Interfacial studies of Al₂O₃ deposited on 4H-SiC(0001)

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ABSTRACT

Al₂O₃ films deposited on 4H-SiC(0001) by atomic layer deposition (ALD) were characterized by x-ray photoelectron spectroscopy (XPS), and high resolution transmission electron microscopy (HRTEM). The effect of medium and high temperature (873, 1273 K) annealing on samples with oxide thicknesses of 5-8nm and 100-120nm was studied. XPS indicated presence of a thin (~1nm) SiOₓ layer on the as-grown samples which increased to ~3 nm after annealing above crystallization temperature (1273 K) in Ar atmosphere. Upon annealing the stoichiometry of the interfacial oxide approaches that of SiO₂. HRTEM showed that the thickness of the interfacial oxide formed after annealing at 1273 K was not uniform. No significant increase in the thickness of the interfacial oxide, was observed after annealing at 873 K in a N2 (90%) / H2 (10%) atmosphere.

I. INTRODUCTION

As compared to the Si/SiO₂ interface, the density of interface states (Dᵢₙ) at the SiO₂/SiC interface is at least one or two orders of magnitude higher (~10¹² eV⁻¹cm⁻²) [1]. Two dominant sources of electrically active defects have been suggested; C clusters and the so called near interface traps (NITs) [1]. Due to incomplete oxidation of C atoms at the interface graphite-like clusters and/or sp²-bonded clusters form. The C clusters are believed to contribute to
interface states over the entire SiC band gap while the NITs are presumed to be responsible for the abrupt increase in $D_{it}$ towards the edge of the conduction band ($E_c$), especially for 4H-SiC which, has a relatively wide energy band gap (~3.26 eV at 300K). The NITs are assumed to be intrinsic defects in the near-interfacial oxide layers (~1.5-2 nm from the SiC surface) [2]. These states act as traps (acceptors) for electrons and reduce the channel mobility in MOS devices. Nitridation of the SiC/SiO$_2$ interface, carried out either by post-oxidation annealing in NO or N$_2$O, or by direct oxidation in N$_2$O atmosphere, is shown to improve the interface properties significantly, although with a limited success [3,4]. However, Sveinbjörnsson et al. [5] have recently shown that growth of SiO$_2$ layers in alumina environment can reduce $D_{it}$ drastically and improve substantially the channel mobility. However, Na impurities cause severe device instabilities in these samples during negative gate bias stressing. In general, when exposed to high electric fields and high temperatures, accelerated degradation of the SiO$_2$ layers occurs irrespective of the growth environment used. Hence, investigations for alternative dielectrics have become of great interest. Amongst other pure metal oxides, Al$_2$O$_3$ is the most chemically and thermodynamically stable insulator [6]. Moreover, Al$_2$O$_3$ exhibits a large dielectric constant ($\varepsilon \sim 10$), a large band gap (~6.2 eV), and compared to ZrO$_2$ or HfO$_2$, the highest conduction and valence band offsets, $\Delta E_c = 1.7$ eV and $\Delta E_v = 1.2$ eV, respectively, when adjusted to 4H-SiC [7]. Several studies of Al$_2$O$_3$ on Si have reported presence of metal clusters, C contamination and defect states like Al-Al and OH bonds in Al$_2$O$_3$, bulk grown by ALD with water as a source of oxygen [8]. In contrast, by growing Al$_2$O$_3$ layers using O$_3$ as oxidant, a decrease in leakage-current density by one to two orders of magnitude and also a smaller flat band voltage have been found [9]. High temperature annealing of Al$_2$O$_3$ deposited on Si initiates crystallization of the oxide layers at 1073 K (30 min) with a completion at 1273 K after 15 min [10]. However, good thermal stability and low leakage currents for Al$_2$O$_3$ devices have been achieved also after crystallization of the Al$_2$O$_3$ layer at 1273 K [11]. Further annealing, at the crystallisation temperature and above, increases the dielectric constant of the Al$_2$O$_3$ films ($\varepsilon \sim 11-14$) [12]. Recent results by Hino et al [13] for 4H-SiC MOSFETs with Al$_2$O$_3$ as gate dielectric, yield a peak field effect mobility of $78\pm10$ cm$^2$/Vs which, although promising, is substantially below that of $\sim 150$ cm$^2$/Vs for state of the art 4H-SiC MOSFETs with SiO$_2$ as gate dielectrics. In this work we used XPS, TEM and SIMS to investigate the effect of annealing on the nature of the Al$_2$O$_3$/SiC interface. **Our investigations were focused on the SiO$_x$ formation along the interface and films with different Al$_2$O$_3$ thicknesses 5 and 100-120 nm were used for the XPS and the TEM analysis respectively.**
II. EXPERIMENTAL

Al₂O₃ was grown by ALD on Si-faced, n-type (N-doped) and p-type (Al-doped) 4H-SiC substrates, with a 10µm thick epi-layer (net doping level 2x10¹⁵cm⁻³) on a highly doped substrate (net doping level 1x10¹⁸cm⁻³), and oriented 8° off the (0001) direction. The 4H-SiC substrates were cleaned using HF followed by rinsing in de-ionized water and in-situ O₃ treatment immediately before the Al₂O₃ deposition. The O₃ treatment consisted of a total 60 seconds of 500 sccm O₃ (ca. 15 vol% O₃ in O₂) at the growth temperature. Al₂O₃ was grown using two different trimethylaluminum (TMA) precursors with purities 98% and 99.999%, and O₃ at 500 sccm flow as an oxidant at a reactor temperature of 573 K. The pulsing scheme for the ALD growth was 0.5 s of TMA, 0.5 s purge, 4 s of O₃, and 1.5 s purge. N₂ (300 sccm) was used as a carrier gas providing a base pressure of ca. 2 mbar.

Post-deposition annealing treatments have been carried out at 873 K in N₂ (90%) / H₂ (10%) atmosphere and at 1273 K in Ar atmosphere for 1-3 hours.

Cross-section TEM samples were prepared by ion-milling using a Gatan precision ion polishing system with a 5kV gun voltage. HRTEM of the Al₂O₃/SiC interfaces was performed using an analytical 200keV JEOL 2010F TEM. XPS was performed using a Thermo VG scientific Sigma Probe spectrometer with monochromatic Al Kα radiation (hν = 1486.6eV).

Spectra were acquired from bulk and surface regions of the specimen, at take-off angles, relative to the surface normal, of 28 ± 5° and 78 ± 5° respectively as well as in the so-called angle resolved mode of 53 ± 18° which provides higher sensitivity at an intermediate take-off angle. Pass energies of 100 eV and 50 eV were employed for the survey and the high resolution spectra respectively. The spectra were corrected for charging by using a C 1s value for adventitious C equal to 284.8 eV [14].

III RESULTS AND DISCUSSION

Figure 1 shows the Si 2p spectra obtained by ARXPS in AR mode on both as-grown and annealed samples. We calculated the thickness of the silicon sub-oxide following the approach described by Watts and Wolstenholme [15] and an inelastic mean free path value for Si (λ₅) in SiO₂ equal to 3.77nm [16]. For the calculation of the SiOx film thickness (d) the following form of the Beer-Lambert equation was used

\[ d = \lambda₅ \cos\theta \ln(1+R/R∞) \]  

(1)
where: $\lambda_{Si}$ is the inelastic mean free path for Si, $\theta$ the angle of emission, R the Si 2p intensity ratios $I_{SiOx}/I_{SiC}$, $R^\infty$ the Si 2p intensity ratios $I^\infty_{SiOx}/I^\infty_{SiC}$ where $I^\infty$ is the intensity from an infinitely thick substrate. $R^\infty$ was derived from (2)

$$R^\infty = \frac{\sigma_{Si,SiO2} \cdot \lambda_{Si,SiO2}}{\sigma_{Si,Si} \cdot \lambda_{Si,Si}} \quad (2)$$

where $\sigma_{Si,SiO2}$ and $\lambda_{Si,SiO2}$ are the number of Si atoms per SiO$_2$ unit volume and the inelastic mean free path respectively.

The $\sigma_{Si,SiO2} / \sigma_{Si,Si}$ ratio is given by (3)

$$\sigma_{Si,SiO2} / \sigma_{Si,Si} = \left( \frac{D_{SiO2} \cdot F_{Si}}{D_{Si} \cdot F_{SiO2}} \right) \quad (3)$$

where D is the density of the material and F the formula weight.

For the calculations we also assumed that the Si 2p photoelectrons from both SiC and Si oxide film will be attenuated by the same amount as they travel through the Al$_2$O$_3$ film therefore, their intensity ratio will reflect the attenuation of the Si 2p electrons coming from the SiC through the Si oxide film.

Since in the AR mode the electrons are collected over a wide angular range and since the surface mode at high emission angles suffers from elastic scattering of electrons coming from deeper in the sample thus leading to an underestimation of the film thickness, we used only the spectra from the bulk mode for the estimation of the SiO$_x$ thickness. For simplification reasons we also assumed presence of one (sub-) oxide component.

The analysis indicated presence of a ~ 1.2 nm thick Si sub-oxide between Al$_2$O$_3$ and SiC in the as-grown condition. The intensity of the sub-oxide was more pronounced in the bulk mode indicating its formation at the SiC/Al$_2$O$_3$ interface. The thickness of the interfacial Si sub-oxide increased to ~ 3 nm after annealing at 1273 K independently of the annealing duration, whilst the interfacial film thickness after annealing at intermediate temperatures (873 K) was significantly less. Similar analysis performed for estimating the thickness of the as grown Al$_2$O$_3$ film showed a film thickness of 5.1nm which was in excellent agreement with the nominal value (5nm).

The formation of this interfacial film may be attributed to the exposure of Si, terminating the SiC surface, to O$_3$ treatment prior to oxide deposition. The Si 2p spectra of the 1273 K annealed samples exhibit a more intense SiO$_x$ peak positioned at higher binding energy indicating the formation of SiO$_2$. This is attributed to oxidation of part of the SiO$_x$ to SiO$_2$ accompanied by a simultaneous reduction to Si of the SiO$_x$. Pure Si was also present as shown by the peak at about 99 eV which is enhanced for the annealed samples (Figure 1).

Therefore, we conclude that Si originating from the redox reaction diffuses through the Al$_2$O$_3$ towards the surface which is in agreement with the SIMS measurements.
Figure 2 shows the O 1s angle resolved spectrum from as-grown Al₂O₃/4H-SiC samples with two different Al₂O₃ film thicknesses. The energy separation between the main peak and the onset of the plasmon loss is equivalent to the minimum energy required for an electron to travel across the band gap and cause plasmon oscillations, i.e., to a good approximation to the band gap energy [17]. In this context, the Al₂O₃ band gap was measured to be 6.2eV and 6.8eV for 8nm and 5nm thick Al₂O₃ respectively, in the case of as-deposited sample and 6.3eV for the annealed ones (not shown) in good agreement with the literature [18].

The Al 2p (Figure 3) and O 1s peaks (not shown) of the as-grown sample (74 ± 0.1eV) shifted at 0.3 eV towards higher binding energy after annealing whilst the SiC component of the Si 2p peak shifted 0.3-0.4 eV towards lower binding energies. The O 1s – Al 2p energy separation does not change upon annealing as shown in figure 4. Therefore, the above energy shifts are attributed to the thickening of the SiOₓ interfacial layer and the subsequent enhancement of electrostatic charging rather than any alteration of the Al-O bond distance due to e.g. densification of the Al₂O₃ film.

SIMS measurements (not shown) revealed presence of Na, K, Mn and Ni at the Al₂O₃/4H-SiC interface probably originated from the aluminium precursor. The H profile showed a lower concentration in the bulk oxide after annealing in agreement with the O1s XPS spectra (not shown) which exhibited a reduced OH⁻ component after annealing. The H concentration increased significantly at the interface probably due to H diffusion whilst, the Si profile showed an out-diffusion after annealing at 1273 K indicating that Al₂O₃ is not a diffusion barrier for Si in agreement with literature reports of Al₂O₃ deposited on Si [19]. The C profile was not affected by temperature treatment even above crystallization temperature (T>1173 K).

HRTEM images of the interface between the crystalline SiC substrate and the polycrystalline (due to electron beam crystallisation) Al₂O₃ film revealed a ~ 1.3 nm thick amorphous layer, see Figure 5. The thickness of this amorphous layer did not appear to increase after heat-treatment. The discrepancy with the XPS results could be explained by the different Al₂O₃ thicknesses used for the XPS and HRTEM analysis, 5nm and 100-120nm respectively and the shorter diffusion paths in the thinner film and/or to inaccuracies due to the uneven thickness of the interfacial film (film thickness measurement via ARXPS assumes sharp interfaces). As a concluding discussion point we consider the rearrangement of the interfacial SiOₓ layer and accumulation of passivating H species at the interface of the annealed samples to be the reason for the significant reduction of the interface states density.
(< 10^{11} \text{ eV}^{-1}\text{cm}^{-2}) \text{ close to the conduction band edge, } E_c. \text{ The latter was shown by TDRC measurements of 1273 K (Ar) annealed (~100nm) Al}_2\text{O}_3/4\text{H-SiC capacitors [20].}

**IV. CONCLUSION**

We have investigated Al\textsubscript{2}O\textsubscript{3} films deposited on 4H-SiC(0001) by ALD. XPS indicated the presence of a 1 nm thick SiO\textsubscript{x} interlayer on as-deposited 5nm Al\textsubscript{2}O\textsubscript{3}/4H-SiC samples. After annealing at 1273 K in Ar atmosphere, the Si sub-oxide thickness increased to 3 nm whereas HRTEM on thicker samples (100-120nm) showed a 1.4 nm thick interlayer. The thickness of the sub-oxide after annealing at 873 K increased slightly but it remained close to the value of the as-grown samples.

**REFERENCES**

Figure 1. Si 2p high resolution XPS spectra (AR mode) of samples annealed at different temperatures. From bottom up: as-grown, N₂/H₂ 873 K 15 mins, N₂/H₂ 873 K 30 mins, Ar 1273 K 15 mins, Ar 1273 K 30 mins, Ar 1273 K 60 mins

Fig. 2 XPS O1s spectra (AR mode) of as grown 5nm and 8nm Al₂O₃/4H-SiC
FIG. 3: Al 2p high resolution XPS spectra (AR mode) showing a 0.3eV shift upon annealing. From bottom up: as-grown, N₂/H₂ 873 K 15 mins, N₂/H₂ 873 K 30 mins, Ar 1273 K 15 mins, Ar 1273 K 30 mins, Ar 1273 K 60 mins

Figure 4. O1s-Al2p energy separation of samples annealed at different temperatures
Figure 5. Cross sectional HRTEM image of as grown sample showing presence of an amorphous film at the SiC/Al$_2$O$_3$ interface.