Rearrangement of the oxide-semiconductor interface in annealed $\text{Al}_2\text{O}_3/\text{4H-SiC}$ structures

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Al_2O_3 films with different thicknesses have been deposited on *n*-type (nitrogen-doped) 4H-SiC(0001) epitaxial samples by atomic layer chemical vapor deposition at 300 °C and subsequently annealed in Ar atmosphere at temperatures up to 1000 °C. The $\text{Al}_2\text{O}_3/\text{4H-SiC}$ structures were analyzed by x-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and transmission electron microscopy (TEM). The XPS and SIMS results indicate that the average composition in the wider interface area does not significantly change due to the annealing. However, as revealed by the TEM investigations in combination with XPS, the as-grown samples exhibit a double interface created by an intermediate suboxide SiO_x layer ($x < 2$). After annealing, this intermediate suboxide layer breaks up and transforms into SiO_2 islands, resulting in a rather rough interface region and a high concentration of pure Si in the Al_2O_3 film. Furthermore, a pronounced accumulation of H is found in the rough interface region and this may play a key role for the low density of shallow electron states reported for annealed $\text{Al}_2\text{O}_3/\text{4H-SiC}$ structures. © 2007 American Institute of Physics. [DOI: 10.1063/1.2757608]

Because of its wide band gap (~ 3.2 eV for polytype 4H), SiC is suitable for applications related to high power, high frequency, and high temperatures. In recent years, investigations for alternative dielectrics for device applications have become of great interest. Al_2O_3 is one of the few pure metal oxides exhibiting a high dielectric constant ($\epsilon \sim 10$), a relatively wide band gap ($E_g \sim 6.2$ eV), and a good thermal stability; moreover, compared to ZrO_2 or HfO_2 it displays higher conduction and valence band offsets, $\Delta E_c = 1.7$ eV and $\Delta E_v = 1.2$ eV, relative to 4H-SiC.^{1,2} It has been shown that high quality Al_2O_3 films can be grown on SiC by atomic layer chemical vapor deposition (ALCVD).³ In previous studies,^{4–6} electrical characterization such as capacitance-voltage (CV) and thermal dielectric relaxation current measurements of $\text{Al}_2\text{O}_3/\text{4H-SiC}$ capacitors were reported. In fact, annealing in Ar above the crystallization temperature (~ 900 °C) was found to significantly enhance the electrical properties of the $\text{Al}_2\text{O}_3/\text{SiC}$ interface and promote formation of the γ phase of Al_2O_3 . Furthermore, it has been revealed that the interface properties of those annealed structures are superior to the ones of $\text{SiO}_2/\text{4H-SiC}$ interfaces, since the density of electron traps close to the conduction band minimum is reduced,⁴ as required for improved channel mobility in a metal-oxide-SiC field effect transistors. In this study, the $\text{Al}_2\text{O}_3/\text{4H-SiC}$ interface was investigated on as-grown and annealed samples using angle resolved x-ray photoelectron spectroscopy (AR-XPS), transmission electron microscopy (TEM), and secondary ion mass spectrometry (SIMS). An

ultimate goal is to correlate the structural and compositional properties of the interface with the previously reported electrical characteristics.

The Al_2O_3 layers have been grown by ALCVD on Si-faceted, *n*-type 4H-SiC samples with a 10 μm thick epilayer (net doping level of $2 \times 10^{15} \text{ cm}^{-3}$) on a highly doped substrate (net doping level of $1 \times 10^{18} \text{ cm}^{-3}$), oriented 8° off the (0001) direction, purchased from Cree, Inc. Details of the cleaning and growth procedure can be found elsewhere.^{4,5} For the AR-XPS measurements, 5 and 8 nm thick Al_2O_3 layers were grown while thicker layers (~ 110 – 120 nm) were deposited for the TEM and SIMS measurements. Annealing treatments have been carried out in Ar atmosphere at 1000 °C for 15, 30, and 60 min.

SIMS (Cameca IMS 7F) analysis was performed for H, C, and Si using cesium as sputtering ions with an impact energy of 15 keV. The ion beam current was 20 nA, and the beam was rastered over an area of $100 \times 100 \mu\text{m}^2$. Sample charging effects were minimized by electron flooding. Cross-section TEM samples were prepared by ion milling using a Gatan precision ion polishing system with a 5 kV gun voltage. High resolution images of the $\text{Al}_2\text{O}_3/\text{SiC}$ interfaces were taken with an analytical 200 keV JEOL 2010F TEM. XPS was performed using a Thermo VG Scientific Sigma Probe spectrometer with monochromated $\text{Al K}\alpha$ radiation ($h\nu = 1486.6$ eV). This spectrometer is fitted with an angle sensitive XPS facility that allows AR-XPS data to be acquired without repositioning the sample. Spectra were acquired from bulk and surface regions of the specimen, at takeoff angles, relative to the surface normal, of $28 \pm 5^\circ$ and $78 \pm 5^\circ$, respectively, as well as in the so-called angle re-

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FIG. 1. High resolution Si 2p spectra (AR mode) showing presence of Si suboxide for both as-grown and annealed in Ar atmosphere Al_2O_3 films deposited on 4H-SiC(0001).

solved mode of $53 \pm 18^\circ$ which provides higher sensitivity at an intermediate takeoff angle. The spectra were corrected for charging by using a C 1s value for adventitious carbon of 284.8 eV.⁷

Figure 1 shows Si 2p spectra obtained by AR-XPS in AR mode with both as-grown and annealed Al_2O_3 /4H-SiC samples. We calculated the total thickness of the silicon suboxide, assuming uniform distribution, following the approach described in Watts and Wolstenholme⁸ and using an inelastic mean free path value for Si (λ_{Si}) in SiO_2 of 3.77 nm.⁹ Both bulk and angle resolved spectra (bulk spectra not shown) revealed a total thickness of ~ 1.2 nm thick Si suboxide between Al_2O_3 and SiC in the as-grown condition. The intensity of the suboxide was more pronounced in the bulk mode indicating its formation at the Al_2O_3 /SiC interface. The apparent thickness of the interfacial Si suboxide increases to ~ 3 nm after annealing at 1000 °C independently of the annealing duration (15, 30, and 60 min), assuming again uniform distribution. The formation of this interfacial layer in the as-deposited samples is attributed to the exposure of the Si face to O_3 treatment prior to oxide deposition. Steric hindrance effect may also be enhanced by using SiC substrate orientated 8° off the (0001) direction in comparison to the Si (111) surface.

Si 2p spectra of the annealed samples exhibit a more intense Si^{4+} peak compared to the suboxide peaks indicative of SiO_2 formation. Hence, a further oxidation of the silicon suboxide during the annealing procedure is suggested. Furthermore, the presence of pure Si after annealing is shown in Fig. 1 by the peak at about 99 eV. Hence, it is concluded that during annealing (at 1000 °C in Ar) the 1 nm thick SiO_x interlayer, being less thermodynamically stable than SiO_2 , transforms into SiO_2 ; however, the oxygen supply needed to form SiO_2 is limited and thus leading to the presence of excess pure Si, as confirmed by SIMS measurements.

The O 1s spectra (angle resolved mode) from as-grown and 1 h annealed Al_2O_3 /4H-SiC samples were investigated (not shown here). The as-deposited sample exhibits a broader

FIG. 2. SIMS profiles of (a) Si and (b) H in both as-grown and 3 h annealed at 1000 °C Al_2O_3 /4H-SiC samples in Ar atmosphere. The H profile of the as-grown SiO_2 /4H-SiC sample was displaced in order to compare the H concentration at the SiO_2 /4H-SiC interface with the Al_2O_3 /4H-SiC interfaces.

peak than the annealed samples indicating a diminution of OH groups after heat treatment. Among the annealed samples (15, 30, and 60 min) the O 1s peak does not change. An increasing hydroxide concentration towards the outmost surface (not shown) most likely results from the formation of $\text{Al}(\text{OH})_3$ at the oxide outmost surface layer due to ambient water vapor.

SIMS measurements have been performed on as-grown and annealed samples. Here, we focus on the hydrogen and silicon profile across the oxide into the bulk 4H-SiC (Fig. 2). The hydrogen profile exhibits a lower concentration in the bulk oxide after annealing but the concentration increases at the Al_2O_3 /4H-SiC interface. Furthermore, the peak width of the interfacial H peak is also increased after annealing, possibly suggesting a thicker interfacial layer. The Si profile shows a significant out diffusion after annealing at 1000 °C. Here, it is obvious that Al_2O_3 is not an efficient diffusion barrier for Si. Jakschik *et al.*¹⁰ observed a similar behavior upon annealing Al_2O_3 deposited on silicon expecting Si diffusion along the grain boundaries. The carbon profile (not shown) was not affected by heat treatments even above the crystallization temperature (900 °C). The H profile in an as-grown SiO_2 /4H-SiC control sample is included for comparison in Fig. 2 (the SiO_2 layer with a thickness of ~ 50 nm was grown by thermal oxidation at 1150 °C) and it shows a similar distribution as in the as-grown Al_2O_3 /4H-SiC samples.

Finally, TEM investigations have been conducted. In Fig. 3(a), the interfacial region of an as-grown sample is shown, whereas Fig. 3(b) shows a similar sample annealed for 60 min at 1000 °C. A combination of ion-beam thinning and electron beam exposure resulted in a rapid crystallization of the deposited films but did not affect the interface region. The high-resolution transmission electron microscopy (HR-TEM) images of the as-grown samples show an almost uni-

FIG. 3. HRTEM pictures of (a) as-grown and (b) 1 h annealed (1000 °C, Ar) $\text{Al}_2\text{O}_3/4\text{H-SiC}$ samples.

form and amorphous interfacial layer between the crystalline SiC substrate and the Al_2O_3 film with an approximate thickness of 1 nm [Fig. 3(a)] in very good agreement with the XPS measurements. In Fig. 3(b), the HRTEM micrograph reveals that the originally uniform interfacial layer is broken up into islands along the interface after annealing, while the average thickness did not increase significantly compared to the as-grown sample. The islands have a height of 0.4–1.3 nm and a lateral extension of 2–6 nm. The diffraction pattern presented in Fig. 3(b) mainly contains contributions from the SiC substrate. The extra reflections are attributed to the crystallized Al_2O_3 film. No amorphous rings have been imaged originating from the intermediate oxide islands. The HRTEM images also revealed that the aluminum oxide thickness decreased during heat treatment. Whereas the Al_2O_3 oxide thickness for the as-grown sample was ~ 117 nm, that for the sample heat treated for 1 h was ~ 95 nm, corresponding to an 18% decrease which is in agreement with a previous study based on x-ray methods.¹¹ In the same study, the as-grown Al_2O_3 layer was found to be amorphous whereas after annealing at 900 °C in Ar atmosphere the Al_2O_3 started to crystallize. As also reported by Snijders *et al.* the transition from amorphous to polycrystalline Al_2O_3 layer is accompanied by a reduction of the free volume in the oxide, resulting in an increase of the oxide atomic density.¹²

For both XPS and SIMS, the recorded signals are integrated over a certain surface plane parallel or in a specific angle to the sample surface/interface and they do not provide lateral information, in contrast to that of TEM. In the light of the presented results, it is concluded that a rather large rearrangement occurs in the interface region during annealing [see Figs. 3(a) and 3(b)]. The apparent increase in the thick-

ness of the SiO_x intermediate layer as suggested by the XPS is, therefore, interpreted as being due to the formation of SiO_2 islands with a lateral extension of a few nanometers yielding a rather rough interfacial region. This interpretation is consistent with the indications of SiO_2 formation in Fig. 1 and also with the SIMS result in Fig. 2. The H profile in Fig. 2 can be used as an indicator for the interface position and width. For the annealed sample, the amount of H at the interface increases and is wider spread than for the as-grown sample, suggesting trapping in a wider depth region after annealing. In fact, this holds even more compared to the $\text{SiO}_2/4\text{H-SiC}$ control sample and the high accumulation of H may play a key role for the low density of shallow electron states in annealed $\text{Al}_2\text{O}_3/\text{SiC}$ samples, due to efficient passivation of the boundaries between the SiO_2 islands and the 4H-SiC substrate. Further, this interpretation implies that the shallow electron states do not form at the boundaries between Al_2O_3 and 4H-SiC, in accordance with recent theoretical findings,^{13,14} or that also these boundaries are passivated by H. A further optimization of the SiC surface treatment prior to deposition of Al_2O_3 is believed to improve the interface morphology and also the electrical properties. In particular, a strong attention should be given to minimization of the SiO_x formation at the interface.

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