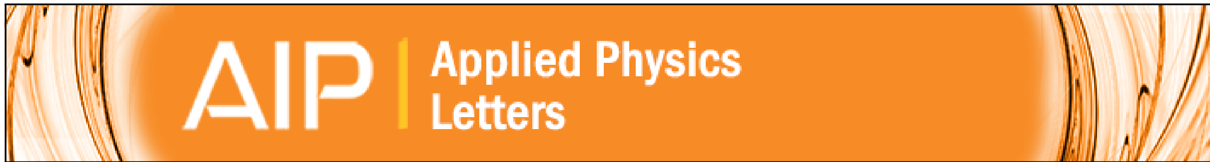

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Enhanced hydrogen bonding strength observed in hydrogenated SiC and SiO_2/SiC structures

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Thermally induced H incorporation, depth distribution, and loss in SiC and in thermally grown SiO_2 films on SiC were investigated using isotopic substitution and nuclear reaction analyses. Hydrogen (deuterium) is found near the SiO_2 film surface or close to the SiO_2/SiC interface depending on the oxidation/D_2-annealing sequence, being much more strongly bound to SiC-based structures than to their Si counterparts. C compounds near the interface seem to play a significant role on the physicochemical and consequently on the electrical characteristics of the D passivated SiO_2/SiC interface. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2645341]

Silicon carbide (SiC) is a wide-band-gap semiconductor with excellent properties for electronic device applications involving high temperature, power, and/or frequency.[1] One of the main advantages that sets SiC apart from other wide-band-gap semiconductors as a replacement for Si, currently the most used semiconductor, is that a layer of silicon dioxide (SiO_2) can be thermally grown on SiC, providing an excellent insulating material to be used as a gate dielectric in metal-oxide-semiconductor (MOS) structures. However, the electronic interface state density (D_{it}) of SiO_2 films thermally grown on SiC is still too high, and the inversion channel mobility of carriers (μ) in SiC is still too low to allow for a wide application of SiC as a basic semiconductor material for MOS device fabrication.[2] This high D_{it} has been mainly attributed[3–6] to the presence of residual C in the SiO_2/SiC interface region. Different postoxidation annealing (POA)processes have been proposed, all aimed at improving the electrical characteristics of the SiO_2/SiC interface. Previous works reported D_{it} reduction by a factor of 3,[7] as well as a raising by a factor of 4 of μ (Ref. 8) following POA in H_2 of SiO_2/n-SiC(0001) structures. Despite these beneficial effects, it remains clear that H_2 annealing of SiC-based MOS structures is not as effective as in the case of their Si-based counterparts. Minimal improvements at best were reported due to H_2 annealings at temperatures below 700 °C.[3] Thus, understanding the physico-chemical interactions of H with thermally grown SiO_2/SiC structures is crucial for modifications of existing device fabrication procedures. In the present letter, a quantitative investigation of H incorporation, distribution in depth, and loss from these structures, before and after thermal oxide growth, is reported.

Starting samples were Si-faced (0001) *n*-type on-axis 6*H*-SiC manufactured by CREE Research Inc., cleaned with the RCA process, and lastly etched in a 5% HF aqueous solution and rinsed in water. These samples were 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. 6 nm thick SiO_2 films were thermally grown (1100 °C, 1 h, 100 mbar) in dry O_2 enriched to 97% in the ^{18}O isotope (termed growth step), followed by an annealing (200–1000 °C, 45 min, 200 mbar), in H_2 enriched to 99.6% in the deuterium ($D={}^2H$) isotope (termed D_2 annealing). This first sequence is named "O_2/D_2." By inverting the gas sequence, keeping the same parameters, a second group of samples was produced, namely "D_2/O_2." Performing a further D_2 annealing of samples prepared following the D_2/O_2 route, a third group was created, namely, "$D_2/O_2/D_2$." Finally, the fourth group was composed of SiC samples annealed only in D_2, skipping the oxidation step, hereafter called "D_2." The use of ^2H and ^{18}O rare isotopes allows to distinguish them from the same chemical species incorporated in the samples during air exposure. D-loss investigations were carried out by annealing the D-loaded samples in Ar (200–1000 °C, 20 min, 1 bar). D quantification was accessed by nuclear reaction analysis[9] (NRA) using the $D(^3He,p)^4He$ nuclear reaction at 700 keV, yielding a sensitivity of $\sim10^{12}$ D/cm^2 with an experimental error of 10%. ^{18}O quantification was also accessed with NRA, using the $^{18}O(p,\alpha)^{15}N$ nuclear reaction at 730 keV, yielding a sensitivity of $\sim10^{13}$ $^{18}O/cm^2$ with an experimental error of 5%. D depth distributions in SiO_2/SiC were determined using NRA in conjunction with step-by-step HF etching of the SiO_2 film.[9]The present depth resolution in the D profiling is ~1 nm.

The temperature dependence of D incorporation in SiO_2/SiC and in SiC is shown in Fig. 1. The O_2/D_2 route (left-hand *y* axis) is in striking contrast to D incorporation in SiO_2/Si,[10] where two peaks of D incorporation were observed, one at 450 °C ($\sim8\times10^{13}$ D/cm^2) and another at 800 °C ($\sim14\times10^{13}$ D/cm^2). Furthermore, the areal density of incorporated D at 450 °C is larger in SiO_2/Si than in SiO_2/SiC structures. Thus, the inefficiency of H_2 annealing at temperatures below 700 °C (Ref. 7) for passivating electronically active defects in the SiO_2/SiC interface region may be related to the lower D incorporation in SiO_2/SiC ($\sim10^{13}$ D/cm^2) as compared to that in SiO_2/Si

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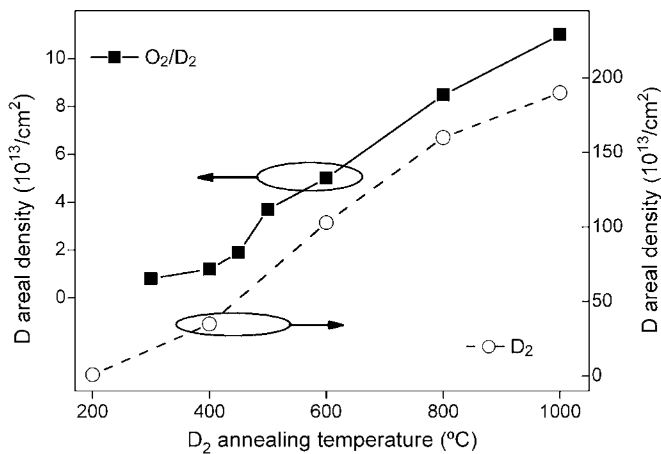

FIG. 1. D areal densities as a function of the D_2-annealing temperature in the case of O_2/D_2 samples (filled squares and solid line, left-hand *y* axis) and D_2 samples (open circles and dashed line, right-hand *y* axis). Lines are only to guide the eyes.

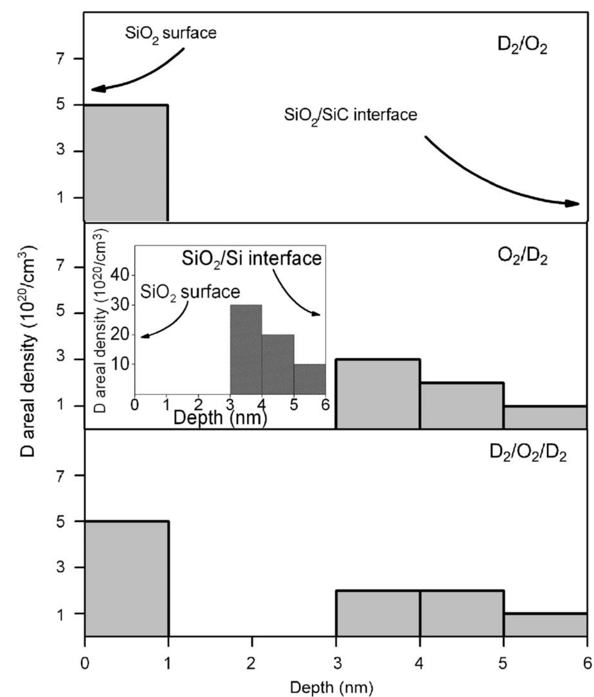

FIG. 2. D depth distribution in samples D_2/O_2 (top), O_2/D_2 (middle), and $D_2/O_2/D_2$ (bottom) obtained by step-by-step chemical etching of the SiO_2 films in conjunction with NRA. D_2 anneals were performed at 600 °C. The inset in the middle figure is the D depth distribution in SiO_2/Si samples annealed in D_2 at 450 °C.

($\sim 10^{14}$ D/cm^2). Based on electrical measurements,[3,7] one may anticipate that defects responsible for the D_{it} observed in SiO_2/SiC structures are different from the P_b centers that exist at the SiO_2/Si interface, since they seem to be more stable against H_2 annealing. Partial passivation of SiO_2/SiC D_{it} is only achieved when H_2 annealing is performed at temperatures above 700 °C, when the incorporation of D reaches $\sim 10^{14}$D/cm^2, approaching the D-incorporation amounts in SiO_2/Si. However, it must be pointed out that the use of Pt as gate contact, leads to a higher D incorporation ($\sim 3\times 10^{14}$ D/cm^2) even at a lower annealing temperature (500 °C), a fact attributed to the catalytic effect of Pt in dissociating H_2.[6] Nevertheless, the electrical passivation is still lower, namely, a reduction of D_{it} by a factor of 3 in the case of *n*-type SiC as compared to a factor of 10 in the case of Si. Recent work[4] reported a 20 times reduction of the signal related to C dangling bonds in SiO_2/n-type SiC after H_2 annealing at 400 °C. However, the absence of electrical passivation using POA in H_2 at 400 °C indicates that the contribution of dangling bonds to D_{it} in SiO_2/SiC is very moderate. Therefore, the electrical passivation obtained at temperatures above 700 °C in SiO_2/SiC is probably related to different types of defects at and/or near the SiO_2/SiC interface, such as C compounds or oxide traps. This point will be discussed further below. No correlations of D incorporation with SiO_2 film thickness (up to 30 nm) or D_2-annealing pressure (up to 1 bar) were found. However, an increase from 1 to 6×10^{13} D/cm^2 was observed when the $^1H_2$ partial pressure in the furnace was lowered due to a lowering in the base pressure before the oxidation step from 6×10^{-6} to 2×10^{-7} mbar.

Annealing SiC(0001) wafers in H_2 at 1000 °C (Ref. 11) is an effective route to electrically passivate the SiC surface and to make it resistant to oxidation during air exposure. Figure 1 right-hand *y* axis shows the dependence of D uptake in SiC with temperature. The areal densities of incorporated D in SiC are more than one order of magnitude higher than those in SiO_2/SiC structures. Previous works[11,12] reported the presence of Si–H bonds and absence of C–H bonds in 6H-SiC(0001) annealed in H_2 at 1000 °C, leading to the conclusion that, in the present case, all D is bonded to Si at the surface of the SiC substrate.

Depth distributions of D in SiO_2/SiC samples from groups D_2/O_2, O_2/D_2, and $D_2/O_2/D_2$ are presented in Fig. 2. D profile for sample D_2/O_2 (top of Fig. 2) shows that all incorporated D is within 1 nm of the SiO_2 film surface, whereas no D was found in a Si sample which underwent the same treatment, within the sensitivity of NRA. Thus, the nature of Si–D bonding on SiC is different from that on Si, implying that for SiC, the chemical environment of D possibly contains Si and C. Strongly bound D in SiO_2/SiC structures justifies the appreciable amount (5×10^{13} D/cm^2) still remaining in the system after the thermal oxide growth step. The mechanism by which D reaches the SiO_2 film surface during thermal oxide growth is not thoroughly understood. However, the experimental evidence given here indicates that the oxide growth occurs underneath a Si–D surperficial layer containing C (and probably O). This result is corroborated by work[13] where the exposure to O_2 of hydrogenated $3C-SiC(3\times 2)$ reconstructed surfaces led to the insertion of O atoms below the top surface without any loss in the H coverage at room temperature. The harsher treatment performed in the present work leads to a partial removal of the incorporated D. However, there is still D remaining at the surface that must be related to a strong bonding configuration in which C plays an important role.

For the O_2/D_2 route, all incorporated D is found within 3 nm of the SiO_2/SiC interface. The incorporated-D areal densities of the D_2/O_2 and O_2/D_2 routes, on the other hand, are comparable. The inset in the middle figure in Fig. 2 shows that the D profile in a SiO_2/Si sample annealed in D_2 is similar in shape but differs in D areal density. D at the SiO_2/SiC interface may be bonded to previously existing dangling bonds therein although, as discussed above, their effect on the electrical characteristics is marginal compared with the effect of D at the SiO_2/Si interface. According to

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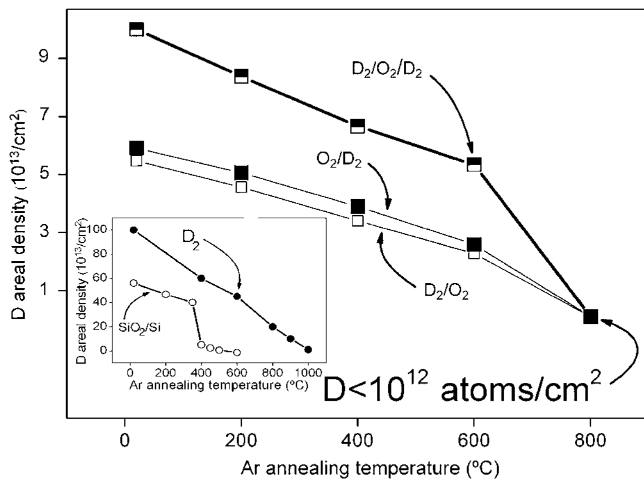

FIG. 3. D areal densities remaining in the samples as a function of the Ar annealing temperature as the last processing step for the D_2/O_2 (open squares), O_2/D_2 (filled squares) and $D_2/O_2/D_2$ (half-filled squares) routes, in which D_2 annealings were performed at 600 °C. Inset: D areal densities as a function of Ar annealing temperature for the D_2 route (filled circles) and SiO_2/Si annealed in D_2 at 450 °C (open circles) (from Ref. 9). Solid lines are only to guide the eyes. Points at room temperature are from samples not submitted to Ar annealing.

the model of Ref. 3, the major contributors for D_{it} at the SiO_2/SiC interface are C clusters and oxide traps. The existence of a transition region, about 3 nm thick,[14] between thermally grown, stoichiometric SiO_2 films and bulk SiC was attributed[14–16] to the presence of C compounds, such as C clusters and silicon oxycarbides. D can react with these C clusters at high temperatures, reducing the original size of the clusters and thus reducing D_{it} in the upper part of the band gap but having little effect in the lower part of the band gap.[17] Nitrogen was also proposed[18] to passivate electrically the SiO_2/SiC interface, shifting C interstitials and C-cluster contributions from the upper to the lower part of the band gap. In the same way, D reduces D_{it} in SiO_2/n-type SiC but has no beneficial effect when p-type SiC is used.[3] Thus, D seems to passivate defects related to C compounds, while passivation of dangling bonds, that also occurs, has a minimal effect on the reduction of D_{it} near the conduction band, as mentioned before.

For the $D_2/O_2/D_2$ set of samples one can observe that the presence of D at the surface of the SiO_2 film, due to the first annealing step, has very little effect on the subsequent incorporation of D after thermal oxidation, indicating that the incorporation of D due to a POA in D_2 depends more on the properties of the SiO_2/SiC interface than on the surface or bulk properties of the SiO_2 film.

Aiming at investigating thermally induced D loss from SiO_2/SiC structures, D areal densities in samples from all annealing routes further submitted to annealing at various temperatures in Ar are given in Fig. 3. Temperature dependence of the D loss in most annealing routes (except for the D_2 route) indicates that D bonded at the SiO_2 surface (D_2/O_2 and $D_2/O_2/D_2$ samples) and that at the SiO_2/SiC interface region (O_2/D_2 and $D_2/O_2/D_2$ samples) have similar chemical environments. In the inset are presented D-loss data in SiO_2/Si (Ref. 9) annealed in D_2, indicating that the desorption process is almost complete at 600 °C, while in the SiO_2/SiC (O_2/D_2 route) this happens at 800 °C. D desorption from SiC samples prepared in the D_2 route is also presented in the inset, indicating strongly bonded D at the SiC surface. Annealing of this sample in Ar at 1000 °C still leaves 1×10^{13} D/cm^2 bonded to the SiC surface. This is another indication that D bond in SiC is stronger than in SiO_2/SiC and much stronger than in Si.

In summary, D uptake in SiO_2/SiC and in SiC was seen to increase monotonically with increasing D_2-annealing temperatures, in striking contrast with previous results for SiO_2/Si and Si. Thermally induced loss of incorporated D points to a much more stable D bonding in SiO_2/SiC than in SiO_2/Si. Additionally, since the temperature dependence of D loss from SiO_2/SiC structures is very similar for different D-incorporation routes, one can conclude that D bonded at the oxide surface and close to the SiO_2/SiC interface must have similar chemical environments that should contain C atoms. The effect of high temperature H_2 annealing on the reduction of D_{it} is then attributed mainly to passivation of C compounds. Furthermore, D bonded to the SiC surface showed the most stable configuration. All these findings are clear evidence of the important role played by near-interface C compounds on the electronic characteristics of SiC-based MOS structures: These compounds give origin to entirely different electrical activities, due to the different physicochemical environments for the passivating H, which is bonded much more tightly in SiC and in SiO_2/SiC than in their Si counterparts. We are presently investigating the effect of different metal gates in the incorporation and distribution of H in oxide films aiming to correlate the results with existing electrical measurements and with those of the present letter.

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