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Enhancement in interface robustness regarding thermal oxidation in nanostructured $\text{Al}_2\text{O}_3$ deposited on 4H-$\text{SiC}$

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Experimental evidences of enhanced stability of $\text{Al}_2\text{O}_3$/SiC structures following thermal annealing are presented. 5- and 40-nm-thick $\text{Al}_2\text{O}_3$ films evaporated on the Si- and C-terminated faces of 4H-$\text{SiC}$ were annealed up to 1000 °C in different atmospheres, leading to crystallization and densification of $\text{Al}_2\text{O}_3$, with an increase in the band gap. Exposure to $\text{O}_2$ at high temperatures produced SiO$_2$ and AlSi$_x$O$_y$ at the $\text{Al}_2\text{O}_3$/SiC interface, with less silicate on the Si-terminated face. Annealing in $\text{N}_2$ before exposure to $\text{O}_2$ hindered oxygen diffusion and exchange, leading to more stable thin film structures from the point of view of atomic transport. © 2009 American Institute of Physics. [DOI: 10.1063/1.3195702]

Significant research effort is being made to exploit the excellent properties of silicon carbide (SiC) for power electronics. With a band gap approximately three times larger than that of silicon (Si), SiC also presents higher breakdown electric field and thermal conductivity. Among wide-bandgap materials, only SiC can be thermally oxidized to produce silicon oxide (SiO$_2$) as in the case of Si. This has raised expectations regarding the realization of SiC-based metal-oxide-semiconductor field effect transistors (MOSFETs). However, channel mobilities in actual devices are only a fraction (approximately 1%) of the bulk carrier mobility in SiC. The imperfect nature of the thermal SiO$_2$/SiC interface is considered to be the main source of channel resistance in SiC MOSFETs. Recently, combined transmission electron microscopy and electron energy loss spectroscopy analyses revealed that thermal oxidation also involves structural degradation of the top few atomic layers of the SiC substrate.

Deposition of a suitable material to act as a gate dielectric on SiC should eliminate the issues associated with thermal oxidation. Aluminum oxide ($\text{Al}_2\text{O}_3$) is attractive as a dielectric because it simultaneously presents a significant dielectric constant ($k = 9$) and large band offsets to 4H-$\text{SiC}$ in comparison to common high-$k$ materials. There are open questions, however, with respect to both fabrication and reliability of $\text{Al}_2\text{O}_3$ as the gate dielectric for SiC devices submitted to the extreme conditions intrinsic to power electronics.

An interfacial Si suboxide layer between $\text{Al}_2\text{O}_3$ prepared by atomic layer deposition (ALD) and the Si-terminated face of 4H-$\text{SiC}$ was evidenced by x-ray photoelectron spectroscopy (XPS). The interlayer thickness increased after annealing at 1000 °C in Ar, which also triggered Si diffusion into the dielectric layer as evidenced by secondary ion mass spectrometry. The thickness of a SiO$_2$ interlayer has significant impact on channel mobility for $\text{Al}_2\text{O}_3$/4H-$\text{SiC}$ MOSFETs. Thus, controlling the transport of oxygen through $\text{Al}_2\text{O}_3$ is mandatory. Besides the formation of an interlayer and compositional changes in the dielectric, thermal annealing also induces structural modifications in $\text{Al}_2\text{O}_3$, as shown by Jakschik et al. In particular, an increase in the dielectric constant was observed accompanying crystallization and densification.

In this scenario, we investigated $\text{Al}_2\text{O}_3$/4H-$\text{SiC}$ structures with respect to atomic transport and interface modification induced by thermal annealing in $\text{O}_2$ or $\text{N}_2$. $\text{Al}_2\text{O}_3$ films were deposited on both (0001) (Si-face) and (0001) (C-face) of 4H-$\text{SiC}$ to investigate the influence of substrate polarity on interface formation and stability. Oxygen incorporation was detected using $\text{O}_2$ enriched in $^{18}\text{O}$, whose natural abundance is 0.2%. That enabled us to use nuclear reaction analysis and distinguish oxygen originally in the $\text{Al}_2\text{O}_3$ film from that incorporated during annealing. All results were compared with those of counterpart $\text{Al}_2\text{O}_3$/Si samples.

4H-$\text{SiC}$ polished on both (0001) and (0001) faces and Si(001) substrates were cleaned in a mixture of H$_2$SO$_4$ and H$_2$O$_2$ followed by the RCA process. After etching in a 5% HF aqueous solution for 1 min, samples were rinsed in de-ionized water for 30 s and loaded in the deposition chamber. $\text{Al}_2\text{O}_3$ films were deposited from an alumina source by electron beam physical vapor deposition, which is not aggressive to the substrate (i.e., minimizes damage) and is free of intrinsic contaminants such as carbon and hydrogen, typical of chemical methods. Deposition parameters were adjusted in order to produce stoichiometric $\text{Al}_2\text{O}_3$ films as determined by Rutherford backscattering spectrometry. XPS was performed in an Omicron SPHERA station using Mg $K\alpha$ radiation. Data fitting was performed using a branching ratio $2p_{1/2}/2p_{3/2} = 0.5$ (the statistical ratio) and a spin-orbit splitting of 0.6 eV. The samples characterized by XPS had 5-nm-thick $\text{Al}_2\text{O}_3$ layers, while 40-nm-thick films were used for x-ray diffraction (XRD) and reflectivity and nuclear reaction analysis. X-ray reflectivity (XRR) analyses were performed in a Shimadzu XRD 6000 equipment using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) and scanning in 0.02° steps. Thermal processing was performed in a resistively heated quartz tube.
furnace for 1 h under a static pressure of 100 mbar of either N$_2$ (<1 ppm of H$_2$O) or O$_2$ enriched to 97% in the isotope of mass 18 (termed $^{18}$O$_2$). The depth distribution of $^{18}$O in annealed samples was determined by nuclear reaction profiling using the resonance at 151 keV in the cross-section curve of the $^{18}$O($p,\alpha$)$^{15}$N nuclear reaction.

Figure 1 shows Si 2p XPS spectra for 5-nm-thick Al$_2$O$_3$ films on SiC before or after annealing in O$_2$ at 600 or 1000 °C. We found no significant evidence of an interlayer between Al$_2$O$_3$ and SiC substrates in as-deposited samples. A Si substrate counterpart, on the other hand, showed aluminum silicate (AlSi$_3$O$_7$). The formation of such a compound was also observed with Al$_2$O$_3$/Si structures prepared by chemical vapor deposition at 400 °C. This observation should be related to the lower reactivity of SiC when compared to Si. In Fig. 1 three components can be distinguished in the spectra. We assign them to silicon oxide, AlSi$_3$O$_7$, and the silicon carbide substrate.

Annealing in O$_2$ affected the Si 2p spectrum of all samples as compared to as-deposited ones. Al 2p and O 1s spectra, on the other hand, remained unchanged. Interface modification took place at 600 °C, where, based only on intrinsic carrier concentration, SiC devices can operate theoretically. The degree of modification depends on annealing temperature and substrate polarity. At fixed temperature, AlSi$_3$O$_7$ is more abundant in the C-faced sample (as determined by comparing the components’ areas) while for a given substrate termination, the higher the annealing temperature, the higher the relative amount of silicate. That is, SiO$_2$ formation is hindered at the highest annealing temperature (similar results were obtained on Si substrate, not shown here). According to the data discussed below, this observation is at least partially due to crystallization of Al$_2$O$_3$.

AlSi$_3$O$_7$ formation can be explained by chemical reaction between Al$_2$O$_3$ and SiC. SiO$_2$ formation would be likely due to reduction in Al$_2$O$_3$ by SiC or reaction between the substrate and oxygen diffusing from the gas phase. As XPS data only show Al in the fully oxidized state, experimental evidence favors the latter hypothesis. Our observation that AlSi$_3$O$_7$ is more abundant in the C-terminated face of SiC can be explained by faster kinetics in the reaction of SiC with Al$_2$O$_3$, as observed for the reaction with oxygen in thermal oxidation. As for the fact that less SiO$_2$ forms at high annealing temperature, additional data discussed below indicate that a bulk transformation in Al$_2$O$_3$ limits the supply of oxygen from the gas phase (i.e., diffusion is hindered).

Figure 2 shows nuclear reaction data regarding $^{18}$O in 40-nm-thick Al$_2$O$_3$ films annealed at the indicated temperatures. Alpha particle yield in the figure is proportional to $^{18}$O concentration; depth in the sample scales with proton energy. The curves shown correspond to the actual concentration versus depth information convoluted with instrumental and proton energy loss functions. According to Fig. 2, processing at 600 °C leads to a relatively shallow distribution of $^{18}$O in Al$_2$O$_3$ (i.e., the interface with SiC is barely reached); the maximum concentration of $^{18}$O occurs at the sample surface. Annealing at 900 °C produces a constant distribution of $^{18}$O in Al$_2$O$_3$ that corresponds to 1.4 times the peak concentration observed at 600 °C. Data taken after annealing at 1000 °C indicate a bulk concentration of $^{18}$O that is intermediate between those seen at 600 and 900 °C. This result contrasts with the observation that oxygen incorporation and ex-
change in Al₂O₃ films deposited by ALD on Si tends to increase with annealing temperature.

Aiming at clarifying the observation above, two samples were annealed sequentially for 1 h in 100 mbar of N₂ followed by ¹⁸O₂. As shown in Fig. 2, the annealing step in inert gas significantly reduced the amount of ¹⁸O incorporated to the oxide film. In addition, ¹⁸O became essentially confined to the sample surface. This result scaled with annealing temperature in N₂: thermal treatment at 900 °C resulted in more ¹⁸O incorporated to the sample surface than the sample annealed in N₂ at 1000 °C following the same oxidation step. XRD showed a signal near $2\theta=67.5^\circ$ (Cu Kα radiation) that was attributed to Al₂O₃ which intensity increased with increasing annealing temperature. This indicates that, despite grain boundaries, crystallized Al₂O₃ is more robust regarding incorporation of oxygen. Our understanding is that Al₂O₃, formation, Al₂O₃ crystalization, and ¹⁸O incorporation occur simultaneously, the latter two being competitive processes to a certain extent. From Fig. 2 (top), for annealing at 900 °C the kinetics is such that ¹⁸O incorporation is at maximum. At 1000 °C, crystallization is accelerated relative to oxygen diffusion and by the time that ¹⁸O reaches the subsurface region of Al₂O₃ the number of reaction sites has been reduced. The crystallization process was accompanied by film densification, as seen in Ref. 7.

XRR measurements (Fig. 3) indicated a reduction of approximately 25% in the Al₂O₃ film thickness after annealing at 1000 °C. Finally, the band gap extracted from the O 1s XPS loss feature was seen to increase from 6.5 eV in as-deposited to 7.4 eV in annealed samples. These values were obtained from the energy difference between the O 1s photoelectron peak and the onset of the plasmon loss, which is a good approximation to the band gap energy. In Fig. 3, the comparison of O 1s loss spectra is made between an as-deposited Al₂O₃ (40 nm)/SiC sample and the same structure after annealing in ¹⁸O₂ at 1000 °C. Similar loss spectra were observed for all annealed samples. This significant increase should be related to the elimination of band-tail states accompanying oxide crystallization.

In summary, we investigated oxygen transport in Al₂O₃ and thermally driven chemical reactions in the Al₂O₃/SiC interface region. Thermal annealing in the presence of O₂ led to the formation of AlSiOₓ and SiO₂, with more silicate observed on the C-terminated face of 4H-SiC. Differences such as this are significant regarding the choice of SiC polytype and face for device fabrication. Exposure to high temperatures promoted crystallization and densification of Al₂O₃. When performed in N₂, this annealing significantly lowered the penetration of oxygen in the film. An engineered thermal annealing step that stabilizes Al₂O₃ with respect to oxygen transport without compromising the Al₂O₃/SiC interface with AlSiOₓ formation might improve the prospects of this oxide-wide band gap semiconductor combination for power electronics.

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