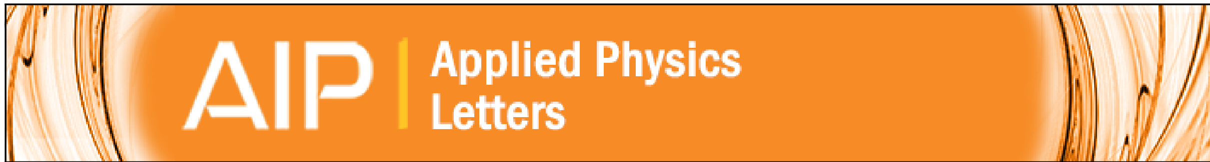

Interaction of SiC thermal oxidation by-products with SiO_2

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APPLIED PHYSICS LETTERS **92**, 252909 (2008)

Interaction of SiC thermal oxidation by-products with SiO_2

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We investigated oxygen incorporation and exchange during thermal growth of silicon oxide films on silicon carbide. This investigation was carried out in parallel with the thermal growth of silicon oxide films on silicon for comparison. We provide experimental evidence that oxidation by-products of silicon carbide out-diffuse and interact with the silicon oxide overlayer, incorporating C and O. This and other results are in sharp contrast to those obtained for silicon samples, constituting a key issue in the stability of any dielectric material used on silicon carbide. *© 2008 American Institute of Physics*. [DOI: 10.1063/1.2945643]

Thermal growth of dielectric films on semiconductor substrates plays a central role in device technology. Such a process has enabled the microelectronics revolution through the formation of a virtually defect free interface between Si and its oxide.[1,2] Thermal oxide growth is also an important processing step of SiC, a semiconductor material with interesting properties for applications where devices are submitted to extreme operation conditions (high temperature, high frequency, high voltage, and/or high power).[3] Despite the similarities of the oxides formed on both materials, one of the building blocks for the success of the SiO_2/Si technology is the main problem for SiC-based devices: the dielectric/semiconductor interface. Large densities of electrically active defects are observed in SiC metal-oxide-semiconductor structures. The physical origin for such defects is mainly attributed to residual carbon in the oxide layer.[4] Several groups investigated the atomic mechanisms involved in the SiO_2 thermal growth on SiC, aiming at elucidating how C compounds are formed in the SiO_2/SiC structure.[5–7] Theoretical investigations[5,8] indicate that CO released from the advancing interface during SiO_2 thermal growth would diffuse through the oxide, interacting with it and forming C clusters. This theoretical result is supported by different experimental analyses[9,10] which evidenced high C concentrations along thermally grown SiO_2/SiC interfaces. This C enrichment was also related to a graded transition between the oxide layer and the SiC substrate.[6] Besides C clusters, compounds such as silicon oxycarbides are also present close to the interface region.[11] The complex composition of the region adjacent to the SiC substrate constitutes a thicker reaction layer for diffusing species as compared to Si. In order to conveniently modify the preparation routes of dielectric films thermally grown on SiC, in the quest for lower densities of electrically active defects, a deeper comprehension of the mechanisms involved in this process is still needed. For example, the identification of mobile species and the knowledge of how they interact with the SiO_2/SiC structure during thermal growth of SiO_2 are essential issues to be addressed. In the present work, we investigated the incorporation and exchange of oxygen during dry thermal growth of SiO_2 on SiC by means of isotopic tracing and nuclear reaction profiling (NRP) techniques. The main objectives were to investigate the oxygen exchange at the SiO_2/SiC interface, comparing these results with those of SiO_2/Si counterpart structures and identify possible interactions of SiC oxidation by-products with the SiO_2/SiC structure. Our results provide direct evidence of oxygen replacement in the bulk of the growing oxide (in sharp contrast with SiO_2 films on Si) and carbon incorporation to the SiO_2 overlayer. Both processes are due to the formation of SiC oxidation by-products that react with the oxide layer in their way out of the film.

4*H*-SiC $(000\underline{1})$ and Si (001) *n*-type substrates were cleaned following the standard Radio Corporation of America routine, followed by a dip for 30 s in a 5% HF aqueous solution and water rinsing for 30 s, aiming at removing the native oxide. Thermal oxidations were performed in a resistively heated quartz tube furnace under a static pressure of 100 mbar of either natural O_2 (<1 ppm of water, termed $^{16}O_2$, ^{16}O natural abundance $\sim$99,8%) or ^{18}O enriched (97%) O_2 (termed $^{18}O_2$). SiO_2 films were also deposited by plasma enhanced chemical vapor deposition (PECVD) using NO_2 and SiH_4 as precursors. ^{18}O profiles were determined by NRP using the resonance at 151 keV in the cross section curve of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction.[12] This technique enables ^{18}O profiling with a depth resolution of $\sim$1 nm close to the sample surface. Carbon depth profiling was performed using the resonance at 4.26 MeV of the $^{12}C(\alpha,\alpha)^{12}C$ nuclear reaction. After using a specific spectral analysis method,[13] C profiles with depth resolution of $\sim$10 nm could be achieved.

Figure 1 shows experimental (symbols) and simulated[12] (lines) excitation curves of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction for (a) Si and (b) SiC substrates after oxidation in $^{16}O_2$ followed by a second oxidation step in $^{18}O_2$. Excitation curves in (a) and (b) show two peaks each: one close to 151 keV, corresponding to ^{18}O in the oxide surface region, and one at 163 keV, corresponding to ^{18}O in the SiO_2/semiconductor interface region. The surface signal for ^{18}O is related to isotopic exchange mediated by defects that are confined to this region of the oxide.[2] The profiles in Figs. 2(a) and 2(b) (ob-

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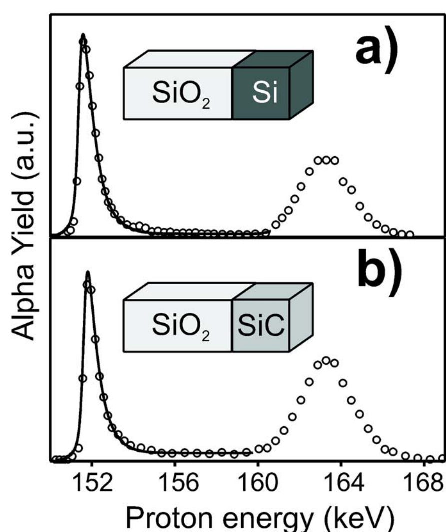

FIG. 1. (Color online) Experimental excitation curves (symbols) of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction and the corresponding simulations (lines) for silicon oxide films thermally grown on (a) Si (100) and on (b) 4*H*-SiC (000$\underline{1}$). Samples were first oxidized at 1100 °C in $^{16}O_2$ (20 h for SiC and 3 h for Si) and then reoxidized at 1000 °C in $^{18}O_2$ (4 h for SiC and 1 h for Si). ^{18}O profiles used for the simulations of excitation curves are shown in Fig. 2. a.u. stands for arbitrary units.

tained from the respective excitation curves of Fig. 1) show almost identical complementary-error-function-like near-surface distributions, evidencing the similarity, in this region, of amorphous silica thermally grown on Si and on SiC. ^{18}O fixation near the SiO_2/semiconductor interface is due to interstitial diffusion of O_2 across the growing oxide and reaction with the semiconductor substrate, forming $Si^{18}O_2$ in accordance with the model of Deal and Grove.[14] The interface signals in Figs. 1(a) and 1(b) are also indistinguishable. ^{18}O profiles close to the oxide/semiconductor interface could not be unambiguously determined from the data in Fig. 1 because depth resolution in NRP degrades as the path length of the incident ion increases in the sample.[15] However, a more detailed analysis reveals differences between the oxidation of Si and SiC that can be understood based on chemical reactions between carbon-containing by-products of SiC oxidation and the growing oxide layer. According to Figs. 2(a) and 2(b), the concentration of ^{18}O in the bulk of the oxide layer grown on SiC is 1.5% of the oxygen concentration in SiO_2,

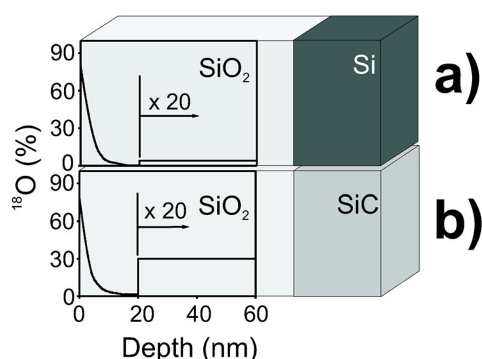

FIG. 2. (Color online) ^{18}O profiles used for simulation of the experimental excitation curves of Fig. 1. Behind each profile, there is a sketch of the analyzed sample indicating the probed region. ^{18}O concentration in all profiles is normalized to O in stoichiometric SiO_2. The sample assignment is the same used in Fig. 1.

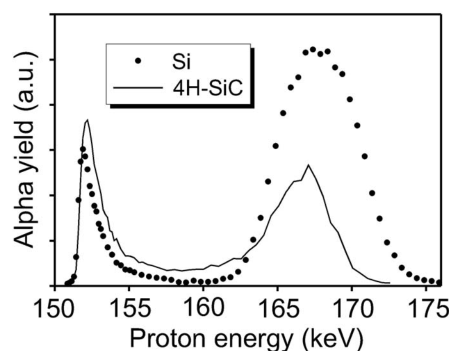

FIG. 3. Experimental excitation curves of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction for SiO_2/Si (symbols) and SiO_2/SiC (line) structures prepared as follows. After SiO_2 deposition by PECVD, both samples were oxidized in 100 mbar of $^{18}O_2$ for 8 h at 1000 °C. a.u. stands for arbitrary units.

while in the Si counterpart sample, ^{18}O is limited to its natural abundance of 0.2%. The Si control sample reproduces data in the literature[2] and confirms that there is no exchange between O in the bulk of stoichiometric SiO_2 and ^{18}O from the gas phase. The result observed for SiC must be attributed to one or more of (a) incomplete substrate oxidation with $^{16}O_2$ (i.e., residual Si–C bonding) that is oxidized during the $^{18}O_2$ step, (b) exchange of in-diffusing ^{18}O with C incorporated in the SiO_2 layer by out-diffusing CO, and (c) reaction of out-diffusing $C^{18}O$ with the SiO_2 overlayer. Available evidences[5,8–11] favors mechanisms (b) and (c). We hypothesize that the higher ^{18}O concentration in the bulk region of the oxide layer of the SiC-based sample is due to chemical reaction mediated by carbon due to mechanisms (b) and (c) discussed above.

Additional evidence that oxide modification is triggered by substrate oxidation was obtained by exposing the samples sequentially oxidized in $^{16}O_2$ and $^{18}O_2$ to one more step in $^{16}O_2$. When the third treatment was carried out at 800 °C for up to 8 h, leading to negligible oxidation of the SiC substrate, no loss of ^{18}O was detected. Performing the last oxidation step at 1000 °C for 4 and 8 h resulted in the loss of 3.07 and 3.67×10^{15} $^{18}O/cm^2$, respectively. These values were obtained by subtraction of the interface peak areas of the excitation curves before and after the last oxidation step. It should be noted that from a qualitative standpoint, analogous experiments with Si substrates did result in ^{18}O loss.[16] Nevertheless, neither temperature nor oxidation time presented such an influence on Si samples. Besides, the amount of ^{18}O lost at 1000 °C is twice that observed for Si counterpart samples, despite the fact that the oxidation rate is significantly higher for the latter. While the evidence indicates more than one mechanism for isotopic exchange, there is a clear correlation between it and the SiC substrate.

A final batch of samples was prepared using PECVD to deposit identical SiO_2 layers on both Si and SiC substrates. Thus, differences arisen from an additional thermal oxidation step can be solely attributed to the interaction of O_2 with the semiconductor substrate. Figure 3 shows excitation curves of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction for Si (symbols) and SiC (line) based samples. One sample of each semiconductor substrate was prepared by firstly depositing a 100 nm SiO_2 layer by PECVD. After that, both samples were oxidized for 8 h in 100 mbar of $^{18}O_2$ at 1000 °C. The obtained excitation curves presented two peaks, as shown in Fig. 1. The Si sample presents an ^{18}O concentration in the bulk region of

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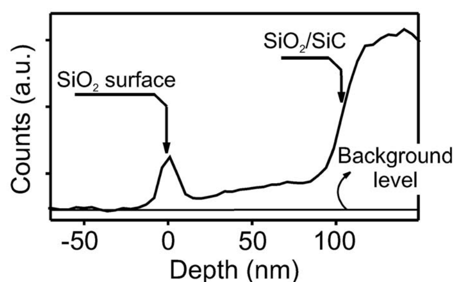

FIG. 4. C profile obtained using the resonance at 4.26 MeV of the $^{12}C(\alpha,\alpha)^{12}C$ nuclear reaction from the 4*H*-SiC based sample of Fig. 3. a.u. stands for arbitrary units.

the oxide film ($\sim 0.3\% \pm 0.05\%$ of the oxygen concentration in SiO_2) slightly higher than the natural abundance (0.2%) of this isotope. This observation evidences the higher density of interaction sites for ^{18}O containing species in the deposited SiO_2 layer in comparison to thermal oxides. The excitation curve obtained from the SiC-based sample suggests an ^{18}O asymmetric distribution close to the SiO_2/SiC interface. A tail towards the oxide surface is also observed. Besides, the ^{18}O concentration is higher than that observed for its Si counterpart sample in the whole depth of the SiO_2 layer including the oxide surface region. One should note that in the Si sample neither remarkable asymmetry in the high energy portion of the excitation curve nor significant ^{18}O concentration above its natural abundance in the bulk region of the oxide layer were observed. This result proves that indeed a by-product of the SiC oxidation containing ^{18}O interacts with the SiO_2 overlayer, promoting incorporation of this isotope in the deposited oxide.

Figure 4 shows the distribution of ^{12}C in the SiC based sample of Fig. 3. The C peak at the sample surface is observed as a result of unavoidable carbonaceous contamination adsorbed during the analysis performed *ex situ*. The leading edge at ~ 104 nm corresponds to the beginning of the C signal from the SiC substrate. If the deposited SiO_2 layer was free from C, the signal between the surface peak and the substrate edge should be at the background level, as indicated in the figure. However, the C profile clearly indicates that this element is incorporated in the SiO_2 layer after annealing of the SiO_2/SiC structure in oxygen.

In summary, remarkable differences between thermal oxidation of Si and SiC were evidenced. In the former case, oxidation parameters have no significant influence on the amount of oxygen exchanged close to the oxide/semiconductor interface. This is not true for SiC: temperature and time strongly affected isotopic exchange, evidencing a more complex mechanism intervening in this process. The chemical ambiance of the SiO_2/SiC interfacial region certainly plays a decisive role. Furthermore, we provided direct experimental evidence that oxidation by-products of SiC, most probably CO,[5,8,17] out diffuse and interact with the SiO_2 overlayer, either deposited or thermally grown. Oxygen exchange resulting from CO interaction with SiO_2/Si structures was already observed,[17] further strengthening the hypothesis that CO is the relevant species responsible for the present experimental observations. However, the existence of other relevant species (CO_2, for example) cannot be ruled out. This result clearly distinguishes the thermal oxidation processes of Si and SiC. In the latter case, additional reactive species and reaction sites must be taken into account besides molecular oxygen for appropriate modeling of the thermal oxide growth. This behavior evidences a complex reaction environment at the SiO_2/SiC interfacial region that is prone to influence any dielectric material used on SiC substrates.

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[1] M. L. Green, E. P. Gusev, R. Degraeve, and E. L. Garfunkel, J. Appl. Phys. **90**, 2057 (2001).
[2] I. J. R. Baumvol, Surf. Sci. Rep. **36**, 1 (1999).
[3] R. Singh, Microelectron. Reliab. **46**, 713 (2006).
[4] P. Deák, J. M. Knaup, T. Hornos, C. Thill, A. Gali, and T. Frauenheim, J. Phys. D **40**, 6242 (2007).
[5] J. M. Knaup, P. Deák, T. Frauenheim, A. Gali, Z. Hajnal, and W. J. Choyke, Phys. Rev. B **71**, 235321 (2005).
[6] C. Radtke, I. J. R. Baumvol, B. C. Ferrera, and F. C. Stedile, Appl. Phys. Lett. **85**, 3402 (2004).
[7] M. Di Ventra and S. T. Pantelides, Phys. Rev. Lett. **83**, 1624 (1999).
[8] S. Wang, M. Di Ventra, S. G. Kim, and S. T. Pantelides, Phys. Rev. Lett. **86**, 5946 (2001).
[9] K. C. Chang, N. T. Nuhfer, L. M. Porter, and Q. Wahab, Appl. Phys. Lett. **77**, 2186 (2000).
[10] W. Lu, L. C. Feldman, Y. Song, S. Dhar, W. E. Collins, and W. C. Mitchell, Appl. Phys. Lett. **85**, 3495 (2004).
[11] C. Radtke, I. J. R. Baumvol, J. Morais, and F. C. Stedile, Appl. Phys. Lett. **78**, 3601 (2001).
[12] C. Driemeier, L. Miotti, R. P. Pezzi, K. P. Bastos, and I. J. R. Baumvol, Nucl. Instrum. Methods Phys. Res. B **249**, 278 (2006).
[13] C. Driemeier and I. J. R. Baumvol, Nucl. Instrum. Methods Phys. Res. B **266**, 2041 (2008).
[14] B. E. Deal and A. S. Grove, J. Appl. Phys. **36**, 3770 (1965).
[15] R. P. Pezzi, P. L. Grande, M. Copel, G. Schiwietz, C. Krug, and I. J. R. Baumvol, Surf. Sci. **601**, 5559 (2007).
[16] T. Akermark, L. G. Gosset, J.-J. Ganem, I. Trimaille, I. Vickridge, and S. Rigo, J. Appl. Phys. **86**, 1153 (1999).
[17] I. Vickridge, J. Ganem, Y. Hoshino, and I. Trimaille, J. Phys. D **40**, 6254 (2007).

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