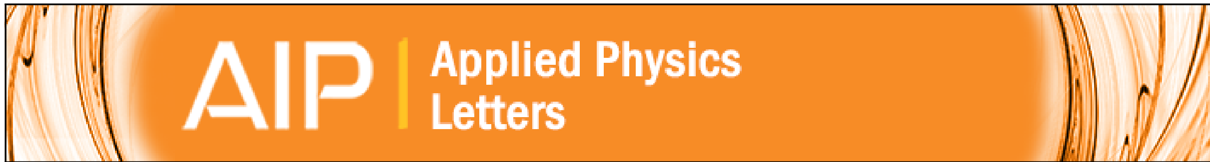

Enhanced initial growth of atomic-layer-deposited metal oxides on hydrogen-terminated silicon

Martin M. Frank, Yves J. Chabal, Martin L. Green, Annelies Delabie, Bert Brijs, Glen D. Wilk, Mun-Yee Ho, Elisa B. O. da Rosa, Israel J. R. Baumvol, and Fernanda C. Stedile

Citation: Applied Physics Letters **83**, 740 (2003); doi: 10.1063/1.1595719
View online: http://dx.doi.org/10.1063/1.1595719
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/83/4?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Interface studies of GaAs metal-oxide-semiconductor structures using atomic-layer-deposited Hf O 2∕Al 2 O 3 nanolaminate gate dielectric
Appl. Phys. Lett. **91**, 142122 (2007); 10.1063/1.2798499

In situ infrared spectroscopy of hafnium oxide growth on hydrogen-terminated silicon surfaces by atomic layer deposition
Appl. Phys. Lett. **87**, 133103 (2005); 10.1063/1.2058226

Island growth in the atomic layer deposition of zirconium oxide and aluminum oxide on hydrogen-terminated silicon: Growth mode modeling and transmission electron microscopy
J. Appl. Phys. **96**, 4878 (2004); 10.1063/1.1787624

Density functional theory study of HfCl 4 , ZrCl 4 , and Al(CH 3) 3 decomposition on hydroxylated SiO 2 : Initial stage of high-k atomic layer deposition
Appl. Phys. Lett. **83**, 542 (2003); 10.1063/1.1587261

Suppressed crystallization of Hf-based gate dielectrics by controlled addition of Al 2 O 3 using atomic layer deposition
Appl. Phys. Lett. **81**, 4218 (2002); 10.1063/1.1522826

NEW Special Topic Sections
NOW ONLINE
Lithium Niobate Properties and Applications: Reviews of Emerging Trends
AIP Applied Physics Reviews

Reuse of AIP Publishing content is subject to the terms at: https://publishing.aip.org/authors/rights-and-permissions. Download to IP: 143.54.44.137 On: Thu, 05 May 2016 14:55:29

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

Martin M. Frank[a),b)] and Yves J. Chabal[b)]
Rutgers University, Department of Chemistry and Chemical Biology, Piscataway, New Jersey 08854

Martin L. Green,[b)] Annelies Delabie, and Bert Brijs
IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

Glen D. Wilk[c)] and Mun-Yee Ho[d)]
Agere Systems, Murray Hill, New Jersey 07974

Elisa B. O. da Rosa, Israel J. R. Baumvol,[e)] and Fernanda C. Stedile
Instituto de Física and Instituto de Química, UFRGS, Porto Alegre, RS, Brazil 91509-900

(Received 21 February 2003; accepted 28 May 2003)

A route is presented for activation of hydrogen-terminated Si(100) prior to atomic layer deposition. It is based on our discovery from *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 SiO_2, the traditional gate dielectric in field effect transistors, approaches its ultimate thickness limit, alternative materials are required to replace SiO_2 and continue device scaling. High-κ materials such as Al_2O_3 and 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., N_2) purge. H_2O is the most commonly used oxidizing agent while $Al(CH_3)_3$ [trimethylaluminum (TMA)] and $HfCl_4$ are the preferred metal precursors for Al_2O_3 and HfO_2, respectively. Growth is based on self-terminating surface reactions.[1] 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-κ interface is desirable to maximize gate stack capacitance. Therefore, growth on H-passivated Si (H/Si) has been attempted[2–9] instead of growth on thin SiO_2 buffer layers. On H/Si, however, growth is nonlinear, exhibiting an incubation period due to inhomogeneous nucleation.[5,6,8,9] Rough films result from the islanded growth mode and unwanted interfacial SiO_2 or silicates are formed.[5–7]

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 Al_2O_3 on H/Si.[10] 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 Al_2O_3 and 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[11] 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 N_2 carrier gas at 1 bar; exposures up to 4×10^4 times higher than used in standard commercial processes; standard exposures are, e.g., 4×10^3 L TMA and 10^4 L water; 1 L=1 Langmuir=10^{-6} 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 D_2O instead of H_2O 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.[10]

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 HfO_2 films. To enhance the sensitivity to Hf, the beam energy was decreased to 1 MeV. In the case of the Al_2O_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),[12,13] calibrated with two

a)Electronic mail: mmfrank@physics.rutgers.edu
b)Also at: Agere Systems, Murray Hill, NJ 07974, and Allentown, PA 18109.
c)Present address: ASM America, Phoenix, AZ 85034.
d)Present address: Chartered Semiconductor Mfg. Ltd., Singapore 738406.
e)Present address: Universidade de Caixas do Sul, RS, 92670 Brazil.

Reuse of AIP Publishing content is subject to the terms at: https://publishing.aip.org/authors/rights-and-permissions. Download to IP: 143.54.44.137 On: Thu, 05 May 2016 14:55:29

 © 2003 American Institute of Physics

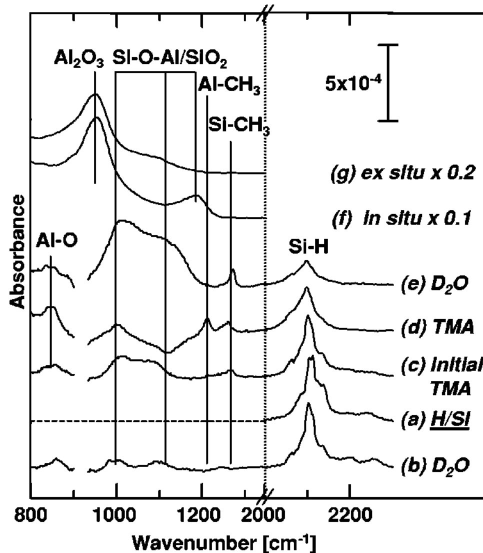

FIG. 1. Transmission IR spectra of H-terminated Si(100) before and after exposure to TMA-water cycles. Bottom spectra taken *in situ* in a model reactor (growth on both front and back surfaces): (a) pristine H/Si; (b) H/Si exposed to an extended D_2O pulse; (c) H/Si exposed to an intermediate amount of TMA (corresponding to a $\sim$30 s pulse in a commercial reactor), followed by extended pulses of (d) TMA and (e) D_2O; and (f) H/Si exposed to 16 TMA–D_2O cycles. Top spectrum (g) taken *ex situ* from a 34 cycle film grown in a commercial ALD reactor, utilizing an initial 3600 s TMA pulse (growth on one wafer surface only; spectra (f) and (g) scaled to ensure comparability of the intensities). Reference surface for oxide phonon region: H-terminated Si; and for Si–H stretching region: Si with native SiO_2. A signal at $\sim 920\ cm^{-1}$ is due to Si–H bending modes of the H/Si(100) *reference* surface and has been removed for clarity.

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 $\pm 15\%$.

The IR spectra (a)–(g) in Fig. 1 summarize the key findings concerning Al_2O_3 nucleation and growth chemistry on HF-etched Si(100).[10] 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-, di-, and trihydrides,[14] and a weaker band at $2250\ cm^{-1}$ arising from oxidized Si–H.[15] Very large D_2O exposures at $300\,^{\circ}C$ [(b) 5×10^8 L] leave the surface nearly unchanged chemically:[16] 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 Å SiO_2 (5×10^{13} O ions per cm^2, ~ 1000–$1200\ cm^{-1}$)[17] and 0.02 monolayers of OD groups (1.3×10^{13} OD per cm^2, not shown) are formed.[10]

In contrast, TMA reacts with H/Si(100) at $300\,^{\circ}C$. An initial TMA exposure [Fig. 1(c), 2×10^5 L] predominantly forms Si–CH_3 ($1266\ cm^{-1}$) at Si defect sites, and higher TMA exposures [(d) 5×10^7 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 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 SiO_2. In the subsequent cycles (f), amorphous Al_2O_3 is grown, while additional subsurface Si oxidation is catalyzed by interfacial aluminum.[10] Al_2O_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 SiO_2 interlayer thickness is smaller.[10,11]

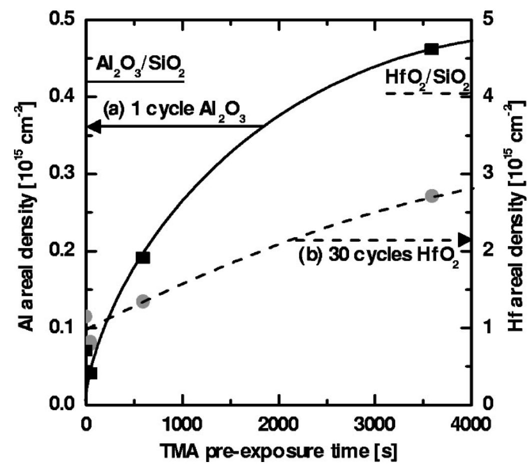

FIG. 2. (a) Left-hand axis: Al areal density dependence, as determined by NRP, on the duration (0.1–3600 s) of the TMA pre-exposure in a single TMA-water cycle, compared with the Al areal density after a regular cycle on a hydrous chemical oxide starting surface (''Al_2O_3/SiO_2''). (b) Right-hand axis: Hf areal density dependence, as determined by RBS, on the duration of the TMA pulse in a single TMA-water cycle and 30 subsequent $HfCl_4$-water cycles, compared with the Hf areal density after 30 $HfCl_4$-water cycles on pristine H/Si ("0 s") and on a hydrous chemical oxide starting surface (''HfO_2/SiO_2''). The lines are guides for the eye.

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 Al_2O_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 (4×10^3 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 Al_2O_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),[5,6,8] 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

Reuse of AIP Publishing content is subject to the terms at: https://publishing.aip.org/authors/rights-and-permissions. Download to IP: 143.54.44.137 On: Thu, 05 May 2016 14:55:29

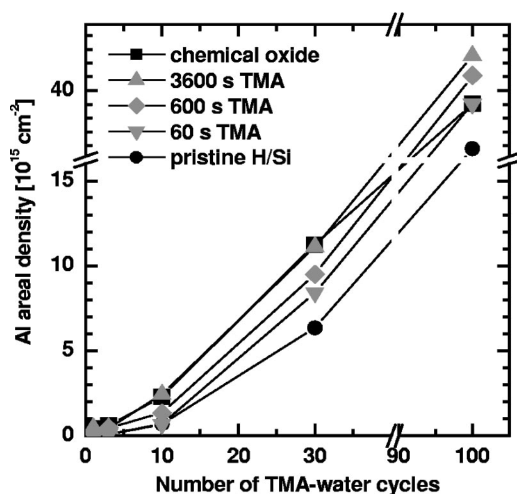

FIG. 3. Al areal density dependence on the number of TMA-water cycles for different starting surfaces: pristine H/Si(100), H/Si(100) pre-exposed to TMA pulses of various durations, and a hydrous chemical oxide. The lines are guides for the eye.

C contamination) compared to Al_2O_3 films grown on pristine H/Si.

Based on our IR and NRP data, a clear picture of Al_2O_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_2O_3. For long TMA pre-exposures (3600 s), nucleation is therefore enhanced after the very first pulse (Fig. 3), supporting linear Al_2O_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 water precursors. We find that the Hf areal density deposited after 30 HfO_2 ALD cycles on TMA-water pre-exposed H/Si surfaces increases with increasing duration of the TMA pulse [Fig. 2(b)], approaching that on a hydrous chemical oxide. This shows that TMA pre-exposure of H/Si results in a better HfO_2 surface coverage and probably also in a reduced film roughness. The $\sim$35% lower HfO_2 growth rate after a 3600 s TMA pre-exposure compared to that on a hydrous chemical oxide may be due to the presence of some Al oxide sites that are less reactive to $HfCl_4$ than hydroxyl groups. TMA, by contrast, can dissociate on hydroxyl-free oxide sites,[21] which would explain the differences in Al_2O_3 and HfO_2 growth enhancement [compare the growth evolution for 30 cycles of Al_2O_3 in Fig. 3 to that of HfO_2 shown in Fig. 2(b)].

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_2O_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-κ devices.

The infrared work was supported by and performed at Agere Systems. M.M.F. was supported by a fellowship within the Postdoc Program of the German Academic Exchange Service (DAAD). The authors wish to thank J. W. Maes (ASM-B) for providing the HfO_2 samples, E. Garfunkel and K. Raghavachari for stimulating discussions, and S. B. Christman and E. E. Chaban for technical support.

[1] A. W. Ott, J. W. Klaus, J. M. Johnson, and S. M. George, Thin Solid Films **292**, 135 (1997).
[2] G. S. Higashi and C. G. Fleming, Appl. Phys. Lett. **55**, 1963 (1989).
[3] E. P. Gusev, M. Copel, E. Cartier, I. J. R. Baumvol, C. Krug, and M. A. Gribelyuk, Appl. Phys. Lett. **76**, 176 (2000).
[4] D. G. Park, H. J. Cho, K. Y. Lim, C. Lim, I. S. Yeo, J. S. Roh, and J. W. Park, J. Appl. Phys. **89**, 6275 (2001).
[5] H. Bender, T. Conard, H. Nohira, J. Petry, O. Richard, C. Zhao, B. Brijs, W. Besling, C. Detavernier, W. Vandervorst, M. Caymax, S. De Gendt, J. Chen, J. Kluth, W. Tsai, and J. W. Maes, Extended Abstracts of International Workshop on Gate Insulator, IWGI 2001, IEEE Cat. No. 01EX537, p. 86.
[6] V. Cosnier, H. Bender, A. Caymax, J. Chen, T. Conard, H. Nohira, O. Richard, W. Tsai, W. Vandervorst, E. Young, C. Zhao, S. De Gendt, A. Heyns, J. W. H. Maes, M. Tuominen, N. Rochat, M. Olivier, and A. Chabli, Extended Abstracts of International Workshop on Gate Insulator, IWGI 2001, IEEE Cat. No. 01EX537, p. 226.
[7] B. W. Busch, O. Pluchery, Y. J. Chabal, D. A. Muller, R. L. Opila, J. R. Kwo, and E. Garfunkel, MRS Bull. **27**, 206 (2002).
[8] L. G. Gosset, J. F. Damlencourt, O. Renault, D. Rouchon, P. Holliger, A. Ermolieff, I. Trimaille, J. J. Ganem, F. Martin, and M. N. Semeria, J. Non-Cryst. Solids **303**, 17 (2002).
[9] M. L. Green, M.-Y. Ho, B. Busch, G. D. Wilk, T. Sorsch, T. Conard, B. Brijs, W. Vandervorst, P. I. Räisänen, D. Muller, M. Bude, and J. Grazul, J. Appl. Phys. **92**, 7168 (2002).
[10] M. M. Frank, Y. J. Chabal, and G. D. Wilk, Appl. Phys. Lett. **82**, 4758 (2003).
[11] M. M. Frank, Y. J. Chabal, and G. D. Wilk, Mater. Res. Soc. Symp. Proc. **745**, N2.4.1 (2003).
[12] I. J. R. Baumvol, Surf. Sci. Rep. **36**, 1 (1999).
[13] As no suitable plateau was found in the cross-section curve of a nuclear reaction on ^{27}Al, NRP was used instead of nuclear reaction analysis.
[14] Y. J. Chabal, G. S. Higashi, K. Raghavachari, and V. A. Burrows, J. Vac. Sci. Technol. A **7**, 2104 (1989).
[15] T. Hattori, T. Aiba, E. Iijima, Y. Okube, H. Nohira, N. Tate, and M. Katayama, Appl. Surf. Sci. **104/105**, 323 (1996).
[16] Small signals in the C–H stretch region are consistent with instrumental instabilities arising from hydrocarbons in the optical path.
[17] K. T. Queeney, M. K. Weldon, J. P. Chang, Y. J. Chabal, A. B. Gurevich, J. Sapjeta, and R. L. Opila, J. Appl. Phys. **87**, 1322 (2000).
[18] W. Mozgawa, M. Sitarz, and M. Rokita, J. Mol. Struct. **512**, 251 (1999).
[19] F. De Smedt, C. Vinckier, I. Cornelissen, S. De Gendt, and M. Heyns, J. Electrochem. Soc. **147**, 1124 (2000).
[20] W. J. Royea, A. Juang, and N. S. Lewis, Appl. Phys. Lett. **77**, 1988 (2000).
[21] R. L. Puurunen, M. Lindblad, A. Root, and A. O. I. Krause, Phys. Chem. Chem. Phys. **3**, 1093 (2001).

Reuse of AIP Publishing content is subject to the terms at: https://publishing.aip.org/authors/rights-and-permissions. Download to IP: 143.54.44.137 On: Thu, 05 May 2016 14:55:29