Water vapor interaction with silicon oxide films thermally grown on 6H-SiC and on Si
G. V. Soares, I. J. R. Baumvol, S. A. Corrêa, C. Radtke, and F. C. Stedile

Citation: Applied Physics Letters 95, 191912 (2009); doi: 10.1063/1.3262971
View online: http://dx.doi.org/10.1063/1.3262971
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/95/19?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Influence of CO annealing in metal-oxide-semiconductor capacitors with SiO2 films thermally grown on Si and on SiC
J. Appl. Phys. 119, 025307 (2016); 10.1063/1.4939836

Deuterium absorption from the D2O exposure of oxidized 4H-SiC (0001), ( 000 1¯ ), and ( 11 2 0 ) surfaces

Water absorption in thermally grown oxides on SiC and Si: Bulk oxide and interface properties

Rhenium ohmic contacts on 6H-SiC
J. Appl. Phys. 96, 5357 (2004); 10.1063/1.1797550

Characterization of hydrogen etched 6H–SiC(0001) substrates and subsequently grown AlN films
J. Vac. Sci. Technol. A 21, 394 (2003); 10.1116/1.1539080
Water vapor interaction with silicon oxide films thermally grown on 6H-SiC and on Si

G. V. Soares,1,a I. J. R. Baumvol,2 S. A. Corrêa,3 C. Radtke,4 and F. C. Stedile4
1Universidade de Caxias do Sul, Caxias do Sul, Rio Grande do Sul 95070-560, Brazil
2Universidade de Caxias do Sul, Caxias do Sul, Rio Grande do Sul 95070-560, Brazil
and Instituto de Física, UFRGS, Porto Alegre, Rio Grande do Sul 91509-900, Brazil
3PGMICRO, UFRGS, Porto Alegre, Rio Grande do Sul 91501-970, Brazil
4Instituto de Química, UFRGS, Porto Alegre, Rio Grande do Sul 91509-900, Brazil

(Received 28 September 2009; accepted 21 October 2009; published online 13 November 2009)

Thermally induced incorporation of isotopically labeled water vapor (D2 18O) species in 7 nm thick SiO2 films thermally grown on 6H-SiC(0001) and on Si(001) were investigated. Higher incorporation of hydrogen and higher isotopic exchange were observed in SiO2/SiC as compared to SiO2/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 SiO2/SiC interface, in contrast with SiO2/Si. The present observations show that strict control of water vapor contents in SiO2/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 (SiO2/SiC) presents a higher interface state density (Dit) (Refs. 1–3) that prevents the broad use of SiC as a semiconductor material, which has been mainly attributed to the presence of silicon oxy-carbides and carbon clusters.2,3 Postoxygen annealing in NO and in H2 leads2,3 to partial passivation of electrically active defects near the SiO2/SiC interface. In order to achieve further improvements in the electrical characteristics of SiO2/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 SiO2 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 SiO2 films on Si (Refs. 5–7) produce negative oxide charge buildup near the SiO2/Si interface and increase Dit. Reliability issues, such as, negative-bias-temperature instabilities were also attributed to the presence of water related species at the SiO2/Si interface.8 These observations should also occur in the SiO2/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 SiO2 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 SiO2 films were thermally grown at 1100 °C in 100 mbar of dry O2 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 18O and 2H (D) rare isotopes, hereafter called D2 18O annealing. The water vapor pressure used in this annealing corresponds approximately to the H2O 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. 18O and D quantification were accomplished by nuclear reaction analyses.10,11 The areal density of 18O was determined by Rutherford backscattering spectrometry in channeling geometry12 using He+ ions at 2 MeV. 18O profiles were determined using the narrow resonance in the cross section curve of the 18O(p, α)15N nuclear reaction at 151 keV.10

Temperature dependence of 18O incorporation in Si 16O2/Si (■) and in Si 18O2/SiC (□) structures is shown in Fig. 1(a), as well as the total O 18O plus 16O amounts incorporated in each case (triangles). Figure 1(b) shows only the total 16O amount in SiO2/Si and in SiO2/SiC structures. In the 20–600 °C temperature range, 18O areal densities increase monotonically for both substrates, being approximately 1.5 times higher in SiO2/SiC as compared to SiO2/Si, while the total O amounts remain constant, indicating that isotopic exchange between 18O from the water vapor and 18O from the SiO2 network is apparently occurring. This is confirmed by the data in Fig. 1(b), where a reduction in total 18O amount is observed in the same temperature range. Previous theoretical and experimental work13–15 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 SiO2 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 energy15 of the following reversible reaction:

[reaction equation]

Electronic mail: gvsoares@uocs.br.
H₂O + Si – O – Si ↔ 2Si – OH.  

Isotopic exchange between oxygen from the vapor phase and oxygen from the SiO₂ film can take place during reaction (1), as indicated by the data in Fig. 1(a) for SiO₂/Si and SiO₂/SiC in the 20–600 °C temperature range. Two possible reactions can be associated with this isotopic exchange process:

\[
D₂^{18}O + Si – 16O – Si ↔ Si^{16}O – D + D₂^{18}O + Si – 18O – Si,  
\]

\[
18OD^- + D^+ + Si – 16O – Si ↔ D₂^{18}O + Si – 18O – Si.  
\]

These reactions assume a defect-free oxide, whereas it is well known that defects in the SiO₂ network enhance the oxygen isotopic exchange during ¹⁸O₂ annealing. The same should happen during D₂¹⁸O annealing. Since the annealing parameters are the same in both cases, other factors should lead to the observed picture, such as SiO₂ network defects concentration.

In the 600–1000 °C temperature range, the ¹⁸O areal densities increase over an order of magnitude in SiO₂/Si samples, whereas the total ¹⁸O 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 SiO₂/Si interface and further reaction with the Si substrate, forming Si¹⁸O₂. In the case of SiO₂/SiC, the ¹⁸O areal density [Fig. 1(a)] increase is comparable with the ¹⁶O 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 SiO₂/SiC. Indeed, Si¹⁸O₂ 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 SiO₂/SiC samples as compared to SiO₂/Si in both regimes, may once again be related to a higher concentration of defects in SiO₂ films thermally grown on SiC.

Figure 2 shows the ¹⁸O profiles for SiO₂/Si (---) and SiO₂/SiC (----) samples annealed in D₂¹⁸O 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 ¹⁸O profile is erfc-like in the SiO₂/Si sample, while a constant, boxlike profile is observed in SiO₂/SiC, evidencing striking differences in water vapor interactions with SiO₂ films thermally grown on Si and on SiC. In SiO₂/Si, the profiles indicate a diffusion-limited process, while in SiO₂/SiC the evidence is for an interface reaction-limited process, whereby ¹⁸O diffuses through the SiO₂ film, reaching the SiO₂/SiC interface. Thus, for SiO₂/Si, we observe surface isotopic exchange, intermediated by peroxy bridges, whereas in SiO₂/SiC a constant concentration in depth (0.4 × 10²² ¹⁸O/cm³), indicates that isotopic exchange takes place in the whole oxide film. For 200 and 600 °C annealing temperatures, the ¹⁸O profile in SiO₂/Si is still erfc-like, but with higher ¹⁸O surface concentrations. This fact confirms that for the low temperature regime, the main process for oxygen incorporation in SiO₂/Si is isotopic exchange confined to near surface regions, with no evidences of reaction between water oxidant species and the Si substrate. ¹⁸O profiles in SiO₂/SiC annealed at 200 and 600 °C evidence that ¹⁸O is incorporated in the near surface and bulk regions of the oxide film, indi-
cating a higher concentration of bulk defects generated in the SiO\textsubscript{2} film during thermal growth on SiC. Similar observations were reported\textsuperscript{18} in SiO\textsubscript{2} films on Si prepared by anodic oxidation, where the higher defective anodic SiO\textsubscript{2} film presented a higher incorporation of water related species during thermal annealings in \textsuperscript{18}O enriched water vapor. The incorporation of carbonaceous species\textsuperscript{19} in the bulk of the SiO\textsubscript{2} films thermally grown on SiC can account for different reaction sites for water incorporation, which are not present in SiO\textsubscript{2}/Si structures. At 1000 °C, \textsuperscript{18}O profiles confirm the complete oxygen isotopic exchange and the formation of Si \textsuperscript{18}O\textsubscript{2} in both systems.

D areal densities as a function of D\textsubscript{2} \textsuperscript{18}O annealing temperature in SiO\textsubscript{2}/Si and SiO\textsubscript{2}/SiC structures are shown in Fig. 3. In the low temperature regime, a higher D incorporation is observed in SiO\textsubscript{2}/Si as compared to SiO\textsubscript{2}/SiC, in contrast with the \textsuperscript{18}O incorporation in the same temperature range. This is not a contradictory observation, since, owing to O isotopic exchange, \textsuperscript{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\textsubscript{2}/Si samples. We attribute this difference in D incorporation in part to the existence of Si dangling bonds near the SiO\textsubscript{2}/Si interface.\textsuperscript{20} Since water molecules can break into \textsuperscript{18}OD\textsuperscript{−} and D\textsuperscript{+}, the latter can diffuse through the SiO\textsubscript{2} film to partially passivate these defects near the SiO\textsubscript{2}/Si interface. \textsuperscript{18}OD\textsuperscript{−} can react with the SiO\textsubscript{2} network, forming Si \textsuperscript{18}OD. Si and C dangling bonds have also been observed\textsuperscript{21} near the SiO\textsubscript{2}/SiC interface, constituting sites for D incorporation. However, significant H amounts are incorporated in SiO\textsubscript{2}/SiC structures only at temperatures above 600 °C.\textsuperscript{22} In this way, the main channel for D incorporation in SiO\textsubscript{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\textsubscript{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\textsubscript{2}/SiC interface becomes higher than in SiO\textsubscript{2}/Si.\textsuperscript{11,22} Furthermore, the lower D incorporation in SiO\textsubscript{2}/Si in the high-temperature regime is a consequence of the depassivation of Pb centers, since the chemical bond between Si and D becomes unstable for temperatures above 500 °C.

In summary, it was shown that SiO\textsubscript{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\textsubscript{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.

The authors would like to acknowledge MCT/CNPq Nanotec, CAPES, and FAPERGS for financial support.

\begin{thebibliography}{99}
\bibitem{1} R. Singh, Microelectron. Reliab. 46, 713 (2006).
\bibitem{7} D. A. Buchanan and D. J. Dimaria, J. Appl. Phys. 67, 7439 (1990).
\bibitem{11} S. M. Myers, J. Appl. Phys. 61, 5428 (1987).
\bibitem{13} D. J. Breed and R. H. Doremus, J. Phys. Chem. 80, 2471 (1976).
\bibitem{17} A. Stesmans and F. Scheerlink, Phys. Rev. B 50, 5204 (1994).
\end{thebibliography}