. stands for arbitrary units.

sample C. A clear signal at 99.8 eV can be observed in the XPS data obtained from this sample (Fig. 3), confirming that the use of H_2O_2 indeed lowered the amounts of SiC_xO_y.

In summary, we have shown the effects of using H_2O_2 as an oxidizing agent on the electrical and physicochemical characteristics of the resulting $SiO_2/4H$-SiC structures. In comparison with similar structures prepared by $4H$-SiC thermal oxidation using H_2O, reduced interface state densities were observed. This effect was correlated with the decrease

in SiC_xO_y compounds at the $SiO_2/4H$-SiC interface region as confirmed by two independent methods. The combination of this passivation method with other well-established treatments like nitridation and annealing in H_2, may further improve the quality of the $SiO_2/4H$-SiC interface.

[1]R. Singh, Microelectron. Reliab. **46**, 713 (2006).
[2]V. V. Afanas'ev, F. Ciobanu, S. Dimitrijev, G. Pensl, and A. Stesmans, J. Phys.: Condens. Matter **16**, S1839 (2004).
[3]W. Lu, L. C. Feldman, Y. Song, S. Dhar, W. E. Collins, W. C. Mitchel, and J. R. Williams, Appl. Phys. Lett. **85**, 3495 (2004).
[4]J. L. Cantin, H. J. von Bardeleben, Y. Shishkin, Y. Ke, R. P. Devaty, and W. J. Choyke, Phys. Rev. Lett. **92**, 015502 (2004).
[5]B. Hornetz, H. J. Michel, and J. Halbritter, J. Mater. Res. **9**, 3088 (1994).
[6]S. Wang, S. Dhar, S. Wang, A. C. Ahyi, A. Franceschetti, J. R. Williams, L. C. Feldman, and S. T. Pantelides, Phys. Rev. Lett. **98**, 026101 (2007).
[7]R. Palmieri, C. Radtke, M. R. da Silva, H. Boudinov, and E. F. da Silva, J. Phys. D: Appl. Phys. **42**, 125301 (2009).
[8]A. Constant, N. Camara, P. Godignon, and J. Camassel, Appl. Phys. Lett. **94**, 063508 (2009).
[9]J. P. Xu, P. T. Lai, C. L. Chan, and Y. C. Cheng, Appl. Phys. Lett. **76**, 372 (2000).
[10]G. Y. Chung, C. C. Tin, J. R. Williams, K. McDonald, M. Di Ventra, S. T. Pantelides, L. C. Feldman, and R. A. Weller, Appl. Phys. Lett. **76**, 1713 (2000).
[11]M. K. Das, Mater. Sci. Forum **457**, 1275 (2004).
[12]K. McDonald, M. B. Huang, R. A. Weller, L. C. Feldman, J. R. Williams, F. C. Stedile, I. J. R. Baumvol, and C. Radtke, Appl. Phys. Lett. **76**, 568 (2000).
[13]P. Jamet, S. Dimitrijev, and P. Tanner, J. Appl. Phys. **90**, 5058 (2001).
[14]S. A. Corrêa, C. Radtke, G. V. Soares, L. Miotti, I. J. R. Baumvol, S. Dimitrijev, J. Han, L. Hold, F. Kong, and F. C. Stedile, Appl. Phys. Lett. **94**, 251909 (2009).
[15]C. Onneby and C. G. Pantano, J. Vac. Sci. Technol. A **15**, 1597 (1997).
[16]C. Radtke, I. J. R. Bumvol, J. Morais, and F. C. Stedile, Appl. Phys. Lett. **78**, 3601 (2001).
[17]S. A. Corrêa, C. Radtke, G. V. Soares, I. J. R. Baumvol, C. Krug, and F. C. Stedile, Electrochem. Solid-State Lett. **11**, H258 (2008).
[18]E. H. Nicollian and A. Goetzberger, Bell Syst. Tech. J. **46**, 1055 (1967).
[19]V. V. Afanas'ev, M. Bassler, G. Pensl, and M. Schulz, Phys. Status Solidi A **162**, 321 (1997).
[20]I. J. R. Baumvol, Surf. Sci. Rep. **36**, 1 (1999).