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Water vapor interaction with silicon oxide films thermally grown on 6H-SiC and on Si

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Thermally induced incorporation of isotopically labeled water vapor ($D_2\,^{18}O$) species in 7 nm thick SiO_2 films thermally grown on 6H-SiC(0001) and on Si(001) were investigated. Higher incorporation of hydrogen and higher isotopic exchange were observed in SiO_2/SiC as compared to SiO_2/Si, at temperatures above 600 °C, which can lead to electrical instabilities, especially in high-temperature devices. At any annealing temperature, oxygen is incorporated in the oxide films, reaching the SiO_2/SiC interface, in contrast with SiO_2/Si. The present observations show that strict control of water vapor contents in SiO_2/SiC is mandatory in order to achieve further improvements in the SiC-based device technology. © *2009 American Institute of Physics*. [doi:10.1063/1.3262971]

Silicon carbide (SiC) is a wide band gap semiconductor suitable for extreme conditions application devices.[1,2] However, the interface between silicon oxide films thermally grown on SiC (SiO_2/SiC) presents a higher interface state density (D_{it}) (Refs. 1–3) that prevents the broad use of SiC as a semiconductor material, which has been mainly attributed to the presence of silicon oxycarbides and carbon clusters.[2,3] Postoxidation annealing in NO and in H_2 leads[3,4] to partial passivation of electrically active defects near the SiO_2/SiC interface. In order to achieve further improvements in the electrical characteristics of SiO_2/SiC structures, the influence of previously neglected factors should be investigated. Among them, the role of water vapor in the physicochemical and electrical properties of SiO_2 films thermally grown on SiC appears as a serious issue, since the relative humidity of a typical clean room fabrication facility is between 30% and 50%. It has been reported that water related species in SiO_2 films on Si (Refs. 5–7) produce negative oxide charge buildup near the SiO_2/Si interface and increase D_{it}. Reliability issues, such as, negative-bias-temperature instabilities were also attributed to the presence of water related species at the SiO_2/Si interface.[8] These observations should also occur in the SiO_2/SiC case, but they have not been addressed so far. In the present letter we investigate thermally induced incorporation of species from isotopically labeled water vapor in SiO_2 films thermally grown on 6H-SiC(0001) and on Si(001).

Silicon-faced n-type 6H-SiC (0001) and Si (001) wafers were cleaned with standard RCA routine and etched in a 5% HF solution. Samples were then immediately loaded in a static pressure, resistively heated quartz tube furnace, which was pumped down to 2×10^{-7} mbar, before being pressurized with the chosen annealing gas. 7 nm thick SiO_2 films were thermally grown at 1100 °C in 100 mbar of dry O_2 on SiC, exposing the wafers for 1 h, and on Si for 15 min. Then, samples were annealed in vacuum at 700 °C for 30 min prior to submission to a further annealing, always without exposure to the atmospheric air, at temperatures ranging from 20 to 1000 °C, for 1 h, in 10 mbar of water vapor simultaneously enriched in the ^{18}O and ^2H (D) rare isotopes, hereafter called $D_2\,^{18}O$ annealing. The water vapor pressure used in this annealing corresponds approximately to the H_2O partial pressure in air of 30% relative humidity at 25 °C.[9] After annealing, samples were moved from the annealing chamber to the analyses chambers with exposure to the atmospheric air. ^{18}O and D quantification were accomplished by nuclear reaction analyses.[10,11] The areal density of ^{16}O was determined by Rutherford backscattering spectrometry in channeling geometry[12] using He^+ ions at 2 MeV. ^{18}O profiles were determined using the narrow resonance in the cross section curve of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction at 151 keV.[10]

Temperature dependence of ^{18}O incorporation in $Si\,^{16}O_2/Si$ (■) and in $Si\,^{16}O_2/SiC$ (□) structures is shown in Fig. 1(a), as well as the total O (^{18}O plus ^{16}O) amounts incorporated in each case (triangles). Figure 1(b) shows only the total ^{16}O amount in SiO_2/Si and in SiO_2/SiC structures. In the 20–600 °C temperature range, ^{18}O areal densities increase monotonically for both substrates, being approximately 1.5 times higher in SiO_2/SiC than in SiO_2/Si, while the total O amounts remain constant, indicating that isotopic exchange between ^{18}O from the water vapor and ^{16}O from the SiO_2 network is apparently occurring. This is confirmed by the data in Fig. 1(b), where a reduction in total ^{16}O amount is observed in the same temperature range. Previous theoretical and experimental work[13–15] reported on the transport of molecular water as the most stable form, but the breakage of water molecule in OH^- and H^+ is also possible. Reaction between the incoming water molecules and the SiO_2 network is observed during diffusion, leading to the formation of silanol groups (Si–OH).[14] This can take place even at low temperatures (<250 °C) due to the low activation energy[15] of the following reversible reaction:

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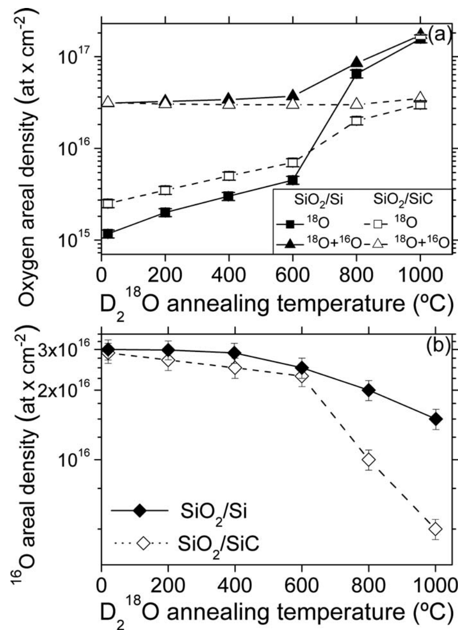
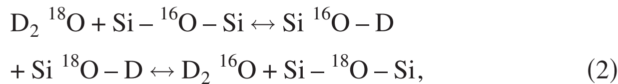


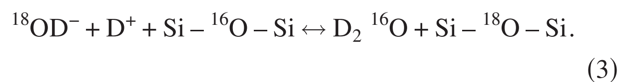
FIG. 1. Oxygen areal densities as a function of the $D_2\,^{18}O$ annealing temperature in SiO_2/Si (solid symbols) and in SiO_2/SiC (open symbols). (a) ^{18}O (squares) and $^{16}O+^{18}O$ (triangles) and (b) ^{16}O (lozenges). Lines are only to guide the eyes. 5% error bars are included.

$$H_2O + Si-O-Si \leftrightarrow 2Si-OH. \quad (1)$$

Isotopic exchange between oxygen from the vapor phase and oxygen from the SiO_2 film can take place during reaction (1), as indicated by the data in Fig. 1(a) for SiO_2/Si and SiO_2/SiC in the 20–600 °C temperature range. Two possible reactions can be associated with this isotopic exchange process:



$$D_2\,^{18}O + Si-{}^{16}O-Si \leftrightarrow Si\,^{16}O-D + Si\,^{18}O-D \leftrightarrow D_2\,^{16}O + Si-{}^{18}O-Si, \quad (2)$$



$$^{18}OD^- + D^+ + Si-{}^{16}O-Si \leftrightarrow D_2\,^{16}O + Si-{}^{18}O-Si. \quad (3)$$

These reactions assume a defect-free oxide, whereas it is well known that defects in the SiO_2 network[16] enhance the oxygen isotopic exchange during $^{18}O_2$ annealing. The same should happen during $D_2\,^{18}O$ annealing. Since the annealing parameters are the same in both cases, other factors should lead to the observed picture, such as SiO_2 network defects concentration.

In the 600–1000 °C temperature range, the ^{18}O areal densities increase over an order of magnitude in SiO_2/Si samples, whereas the total ^{16}O amount in Fig. 1(b) decrease only 1.5 times, indicating the occurrence of a different process, rather than isotopic exchange. These can be attributed to diffusion of water species toward the SiO_2/Si interface and further reaction with the Si substrate, forming $Si\,^{18}O_2$. In the case of SiO_2/SiC, the ^{18}O areal density [Fig. 1(a)] increase is comparable with the ^{16}O areal density [Fig. 1(b)] decrease for the same temperature range. This is attributed to the higher oxidation resistance of SiC as compared to Si and to a higher oxygen isotopic exchange in SiO_2/SiC. Indeed, $Si\,^{18}O_2$ formation in SiC samples is detected only at 1000 °C, when a slight increase in the total oxygen amount is observed. Furthermore, the higher O isotopic exchange observed in SiO_2/SiC samples as compared to SiO_2/Si in both regimes, may once again be related to a higher concentration of defects in SiO_2 films thermally grown on SiC.

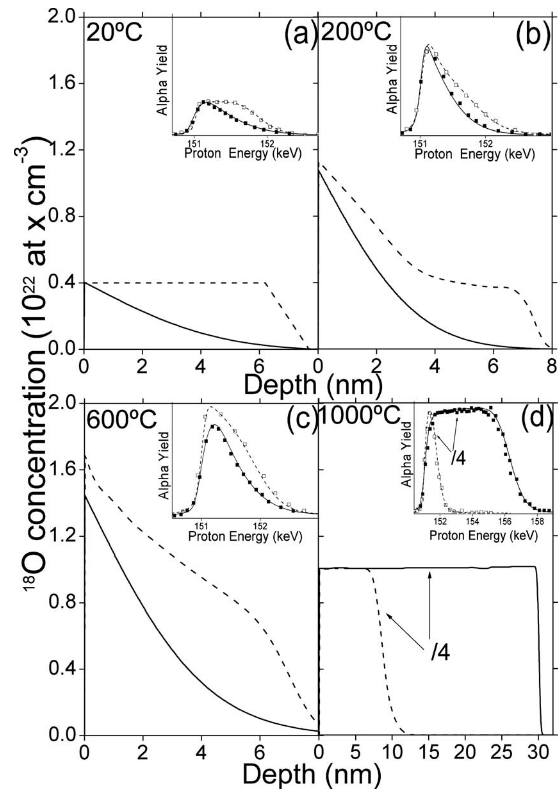


FIG. 2. ^{18}O profiles for SiO_2/Si (solid lines) and SiO_2/SiC (dashed lines) samples annealed in $D_2\,^{18}O$ at (a) 20 °C, (b) 200 °C, (c) 600 °C, and (d) 1000 °C obtained from the simulation of the experimental excitation curves (symbols) of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction around the resonance energy $E_r = 151$ keV presented in the insets. Line types of the insets represent the simulations and are the same as in the ^{18}O profiles. *y*-axis in profiles and excitation curves for samples annealed at 1000 °C (d) are divided by a factor of 4.

Figure 2 shows the ^{18}O profiles for SiO_2/Si (—) and SiO_2/SiC (---) samples annealed in $D_2\,^{18}O$ at 20, 200, 600, and 1000 °C, obtained from the simulation (lines) of the experimental excitation curves (symbols) presented in the insets. At room temperature [Fig. 2(a)], the ^{18}O profile is erfc-like in the SiO_2/Si sample, while a constant, boxlike profile is observed in SiO_2/SiC, evidencing striking differences in water vapor interactions with SiO_2 films thermally grown on Si and on SiC. In SiO_2/Si, the profiles indicate a diffusion-limited process, while in SiO_2/SiC the evidence is for an interface reaction-limited process, whereby ^{18}O diffuses through the SiO_2 film, reaching the SiO_2/SiC interface. Thus, for SiO_2/Si, we observe surface isotopic exchange, intermediated by peroxyl bridges,[16,17] whereas in SiO_2/SiC a ^{18}O constant concentration in depth ($0.4\times10^{22}\,^{18}O/cm^3$), indicates that isotopic exchange takes place in the whole oxide film. For 200 and 600 °C annealing temperatures, the ^{18}O profile in SiO_2/Si is still ercf-like, but with higher ^{18}O surface concentrations. This fact confirms that for the low temperature regime, the main process for oxygen incorporation in SiO_2/Si is isotopic exchange confined to near surface regions, with no evidences of reaction between water oxidant species and the Si substrate. ^{18}O profiles in SiO_2/SiC annealed at 200 and 600 °C evidence that ^{18}O is incorporated in the near surface and bulk regions of the oxide film, indi-

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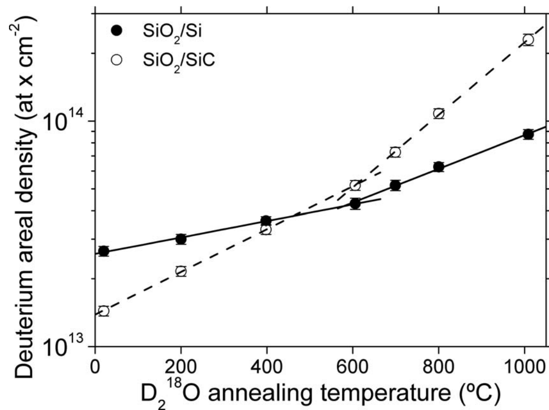

FIG. 3. Deuterium areal density a function of the $D_2\,^{18}O$ annealing temperature in SiO_2/Si (solid circles) and SiO_2/SiC (open circles). Lines are only to guide the eyes. 10% error bars are included.

cating a higher concentration of bulk defects generated in the SiO_2 film during thermal growth on SiC. Similar observations were reported[18] in SiO_2 films on Si prepared by anodic oxidation, where the higher defective anodic SiO_2 film presented a higher incorporation of water related species during thermal annealings in ^{18}O enriched water vapor. The incorporation of carbonaceous species[19] in the bulk of the SiO_2 films thermally grown on SiC can account for different reaction sites for water incorporation, which are not present in SiO_2/Si structures. At 1000 °C, ^{18}O profiles confirm the complete oxygen isotopic exchange and the formation of $Si\,^{18}O_2$ in both systems.

D areal densities as a function of $D_2\,^{18}O$ annealing temperature in SiO_2/Si and SiO_2/SiC structures are shown in Fig. 3. In the low temperature regime, a higher D incorporation is observed in SiO_2/Si as compared to SiO_2/SiC, in contrast with the ^{18}O incorporation in the same temperature range. This is not a contradictory observation, since, owing to O isotopic exchange, ^{18}O incorporation is not necessarily related to D incorporation in the form of silanol groups. Thus, a different site for D incorporation, besides the formation of SiOH, should be present in SiO_2/Si samples. We attribute this difference in D incorporation in part to the existence of Si dangling bonds near the SiO_2/Si interfac.[20] Since water molecules can break into $^{18}OD^-$ and D^+, the latter can diffuse through the SiO_2 film to partially passivate these defects near the SiO_2/Si interface. $^{18}OD^-$ can react with the SiO_2 network, forming $Si\,^{18}OD$. Si and C dangling bonds have also been observed[21] near the SiO_2/SiC interface, constituting sites for D incorporation. However, significant H amounts are incorporated in SiO_2/SiC structures only at temperatures above 600 °C.[22] In this way, the main channel for D incorporation in SiO_2/SiC in the low temperature range should be in the form of SiOD. The picture changes in the high temperatures regime, where a higher D incorporation is observed in SiO_2/SiC samples. This can be explained using the same fact presented above, since at temperatures above 600 °C, the incorporation of D near the SiO_2/SiC interface becomes higher than in SiO_2/Si.[11,22] Furthermore, the lower D incorporation in SiO_2/Si in the high-temperature regime is a consequence of the depassivation of P_b centers, since the chemical bond between Si and D becomes unstable for temperatures above 500 °C.

In summary, it was shown that SiO_2 films thermally grown on Si and on 6H–SiC present striking differences concerning interaction with water vapor, attributed to a higher defect concentration in the SiO_2 film thermally grown on SiC. The above presented observations point out that a strict control of water vapor contents in all fabrication steps is mandatory in order to achieve further improvements in SiC-based devices technology.

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