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The Role Played in the Improvement of the SiO_2/SiC Interface by a Thin SiO_2 Film Thermally Grown Prior to Oxide Film Deposition

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To minimize electrical degradation from thermal oxidation of 4H-SiC, a thin and stoichiometric SiO_2 film was thermally grown, monitored by X-ray photoelectron spectroscopy. To obtain thicker films, SiO_2 was deposited by sputtering. Reduction in the flatband voltage was observed when compared to SiO_2 films thermally grown or deposited directly on 4H-SiC. Post-deposition annealing in Ar reduced the flatband voltage of the samples but induced an electrical degradation in the SiO_2/4H-SiC interface. Nuclear reaction analyzes proved that the thin film thermally grown was not stable during the annealing, exchanging O atoms with the deposited film and with the gaseous ambient.
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The advances in reducing the interface state density (D_{it}) between the silicon carbide (SiC) substrate and a SiO_2 film allowed metal-oxide-semiconductor (MOS) devices based on SiC to be commercially available recently.[1] Nevertheless, channel mobility of SiC devices is still very low when compared to the SiC bulk value (less then 10% of the bulk mobility for SiC, while in the case of Si, it is around 40%).[2] Thus, further improvements must be reached such that SiC based devices can achieve larger channel mobility. Since D_{it} is one of the factors that affects the channel mobility,[3,4] alternative methods to reduce the D_{it} besides the standard post-oxidation annealing (POA) in NO have been investigated.[5–7] Minimizing the electrical degradation due to the SiC thermal oxidation seems to be an important step to achieve this goal. Concerning oxidation parameters, it is known that longer oxidation times lead to higher D_{it} and flatband voltage (V_{fb}),[8] attributed to an increase in the amount of Si intermediate oxide states.[9] We recently observed that this electrical degradation is actually related to the product of oxygen pressure and oxidation time.[10] Thus, if the oxidation is performed only to grow a very thin stoichiometric SiO_2 film, this electrical degradation in the SiO_2/SiC interface should be minimized. In order to obtain a thicker SiO_2 film, the remaining oxide should be deposited up to the desired thickness. In fact, previous studies from another group[11] proved that thermal oxidation prior deposition by chemical vapor deposition (CVD) followed by different annealings can be used to reduce D_{it} in the SiO_2/SiC. In the present work we propose to minimize the electrical degradation from thermal oxidation by growing a very thin and stoichiometric SiO_2 film. In order to obtain a thicker oxide film, SiO_2 was then deposited by sputtering. The formed structure was compared to deposited and thermally grown oxide films on SiC. Investigation of the need of a post-deposition annealing (PDA) in inert ambient to improve the electrical properties[12] and attempts to correlate these results to the thermal stability of the formed structure and atomic transport during the annealing were also performed.

SiC wafers of the 4H polytype, on-axis, polished in the (0001) face (Si face), purchased from CREE Inc. were employed as substrates in samples analyzed by XPS and nuclear reaction analyzes. 4H-SiC commercial wafers from CREE Inc. with an epitaxial layer 4.6 μm thick, doped with nitrogen (1.1×10^{16} cm^{-3}), 8° off-axis on the Si face, were used to obtain samples characterized by electrical measurements. All substrates were cleaned in a solution of H_2SO_4 and H_2O_2 followed by the RCA process.[13] Then samples were etched for 60 s in a 1 vol% aqueous solution of hydrofluoric acid (40 wt% HF, from Merck) and rinsed in deionized water. Immediately after blow drying with N_2, 4H-SiC samples were loaded in a static pressure, quartz tube, resistively heated furnace that was pumped down to 10^{-8} mbar. SiO_2 films were thermally grown on four samples at 1100°C for different oxidation times calculated from the moment the system reached the working temperature (0, 5, 10, and 20 minutes) in 100 mbar of dry O_2 (<1 ppm H_2O) enriched to 97% in the ^{18}O isotope, whose natural abundance is 0.2%, named $^{18}O_2$. The use of ^{18}O allowed the use of nuclear reaction analyzes to investigate the atomic transport in the thermally grown films. The total amount of ^{18}O in resulting samples was determined by NRA using the $^{18}O(p,\alpha)^{15}N$ nuclear reaction at 730 keV,[14] referenced to a standard $Si^{18}O_2$ film on Si. The depth distribution of ^{18}O in samples was determined by nuclear reaction profiling (NRP) using the narrow resonance at 151 keV in the cross section curve of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction. ^{18}O concentration profiles were determined from experimental excitation curves (alpha particle yield versus incident proton energy) using the FLATUS code.[15] SiO_2 films were deposited by RF sputtering using a SiO_2 target. For this, the system was pumped down to 10^{-8} mbar and then Ar was introduced in the chamber at a constant flux, keeping the pressure at 2.7×10^{-3} mbar during sputtering. Stoichiometry and film thickness were evaluated by Rutherford backscattering spectrometry (RBS) of samples with the same films deposited on a carbon substrate. PDA was performed under 400 mbar of Ar for 1 h at 1100°C in the same static reactor used in oxidations. X-ray photoelectron spectroscopy (XPS), used to monitor the conditions to obtain a very thin and stoichiometric SiO_2 film thermally grown on 4H-SiC, were performed in an Omicron-SPHERA station, using Al Kα radiation at 14° take-off angle (sensitive to the sample surface). Aluminum thermal evaporation was used to obtain MOS structures. A mechanical mask was used to form circular capacitors with a diameter of 200 μm. An InGa eutectic was used as a back contact. Samples were electrically characterized using a computer-controlled HP4284A Precision *LCR* Meter for the C-V curves and HP4155A parameter analyzer for the I-V curves.

XPS analyzes of samples oxidized for short oxidation times are presented and compared to a sample without any thermal treatment in Figure 1. The clean sample presents a small amount of silicon bonded to oxygen and/or carbon in different stoichiometries, named silicon oxycarbides compounds (SiC_xO_y), which could not be removed with wet etching in HF, attributed to the high chemical stability of these compounds against wet environments.[16] In the first stage of oxidation investigated, mainly these SiC_xO_y are formed, in agreement with previous work,[17] which are not adequate to be used as an insulator layer prior to the SiO_2 film deposition. As oxidation progresses in time, stoichiometric SiO_2 becomes the main compound observed. Therefore, for being the shortest oxidation time investigated to grow a stoichiometric SiO_2 film, 5 minutes was the oxidation time condition chosen to thermally grow the SiO_2 film before the deposition.

It is possible to observe in the I-V measurements in accumulation presented in Figure 2a that the sample with the 20 nm SiO_2 film

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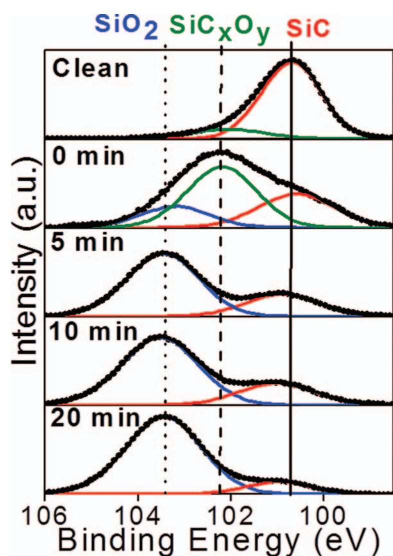

Figure 1. Si 2p photoelectron spectra (a.u. stands for arbitrary units) at a take-off angle sensitive to the surface of Si-faced 4H-SiC samples thermally oxidized at 1100°C in 100 mbar of $^{18}O_2$ for different oxidation times, as indicated. Vertical lines indicate the presence of the compound appearing in the top of the figure: SiC (solid), SiC_xO_y (dashed), and SiO_2 (dotted).

directly deposited on the SiC and previous to Ar annealing presented a very low breakdown voltage, while the sample oxidized prior the deposition presented the highest breakdown voltage, indicating an improvement in the dielectric properties. In the C-V measurements presented in Figure 2b, the sample with the oxide film directly deposited on the SiC presented the highest V_{fb}, indicating the presence of large amounts of negative fixed charge. Even with a significant reduction in the V_{fb} after the PDA in Ar, a high D_{it} can be inferred from the C-V curve slope. On the other hand, samples in which a thin SiO_2 film was thermally grown prior to the deposition (final film thickness around 23 nm) presented a smaller $V_{fb.}$ When compared to a SiC sample thermal oxidized for 4 h (film thickness around 14 nm), samples oxidized for a short time prior to the oxide deposition exhibit smaller $V_{fb,}$ despite the presence of a thicker SiO_2 film. These results confirm that the short oxidation time reduced the electrical degradation and the oxide deposition did not increase significantly the amount of negative fixed charge.

Concerning the PDA in Ar in the sample oxidized previously to the deposition, an unexpected deterioration in the I-V result and electrical degradation in the C-V curve were observed. To further investigate this point, new samples were prepared. A 3 nm SiO_2 film was deposited on SiC samples oxidized in $^{18}O_2$ for different short times, followed by PDA in Ar using the previous condition, and samples were analyzed by nuclear reaction analyzes. In Figure 3a, a loss in the ^{18}O total amount can be observed after the PDA for all samples, indicating that the film thermally grown was not stable during the annealing. Only the ^{18}O depth profile of the sample oxidized for 5 minutes is presented in Figure 3b, since the others were alike. Results indicate, besides ^{18}O loss, an intermixing between SiO_2 films deposited and thermally grown in a similar way to the observed in samples oxidized in $^{18}O_2$ and reoxidized in $^{16}O_2$.[18] The electrical degradation can be related to this thermal instability of the dielectric/SiC structure, probably caused by an out-diffusion of carbonaceous compounds during the thermal treatment.[19] Further investigations are in progress to better understand this effect and to optimize the PDA parameters.

In summary, deposition of SiO_2 films by sputtering on the Si face of 4H-SiC was investigated. The direct deposition on 4H-SiC lead to a low breakdown field and high V_{fb}. When a thin and stoichiometric SiO_2 film was thermally grown before the deposition, a significant

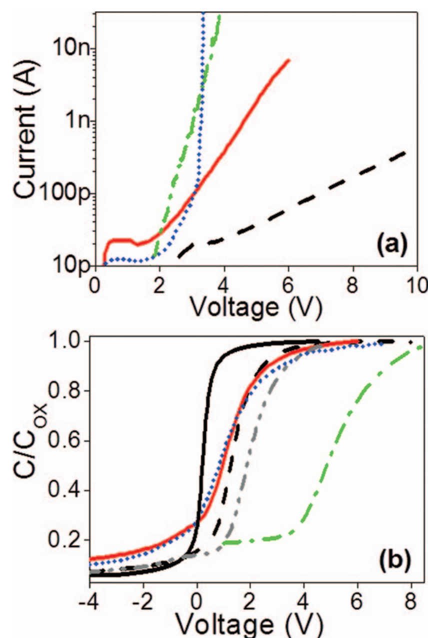

Figure 2. (a) I-V curves and (b) C-V curves of $Al/SiO_2/4H-SiC$ (Si face) structures. 20 nm SiO_2 films deposited by sputtering on SiC not submitted (dotted-dashed green line) and submitted (dotted blue line) to annealing in Ar. SiC samples with SiO_2 films thermally grown under 100 mbar of $^{18}O_2$ at 1100°C for 5 min followed by the same SiO_2 deposition not submitted (dashed black line) and submitted (solid red line) to the same Ar annealing. Ideal C-V curve (solid black line) and the curve of a SiC wafer oxidized under 100 mbar of $^{18}O_2$ at 1100°C for 4 h (~14 nm dot-dot-dashed gray line) are also presented for comparison.

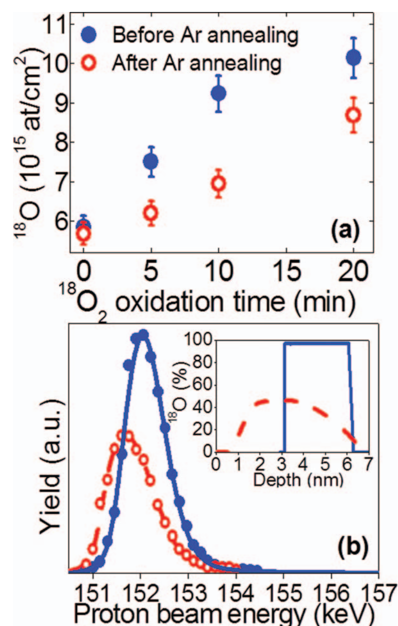

Figure 3. (a) ^{18}O amounts obtained by NRA from samples submitted to different oxidation times under 100 mbar of $^{18}O_2$ at 1100°C followed by sputtering deposition of a 3 nm SiO_2 film. Data from samples before and after a PDA in 400 mbar of Ar for 1 h at 1100°C are presented. (b) Experimental (symbols) excitation curves of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction around the resonance at 151 keV and the corresponding simulations (lines) for the 4H-SiC sample oxidized in 100 mbar of $^{18}O_2$ for 5 min followed by sputtering deposition of a 3 nm thick SiO_2 film before (full blue circles for experimental points and solid blue line for simulation) and after (open red circles for experimental points and dashed red line for simulation) the PDA in Ar. Inset, the resulting ^{18}O profiles from the simulations using the same line types.

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improvement in the breakdown field and reduction in the V_{fb} was observed. When compared to a SiO_2 film thermally grown, the sample oxidized before the deposition presented a smaller V_{fb}, even being characteristic of a thicker SiO_2 film, indicating that this should be an efficient way to minimize the electrical degradation due to the oxidation process. Nuclear reaction analyzes used to investigate the effects of the PDA in Ar proved that the oxygen present in the SiO_2 film thermally grown was not stable during the annealing in Ar, fact that may be attributed to an out-diffusion of carbonaceous compounds.

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