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# Suppression of parasitic Si substrate oxidation in $HfO_2$–ultrathin-$Al_2O_3$–Si structures prepared by atomic layer deposition

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We investigated the effects of $Al_2O_3$ thickness on the suppression of parasitic substrate oxidation in $HfO_2$–ultrathin-$Al_2O_3$–Si structures. The use of $H_2O$ as oxidizing agent in the atomic layer deposition (ALD) chemistry is considered key to preventing the formation of an $SiO_x$ interlayer during oxide deposition. An $Al_2O_3$ layer prepared with 10 cycles of atomic layer deposition (ALD, ~0.74 nm) effectively suppressed substrate oxidation during rapid thermal annealing in $N_2$ for 10 s below 800 °C. Parasitic oxidation was observed at 600 °C for samples with only five cycles or without $Al_2O_3$. Ultrathin $Al_2O_3$ films can be relevant for the integration of $HfO_2$ as gate dielectric in silicon technology. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1944206]

Excessive tunneling of charge carriers through $SiO_xN_y$ thin films presently limits the miniaturization of metal–oxide–silicon field effect transistors. Replacement of $SiO_xN_y$ by a material of higher dielectric constant ($k>9$) has been proposed.[1,2] Other conditions being met, such a high-$k$ material would allow increasing the thickness of the dielectric layer by a factor above $k/7.5$—therefore, reducing tunneling currents—without significantly altering device characteristics. Among high-$k$ dielectric candidates, $HfO_2$ is under intense investigation. In addition to high dielectric constant ($k\sim 22$–25),[3] it exhibits relatively large band gap[4,5] ($E_g \sim 5.6$ eV) and high free energy of reaction with Si.[6] Nevertheless, most $HfO_2$–Si structures reported to date show an interfacial layer, probably formed due to oxidizing species.[7] The interfacial layer generally forms during $HfO_2$ deposition and thickens upon thermal annealing, which is inherent to device fabrication. While such a layer can reduce the density of interface defects and improve the reliability of the $HfO_2$ film,[3] a critical disadvantage is the reduced effective dielectric constant of the resulting dielectric stack. This prompts for an engineered interface between $HfO_2$ and Si.

$Al_2O_3$ presents a moderate dielectric constant ($k\sim 9$), wide band gap, and large band offset energies with respect to Si. It has also been shown to remain amorphous on Si after annealing above 800 °C.[8] Gusev *et al.*[9] reported the deposition of $Al_2O_3$ on Si by atomic layer deposition (ALD) without the formation of an interfacial layer. We are thus investigating ultrathin $Al_2O_3$ layers on Si to prevent interfacial layer formation during $HfO_2$ deposition and thermal annealing.

In this letter, we report the effects of $Al_2O_3$ thickness on the suppression of parasitic substrate oxidation in $HfO_2$–ultrathin-$Al_2O_3$–Si structures. Ultrathin $Al_2O_3$ films of different thicknesses (<1 nm) were deposited on HF-last Si(100) by ALD in an F-120 system (ASM Microchemistry). Atomic layer deposition of $HfO_2$(~4.5 nm) followed on selected samples and directly on Si for control purposes. The hot wall quartz reactor was kept at 300 °C. Trimethylaluminum (TMA, naturally vaporized) and hafnium tetrachloride ($HfCl_4$, kept at 150 °C and carried by $N_2$) were the metal precursors, and $H_2O$ was the oxidizing agent. A reactor purge with $N_2$ preceded substrate exposure to each of the reactants. The samples were submitted to rapid thermal annealing in $N_2$ for 10 s at 600 to 800 °C. Physical characterization before and after annealing was accomplished using x-ray photoelectron spectroscopy (XPS) and cross-sectional high-resolution transmission electron microscopy (HRTEM).

We used XPS to identify chemical bonding in the samples and to determine the thickness[10,11] of the $Al_2O_3$ layers. Figure 1(a) schematically presents three samples used in

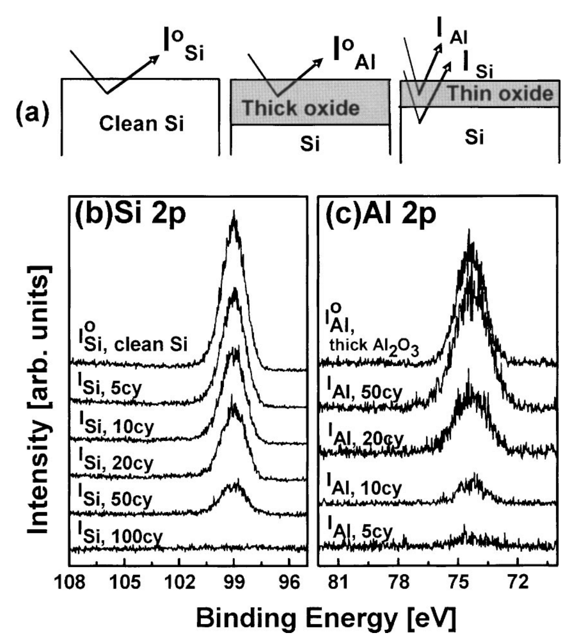


FIG. 1. (a) Schematic illustration of three structures used for $Al_2O_3$ thickness determination by XPS: Clean Si substrate, thick $Al_2O_3$ film on Si, and thin $Al_2O_3$ film on Si (sample of interest); (b) Si 2$p$ and (c) Al 2$p$ XPS data from various thicknesses of as-deposited $Al_2O_3$ on Si ("cy" refers to ALD cycles).

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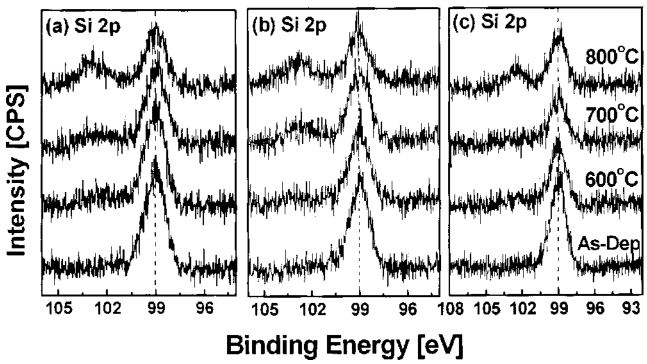


FIG. 2. Si 2*p* XPS data for samples featuring (a) zero, (b) 5, and (c) 10 ALD cycles of $Al_2O_3$ between the Si substrate and the $HfO_2$ overlayer, with annealing temperature as parameter; Si–Si bonding appears at 99 eV, and Si–O at 103 eV.

the thickness determination process: Clean Si substrate, thick $Al_2O_3$ layer on Si, and thin $Al_2O_3$ layer on Si (sample of interest). Figures 1(b) and 1(c) show actual Si 2*p* and Al 2*p* XPS spectra acquired from various samples featuring $Al_2O_3$ layers of different thicknesses. The Si 2*p* and Al 2*p* data evidence only Si–Si and Al–O bonding, respectively, indicating that there is no parasitic oxidation of the substrate during $Al_2O_3$ deposition and that the overlayer is fully oxidized. In the thickness calculations we use 2.9 and 2.8 nm, respectively, as the attenuation lengths for Si 2*p* and Al 2*p* photoelectrons in $Al_2O_3$.[12] These values are reasonably close to those reported[13] by Bender *et al.*: 2.65 and 2.70 nm. The $Al_2O_3$ thicknesses determined are 0.27 and 0.74 nm for 5 and 10 ALD cycles, respectively. A linear fit to the full set of thickness versus number of ALD cycles data (not shown) indicates about three cycles of incubation, i.e., no actual oxide deposition during the first three ALD cycles. Gosset *et al.*[14] also reported a nucleation retardation of four deposition cycles for $Al_2O_3$ on HF-last Si. The retardation has been understood as due to the low reactivity of hydrogen-terminated silicon towards the ALD precursors.

To discuss unintentional interfacial layer formation during $HfO_2$ deposition and thermal annealing, we consider the Si 2*p* XPS data in Fig. 2, acquired from the $HfO_2$–ultrathin-$Al_2O_3$–Si structures as-prepared and after annealing at 600 to 800 °C. Data from as-deposited samples evidences only Si–Si bonding, indicating the absence of interfacial $SiO_x$ irrespective of $Al_2O_3$ layer presence or thickness. We attribute that to the use of $H_2O$ as oxidizing agent in the ALD process. The alternative chemistry with $O_3$ oxidizes the substrate.[15] Si–O bonding becomes evident at 103 eV in Figs. 2(a) and 2(b) after annealing at 600 °C, indicating low thermal stability of the $HfO_2$–Si structure [Fig. 2(a)] and no beneficial effect of 5 ALD cycles of $Al_2O_3$ between $HfO_2$ and Si [Fig. 2(b)]. In contrast, the Si–O XPS component is absent from Fig. 2(c) until the annealing is performed at 800 °C, indicating enhanced thermal stability for the sample incorporating 10 ALD cycles of $Al_2O_3$.

Figure 3 shows cross-sectional HRTEM images of the $HfO_2$–ultrathin-$Al_2O_3$–Si structures as-deposited [Figs. 3(a)–3(c)] and after annealing at 700 °C [Figs. 3(d)–3(f)]; the number of $Al_2O_3$ ALD cycles increases from zero to 5 to 10 in Figs. 3(a)–3(c) and Figs. 3(d)–3(f). Images from as-deposited samples show both $HfO_2$ and $Al_2O_3$ films as amorphous; the thickness labels indicate upper limits for the layer between $HfO_2$ and Si. We recall that the absence of Si–O

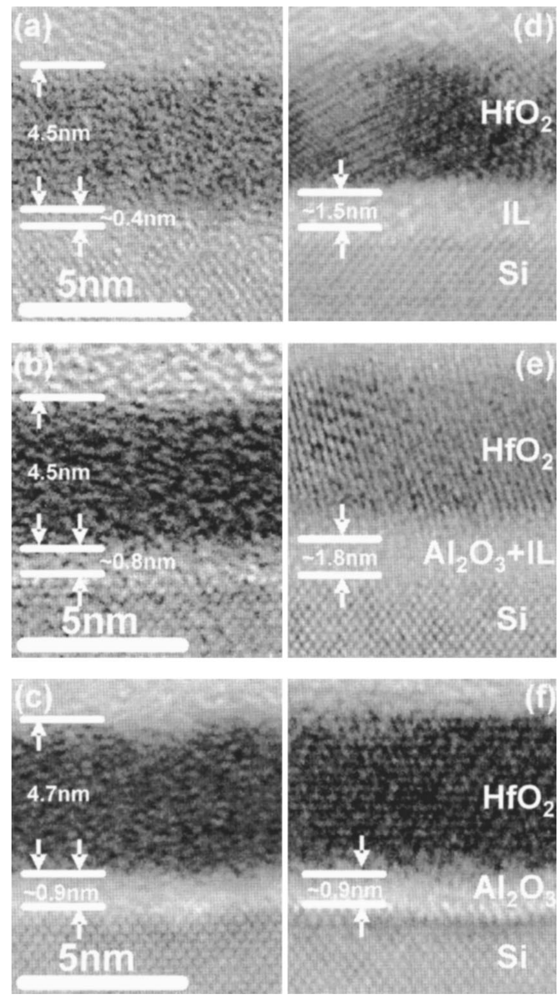


FIG. 3. Cross-sectional HRTEM images of $HfO_2$–ultrathin-$Al_2O_3$–Si structures as-deposited [(a)–(c)] and after thermal annealing in $N_2$ for 10 s at 700 °C; the number of $Al_2O_3$ ALD cycles increases from zero to 5 to 10 in the sequences (a)–(c) and (d)–(f). "IL" stands for interfacial layer.

bonding was inferred from XPS for all as-deposited samples. Figures 3(a) shows a transition layer that is only one to two atomic layers-thick, while Figs. 3(b) and 3(c) show a layer of thickness approaching 1 nm. Regarding Fig. 3(b), it is reasonable to question if 5 ALD cycles produce a qualified, continguous *layer* of $Al_2O_3$; in this sense, the thickness reported from XPS (0.27 nm) should be interpreted as an approximate average. Based on XPS, the thickness of $Al_2O_3$ in Fig. 3(c) is more than twice that in Fig. 3(b). We, therefore, state that most of the lighter area between Si and $HfO_2$ in Fig. 3(b) corresponds to the Si substrate. Concerning the annealed samples, Figs. 3(d) and 3(e) clearly indicates the growth of an interfacial layer, as opposed to Fig. 3(f), in which the interface is stable with reference to the as-deposited sample in Fig. 3(c). HRTEM, therefore, confirms the result provided by XPS, namely that 10 ALD cycles of $Al_2O_3$ between Si and $HfO_2$ prevent the formation of an unintentional interfacial layer during thermal annealing at 700 °C. We finally note that the presence of $Al_2O_3$ does not prevent crystallization of the $HfO_2$ overlayer, which is evident in Fig. 3 for all annealed samples.

In summary, the suppression of parasitic substrate oxidation in $HfO_2$–ultrathin-$Al_2O_3$–Si structures was investigated. Ten ALD cycles of $Al_2O_3$ (0.74 nm) yielded structures presenting thermal stability during rapid thermal annealing in

$N_2$ for 10 s below 800 °C. Samples featuring only 5 ALD cycles of $Al_2O_3$ did not show improvement with respect to the parent $HfO_2$–Si stack. This result suggests an approximate minimal $Al_2O_3$ thickness that could be necessary to integrate $HfO_2$ as gate dielectric in silicon technology.

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