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Enhanced initial growth of atomic-layer-deposited metal oxides on hydrogen-terminated silicon

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A route is presented for activation of hydrogen-terminated Si(100) prior to atomic layer deposition. It is based on our discovery of in situ infrared spectroscopy that organometallic precursors can effectively initiate oxide growth. Narrow nuclear resonance profiling and Rutherford backscattering spectrometry show that surface functionalization by pre-exposure to $10^8$ Langmuir trimethylaluminum at 300 °C leads to enhanced nucleation and to nearly linear growth kinetics of the high-permittivity gate dielectrics aluminum oxide and hafnium oxide. © 2003 American Institute of Physics. [DOI: 10.1063/1.1595719]

As $\text{SiO}_2$, the traditional gate dielectric in field effect transistors, approaches its ultimate thickness limit, alternative materials are required to replace $\text{SiO}_2$ and continue device scaling. High-$\kappa$ materials such as $\text{Al}_2\text{O}_3$ and $\text{HfO}_2$ are attractive candidates, the more so if they can be deposited directly on silicon with monolayer thickness and uniformity control. In atomic layer deposition (ALD), a promising and highly manufacturable technique, a metal precursor and an oxidizing agent are brought to the surface in alternating pulses, separated by an inert gas (e.g., $\text{N}_2$) purge. $\text{H}_2\text{O}$ is the most commonly used oxidizing agent while $\text{Al(CH}_3)_3$ [trimethylaluminum (TMA)] and $\text{HfCl}_4$ are the preferred metal precursors for $\text{Al}_2\text{O}_3$ and $\text{HfO}_2$, respectively. Growth is based on self-terminating surface reactions. Compounds can thus be deposited on complex geometries with a maximum growth rate of one monolayer per pulse, thereby allowing conformal growth with thickness and uniformity control at the angstrom level.

An abrupt Si/high-$\kappa$ interface is desirable to maximize gate stack capacitance. Therefore, growth on H-passivated Si (H/Si) has been attempted instead of growth on thin $\text{SiO}_2$ buffer layers. On H/Si, however, growth is nonlinear, exhibiting an incubation period due to inhomogeneous nucleation. Rough films result from the islanded growth mode and unwanted interfacial $\text{SiO}_2$ or silicates are formed.

In order to improve the initial ALD growth of monolayer thick films through an understanding of the nucleation and growth mechanism, we have recently conducted in situ IR absorption studies of the first few ALD cycles of $\text{Al}_2\text{O}_3$ on H/Si. We have thus shown that growth is not initiated by water, as commonly believed, but rather is initiated by extended metal precursor (TMA) pre-exposure. In the present work, we use this information and combine other experimental techniques to demonstrate that proper functionalization of H/Si by TMA dramatically improves the growth characteristics of $\text{Al}_2\text{O}_3$ and $\text{HfO}_2$ films.

We perform in situ and ex situ film characterization. For in situ work, emphasis is placed on probing surface reactions under high enough exposures to achieve completion of surface reactions, which is particularly important for looking at relatively stable H/Si surfaces. This is done in a home-built ALD reactor equipped with a shutter/purge arrangement to protect the IR windows from comparatively high water and TMA partial pressures (10 and 1 mbar, respectively, in $\text{N}_2$ carrier gas at 1 bar; exposures up to $4 \times 10^4$ times higher than used in standard commercial processes; standard exposures are, e.g., $4 \times 10^3 \text{ L TMA}$ and $10^4 \text{ L water}$; 1 L=1 Langmuir=$10^{-6} \text{ Torr s}$). The IR transmission measurements are carried out at 70° off-normal incidence, with the sample temperature maintained at 50 °C, following each precursor exposure at 300 °C. Use of $\text{D}_2\text{O}$ instead of $\text{H}_2\text{O}$ ensures that all IR bands are separated from the signals caused by trace amounts of water in the optical system, and does not affect growth chemistry.

Films studied by ex situ techniques are grown in commercial ALD reactors (ASM Pulsar2000™). Rutherford backscattering spectrometry (RBS) is performed at IMEC to determine the areal density of Hf in $\text{HfO}_2$ films. To enhance the sensitivity to Hf, the beam energy was decreased to 1 MeV. In the case of the $\text{Al}_2\text{O}_3$ films, the small mass difference between Al and Si precludes the separation of their RBS signals. The Al areal density is therefore determined from the area under excitation curves generated by narrow nuclear resonance profiling (NRP), calibrated with two
standard samples. This is a technique so far not applied to the study of monolayer-thick films. The 992 keV resonance of the $^{27}$Al($p,\gamma$)$^{28}$Si reaction is used and the 3 MV Tandetron accelerator at Porto Alegre delivers the proton beam. The uncertainty in areal density is estimated as ±15%.

The IR spectra (a)–(g) in Fig. 1 summarize the key findings concerning $\text{Al}_2\text{O}_3$ nucleation and growth chemistry on HF-etched Si(100). The initial H/Si surface (a) is atomically rough (exhibiting double-layer roughness), with a broad and structured Si–H stretching band centered at 2110 cm$^{-1}$, associated with mono-,$^4$ di-,$^5$ and trihydrides,$^4$ and a weaker band at 2250 cm$^{-1}$ arising from oxidized Si–H.$^5$ Very large $D_2$O exposures at 300 °C [(b) $5 \times 10^8$ L] leave the surface nearly unchanged chemically: the Si–H stretch signal is unaffected, except for a few percent of isotopic Si–H to Si–D exchange (not shown), and at most 0.1 $\text{SiO}_2$ (5 $\times 10^{13}$ O ions per cm$^2$, $\sim 1000$–$1200$ cm$^{-1}$)$^7$ and 0.02 monolayers of OD groups (1.3 $\times 10^{13}$ OD per cm$^2$, not shown) are formed.$^10$

In contrast, TMA reacts with H/Si(100) at 300 °C. An initial TMA exposure [Fig. 1(c), $2 \times 10^5$ L] predominantly forms Si–CH$_3$ (1266 cm$^{-1}$) at Si defect sites, and higher TMA exposures [(d) $5 \times 10^5$ L] give rise to Al–CH$_3$ species (1217 cm$^{-1}$).$^10$ While oxidized TMA, probably due to gas impurities, leads to the formation of interfacial Si–O–Al bond arrangements (800 and 1000–1100 cm$^{-1}$),$^{10,18}$ inadvertent $\text{SiO}_2$ formation is limited to less than 0.25 Å. Once the H/Si(100) surface has been functionalized by TMA, a water pulse (e) replaces Al-bonded CH$_3$ (but not Si-bonded CH$_3$) by OD and gives rise to subsurface $\text{SiO}_2$. In the subsequent cycles (f), amorphous $\text{Al}_2\text{O}_3$ is grown, while additional subsurface Si oxidation is catalyzed by interfacial aluminum.$^10$ $\text{Al}_2\text{O}_3$ films grown with a long initial TMA pulse in a commercial ALD reactor [(g) 3600 s, $10^8$ L] are very similar to those from our model reactor. The much lower water exposures employed in the commercial reactor ($10^4$ L), however, guarantee that the $\text{SiO}_2$ interlayer thickness is smaller.$^{10,11}$

We conclude that water exposure has essentially no effect on H/Si, while regular and oxidized TMA species strongly modify the surface and initiate oxide growth when supplied in quantities exceeding what is typically used in the commercial process. Consequently, we expect a more homogeneous nucleation and hence more linear growth after a large initial TMA exposure.

To test this conjecture, we use NRP to measure the Al areal density in $\text{Al}_2\text{O}_3$ films grown in a commercial ALD reactor under different initial TMA pulse conditions. Figure 2(a) shows that the Al areal density deposited on H/Si during the first cycle increases with increasing TMA exposure time, confirming surface modification by the TMA pulse. After a 3600 s TMA pulse ($10^8$ L), the Al areal density reaches values observed for standard TMA exposures ($4 \times 10^3$ L) of a hydrous chemical oxide.$^{19}$ Such chemical oxide contains a high concentration of OH sites that are very reactive with metal precursors, which leads to nearly linear high-κ growth.$^6,9$ This is confirmed by NRP data for $\text{Al}_2\text{O}_3$ (Fig. 3).

The key finding reported in Figs. 2 and 3 is direct proof that a similar, complete nucleation can also be achieved on H/Si by long TMA pre-exposure. While the standard H/Si starting surface exhibits the well-known incubation period with a delay of about 15 cycles before the onset of linear growth (Fig. 3, bottom curve),$^{7,6,8}$ this incubation time is shortened and growth gradually approaches nearly linear characteristics as the length of the initial TMA pulses increases to 3600 s. Enhanced oxide nucleation on TMA-modified H/Si is confirmed by ellipsometry. We note that there is no noticeable increase in electrical leakage (e.g., by...
C contamination) compared to Al$_2$O$_3$ films grown on pristine H/Si.

Based on our IR and NRP data, a clear picture of Al$_2$O$_3$ nucleation and growth on H/Si surfaces emerges. A short (e.g., 60 s) TMA pulse deposits only very little Al [Fig. 2(a)], while many Si–CH$_3$ groups are formed [Fig. 1(c)]. These Si-bonded methyl groups are not reactive with water during the initial growth cycles [Fig. 1(e)], thus providing a passivation at least as effective as hydrogen.\(^{20}\) Accordingly, during the first 10 ALD cycles following a 60 s TMA pulse, the growth rate is close to that on pristine H/Si (Fig. 3). At later growth stages, however, we observe the gradual decomposition of most Si–CH$_3$ [Fig. 1(f)]. Reactive Si sites are thus created, resulting in an increased growth rate (Fig. 3). If, instead, longer TMA pre-exposures are used at the onset, then Al–CH$_3$ is formed as well [Fig. 1(d)]. Such Al–CH$_3$ sites readily react with water to form hydroxylated Al$_2$O$_3$. For long TMA pre-exposures (3600 s), nucleation is therefore enhanced after the very first pulse (Fig. 3), supporting linear Al$_2$O$_3$ growth.

TMA-induced activation of H/Si is expected to be of general use for water-based dielectric growth, as hydroxyl groups present after the subsequent water pulse constitute reactive sites for many metal precursors. We have tested this hypothesis for the case of HfO$_2$ deposition from HfCl$_4$ and reactive sites for many metal precursors. We have tested this hypothesis for the case of HfO$_2$ deposition from HfCl$_4$ and water precursors. We find that the Hf areal density deposited TMA pre-exposure compared to that on a hydrous chemical oxide. The lines are guides for the eye.

For long TMA pre-exposures contrast, can dissociate on hydroxyl-free oxide sites,\(^{21}\) which growth rate is close to that on pristine H/Si. After 30 HfO$_2$ ALD cycles on TMA-water pre-exposed H/Si, we find that the Hf areal density deposited TMA pre-exposure compared to that on a hydrous chemical oxide. The lines are guides for the eye.

FIG. 3. Al areal density dependence on the number of TMA-water cycles for different starting surfaces: pristine H/Si(100), H/Si(100) pre-exposed to TMA pulses of various durations, and a hydrous chemical oxide. The lines are guides for the eye.

In conclusion, an in situ approach to understanding surface chemistry in ALD has enabled us to propose a route for Si surface functionalization, based on extended TMA pre-exposure of H-terminated Si. Al$_2$O$_3$ and HfO$_2$ films grown on TMA-modified surfaces exhibit enhanced initial growth kinetics, approaching linear growth. The proposed combination of TMA and HfCl$_4$ precursors may become an important ingredient to minimizing gate leakage in future high-k devices.

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As no suitable plateaus were found in the cross-section curve of a nuclear reaction on $^{27}$Al, NRP was used instead of nuclear reaction analysis.


Small signals in the C–H stretch region are consistent with instrumental instabilities arising from hydrocarbons in the optical path.


