Electrochemical and Solid-State Letters, **9** (6) F45-F48 (2006)
1099-0062/2006/9(6)/F45/4/$20.00 © The Electrochemical Society

ALD of Scandium Oxide from Scandium Tris(*N*,*N′*-diisopropylacetamidinate) and Water

Philippe de Rouffignac, Andrew P. Yousef, Kyoung H. Kim, and Roy G. Gordon*,z

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, USA

Sc_2O_3 films were deposited by atomic layer deposition (ALD) from a new precursor scandium tris(*N*,*N′*-diisopropylacetamidinate) and water. The precursor is thermally stable (>350°C), volatile, with good reactivity to HF-last silicon. A growth rate of 0.3 Å/cycle was obtained at 290°C. The films were pure (C,N < 0.5 atom %) and had a refractive index of 1.8. Reactive ion etching tests on ALD scandia showed an etch rate 18 times slower than ALD hafnia. Electrical measurements showed a high permittivity of ~17, and a leakage current density of $<3 \times 10^{-3}$ A/cm^2 for an equivalent oxide thickness of 1.8 nm at 1.0 V.
© 2006 The Electrochemical Society. [DOI: 10.1149/1.2191131] All rights reserved.

Manuscript submitted January 24, 2006; revised manuscript received February 21, 2006. Available electronically April 3, 2006.

High-quality dielectric films are required in order to continue scaling down gate dimensions, capacitor footprints in dynamic random access memory (DRAM), and for optical applications.[1] Scandium oxide has been identified as a candidate material for these applications. Scandium oxide films also have properties that enable their use as damage-resistant antireflection multilayer coatings in high-power UV lasers, etch-stop layers in multilayer dielectric gratings and resist layers in electron beam lithography.[2,3] While etch-stop and resist layers currently use hafnium oxide, reactive ion etching (RIE) on HfO_2/SiO_2 multilayers causes fluorinated hafnium compounds to accumulate on SiO_2 walls, thereby reducing the laser damage threshold. On the contrary, Sc_2O_3/SiO_2 multilayers produce clean etches with no fluorinated Sc accumulation. Furthermore, etch rate selectivities for HfO_2/Sc_2O_3 were reported to be ~10:1, indicating that scandia films are potential candidates for replacing hafnia films in etch-stop and resist applications.[3] Along with these interesting physical characteristics, Sc_2O_3 possesses electrical properties that are compatible with advanced microelectronic devices.

To eliminate the high gate leakage experienced by ultrathin (<1.5 nm) films in metal oxide semiconductor field-effect transistor (MOSFET) devices it is necessary to incorporate higher dielectric constant materials. The current choices for replacing SiO_2 and SiO_xN_y in high performance transistors are HfO_x[4] and HfO_xN_y.[5,6] Though the hafnium based insulators have promising characteristics, HfO_x tends to crystallize at modest processing conditions. Crystallization of the dielectric layer can lead to increased leakage current densities due to impurity segregation to the grain boundaries.[4] Amorphous HfO_xN_y has been successfully deposited by atomic layer deposition (ALD),[7] but its crystallization after annealing has not been studied. One class of dielectrics that has been identified as having a high dielectric constant, high band offsets with respect to silicon, and high crystallization onset temperatures (>900°C) is the group of lanthanide ternary scandates, $Ln_xSc_yO_3$.[8] These compounds have been grown using physical vapor deposition techniques such as pulsed laser deposition (PLD) and molecular beam epitacy (MBE).[7,9]

Developing an ALD process for the scandates is important for conformal coating over structures with high aspect ratios, such as those required aggressive device geometries. Because scandium oxide is an integral component of these films it is necessary to develop a good ALD scandium oxide process that will produce low impurity films using reasonable deposition conditions. Sc_2O_3 has been deposited using chemical vapor deposition (CVD) from a β-diketonate scandium source[10] with relatively high purity and high growth rates above 450°C. ALD has been more of a challenge. ALD scandium oxide was first reported by Putkonen et al. using a β-diketonate scandim precursor.[11] A follow-up article to that work was recently published using cyclopentadientyl and THD based Sc precursors.[12] In the original paper, the films were stoichiometric, crystalline as deposited and had very low impurity content, however no electrical results were reported. In the following paper $YScO_3$ was deposited and the electrical results were promising, though the breakdown field was below 1.5 MV/cm.

The development of ALD processes for the deposition of high-quality scandium-containing films can be addressed primarily through the introduction of new precursors. In this study, a new precursor, scandium tris(*N*,*N′*-diisopropylacetamidinate) or $Sc(amd)_3$, was investigated for use in an ALD process. Because of the inherent thermal stability of the ligand and ligand-metal bonds, as well as the thermodynamic driving force for breaking nitrogen bonds and forming oxygen bonds, the precursor chemistry is favorable to ALD. In this study, the defining characteristics of ALD, such as self-limiting surface reactions, linear growth rate with cycle number, and conformality, are demonstrated.

The synthesis of the pure precursor was done using the protocol outlined by Lim et al.[13] The precursor was made in high yield (>70%), and it showed good thermal stability (no decomposition at 150°C for 2 months, and it was air stable). Residue from thermogravimetric analysis was only 1.2% after a 10°C/min ramp to 450°C, further confirming that $Sc(amd)_3$ has high thermal stability. The precursor starts to sublime at 125°C and 50 mtorr, and was used at 150°C in the bubbler.

All films were deposited on n-type Si(100) pieces. Silicon was treated with UV-ozone and then dipped in HF (10%) to leave a clean, hydrogen terminated surface. The scandia films were deposited in a horizontal gas flow reactor[14] using scandium tris(*N*,*N′*-diisopropylacetamidinate) $Sc(amd)_3$ and water vapor. Hafnium oxide films were grown using tetrakis(diethylamido)-hafnium and water at 220°C. The reactor pressure was set to 250 mTorr by controlling the flow rate of purified N_2 gas. The film thickness and uniformity were measured using a single wavelength (632.4 nm) ellipsometer (Rudolph, AutoEl III), while the film composition was analyzed by Rutherford backscattering spectroscopy (RBS). Post-metallization annealing was done at several temperatures under a forming gas atmosphere. Electrical characterization was performed by measuring the capacitance-voltage (CV) and leakage current density (J) curves of MOS capacitor stacks. The top contact was formed using a shadow mask and sputtered Pt. The equipment and the configuration for the actual measurements were described by Lim et al.[15]

Figure 1a shows the saturation curve as well as the pulse sequence used for films deposited at 290°C. The dose was varied in some cases by increasing the bubbler temperature and in others by increasing the volume of reactant supplied to the deposition chamber. The water dose was saturated at 10 nmol/cm^2 (not shown) and there was no increase in the growth rate up to 210 nmole/cm^2. The slope of the thickness vs cycle curve (Fig. 1b) gives a growth rate per cycle (GPC) of 0.3 Å/cycle and an intercept that passes near the

* Electrochemical Society Active Member.
z E-mail: gordon@chemistry.harvard.edu

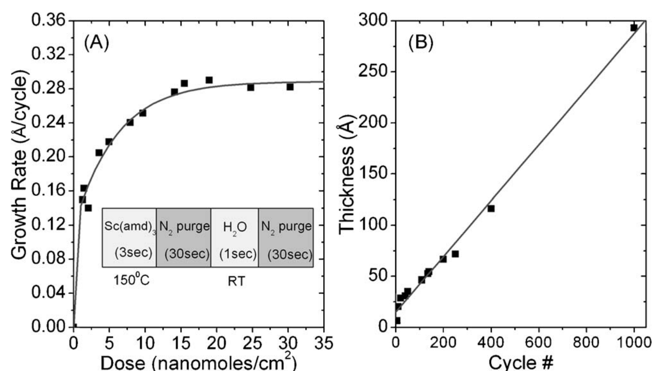

Figure 1. (a) Saturation curve for $Sc(amd)_3$ and ALD pulse sequence used. (b) Thickness as a function of cycle number. Thickness determined by RBS and ellipsometry. Film deposited on HF-last silicon at 290°C.

origin, signifying very little growth inhibition on a hydrogen-terminated surface. Growth on HF-last surfaces is common to this class of precursor,[16] and is a prerequisite for growth of films with little to no interfacial oxide. The growth rate is strongly dependent on temperature (Fig. 2). The graph shows a rapidly increasing growth rate with increasing temperature. This often indicates decomposition of the precursor, but there was no evidence of decomposition up to 350°C according to the following decomposition test. We pulsed $Sc(amd)_3$ without following with a water vapor pulse for 200 cycles and then measured the amount of scandium using RBS. The data show that at the relatively high temperature of 360°C decomposition provides about 3% of the total film thickness. This contrasts with other ALD processes using the amidinate ligands,[13] which usually show significant decomposition above 325°C. The other amidinate precursors also display higher GPCs at low temperatures. Though the scandium atom is smaller than other rare earth metals, it does not fully account for why the growth rate at 290°C is only 0.3 Å/cycle. A major difference when comparing $Sc(amd)_3$ to other rare earth metal amidinates is that the three organic ligands form a more complete shell around the metal center. This may be the root of several properties: the seemingly low volatility, the high thermal stability, and the low reactivity of the precursor.[13] The size and shape of the molecule could allow for better packing in the solid state and an increase in the energy needed to dislodge molecules into the vapor phase. The thermal stability would see an enhancement because a common decomposition pathway is through β-hydride elimination and this is inhibited if the molecule has a more constrained geometry and the ligands are not free to rotate or bend. The solid organic shell would also prevent a facile reaction with the surface because the dative bond between the scandium metal center and the surface would be harder to form.[17] The low reactivity with the surface explains the increase in GPC with temperature seen in Fig. 2. This differs from the traditional definition of ALD which includes a region in the GPC vs temperature curve that is relatively flat. For the GPC to be constant over a range of temperatures the reaction kinetics must be independent of the reaction temperature. However, if the reaction kinetics are temperature dependent and the exposure of the precursor to the surface is constant then the GPC will also be temperature dependent. A review of the literature shows several examples of an ALD process that is kinetically slow and the GPC can be increased by either a several orders of magnitude increase in exposure or an increase in temperature.[18,19]

The stoichiometry was determined to be $Sc_2O_{3.1}$ from RBS of a 40 nm film grown on a carbon substrate after forming gas anneal. The extra oxygen most likely is in the form of trapped hydroxyl groups, and some remain after the 5 min anneal at 425°C. The RBS

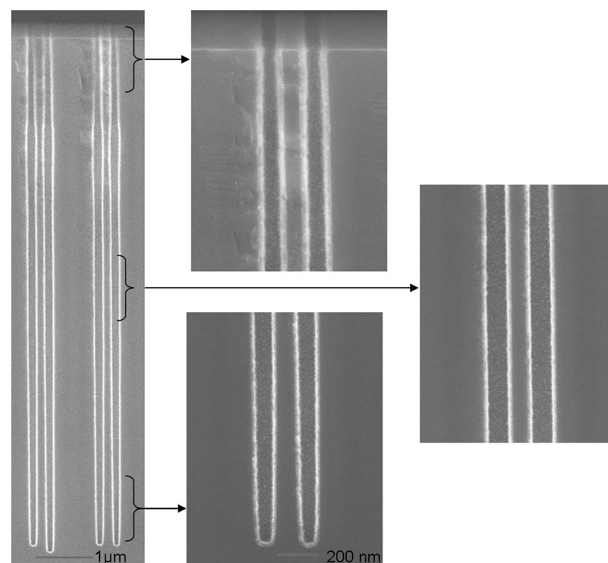

Figure 3. HRSEM of a cross section of a 60:1 aspect ratio via with 30 nm Sc_2O_3 deposited conformally. Via structures courtesy of Infineon Technologies.

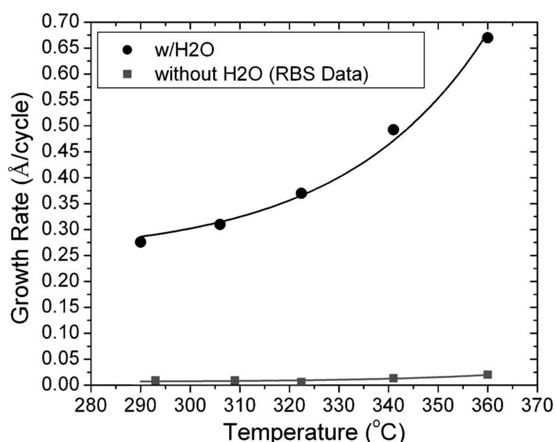

Figure 2. Plot of growth rate dependence on temperature, also shown is the component of growth rate that is due to decomposition. Decomposition data (RBS) was collected using the same cycle times, but no H_2O pulse.

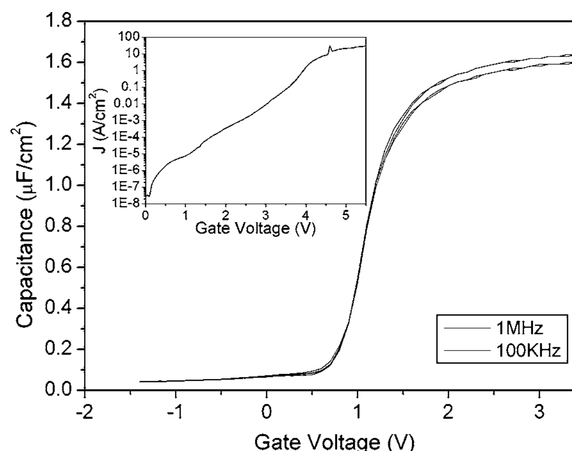

Figure 4. CV curves at 1 MHz and 100 KHz for a 5.5 nm Sc_2O_3 film. MOS capacitors are $(Pt/Sc_2O_3/Si(.01\ \mu\Omega \cdot cm)/Pt)$ with an area of 1.05 $\times 10^{-3}$ cm^2. J vs V_g curve inset, leakage current density less than 0.01 A/cm^2 at 3 V.

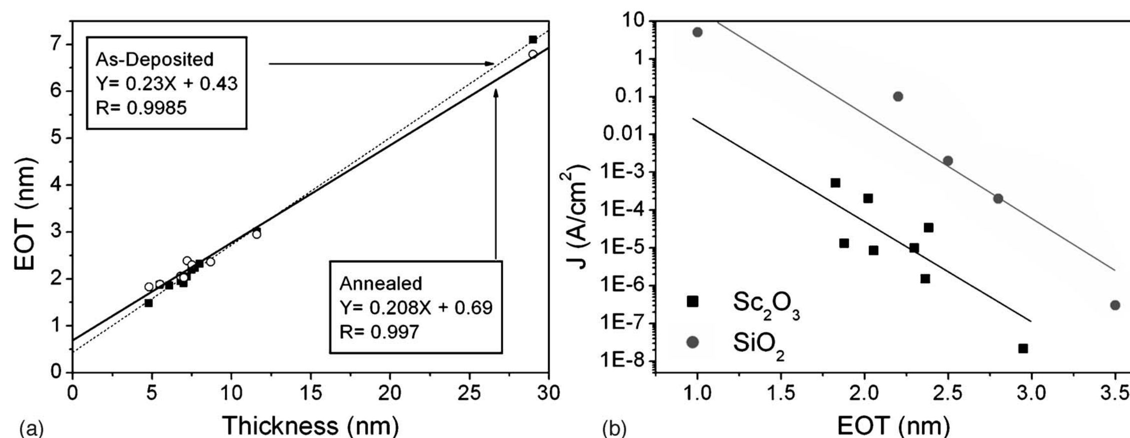

Figure 5. (a) EOT plotted as a function of film thickness. Black squares correspond to as-deposited data and open circles correspond to PMA data. (b) J as a function of EOT for Sc_2O_3 and thermal SiO_2. J for Sc_2O_3 is three orders of magnitude lower for a given EOT than SiO_2.

also showed no carbon shoulder or any detectable nitrogen peaks. This corresponds to less than 1 atom% of carbon or nitrogen in the film. As deposited at 290°C the film is smooth (rms roughness = 2.3 Å) and it shows very small lattice reflections from glancing-angle X-ray diffraction (XRD). After annealing to 450°C and then 1000°C the XRD peaks become more pronounced and the film is fully cubic polycrystalline. The rms roughness also increases to 3.6 Å after the 1000°C anneal. The appearance of crystallinity in the as-grown films is consistent with other vapor deposition methods.[2-4]

A good indicator of whether or not a given ALD process is a true ALD process is the level of conformality that can be achieved.[20] An ALD process that contains a significant decomposition component or CVD component can produce large thickness profiles. Figure 3 shows a high-resolution scanning electron micrograph (HRSEM) image of a cross section of a 60:1 high aspect ratio via with 30 nm of Sc_2O_3 deposited conformally over the feature. The film shows contrasting bands perpendicular to the direction of the film growth. The contrast is caused by the crystallinity of the film. The thickness variation is less then 10% from top to bottom. This marks the first report of a highly conformal Sc_2O_3 thin film grown by any vapor deposition method.

Reactive ion-etching (RIE) tests indicate that ALD scandia has a better etch resistance than ALD hafnia. The RIE condition was as follows: 200 W of microwave power, 50 V of dc bias, 2.0 sccm of O_2, 40.0 sccm of CF_4, and a pressure of 20.0 mTorr. The etch rate was determined by etching for time intervals of 30, 90, 150, 210, 270, and 330 s. The hafnia film etched at a rate of 45 Å/min; while the scandium oxide etched at a rate of 2.5 Å//min, giving an 18:1 etch selectivity of hafnia to scandium oxide.

We examined the electrical properties of thick and ultrathin Sc_2O_3 films grown at 290°C. Figure 4 shows the C-V and J-V curves for a 5.5 nm film after PMA. The C-V curves at 100 kHz and 1 MHz are closely aligned indicating no frequency dispersion, which suggests the film is relatively free of hydroxyl groups.[21] Fitting the C-V curve using the Hauser simulation program[22] showed that the equivalent oxide thickness (EOT) is 1.8 nm and the flat band voltage is +1 V. From the corresponding gate leakage density curve (inset of Fig. 4), the leakage current density is $<3 \times 10^{-3}$ A/cm^2 at (V_g-V_{fb}) of 1 V. This compares favorably to many high-κ materials.[4] The average hard breakdown field of thick films (not shown) was 3.5 MV/cm. Figure 5a is a graph of the film thicknesses and the corresponding EOT values. The slope of the plot was used to extract the bulk dielectric constant. The y-intercept provides an approximate value for the interfacial layer (IL) thickness. The as-deposited film gave a dielectric constant of 16.9 and an IL thickness of 0.4 nm, while the forming gas anneal increased the dielectric constant to 18.7 with a 0.7 nm IL. The higher dielectric constant is most likely due to an increase in crystallinity. Figure 5b provides a comparison of this material to thermal SiO_2 as a gate dielectric. By extrapolating the curve to low EOT values it would seem that this material can be scaled down to <1 nm EOT and J would remain below 0.1 A/cm^2. However, films with a physical thickness of 4.0 nm or less have rapidly decreasing dielectric constants after PMA suggesting significant IL re-growth. The grain boundaries of the film may facilitate oxygen transport to the silicon/Sc_2O_3 interface, and at high temperatures a SiO_2 layer can be easily formed.[23]

Conclusions

In summary, ALD of Sc_2O_3 films using a novel scandium precursor scandium tris(*N*,*N*′-diisopropylacetamidinate) and H_2O has been successfully demonstrated through saturation curves and high conformality. The films showed some crystallinity at all growth temperatures and an increase in both crystallinity and roughness after high-temperature anneal. The saturated growth rate was low at 290°C (0.3 Å/cycle) but was higher for higher deposition temperatures. The high purity of the thin films was examined by RBS and was further confirmed using impurity sensitive electrical measurements. Leakage current densities of $<3 \times 10^{-3}$ A/cm^2 at 1 V gate voltage bias for films with EOT's as low as 1.8 nm were demonstrated. This work presents a feasible approach to the use of this material as a component of ternary oxides and as a protective coating.

Harvard University assisted in meeting the publication costs of this article.

References

1. H. Geng, *Semiconductor Manufacturing Handbook*, McGraw-Hill, New York (2005).
2. Z. Xu, A. Daga, and H. Chen, *Appl. Phys. Lett.*, **79**, 3782 (2001).
3. J. A. Britten, H. T. Nguyen, S. F. Falabella, B. W. Shore, M. D. Perry, and D. H. Raguin, *J. Vac. Sci. Technol. A*, **14**, 2973 (1996).
4. G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.*, **89**, 5243 (2001).
5. C. S. Kang, H. J. Cho, K. Onishi, R. Nieh, R. Choi, S. Gopalan, S. Krishnan, J. H. Han, and J. C. Lee, *Appl. Phys. Lett.*, **81**, 2593 (2002).
6. C. L. Cheng, K. S. Chang-Liao, C. H. Huang, and T. K. Wang, *Appl. Phys. Lett.*, **85**, 4723 (2004).
7. J. S. Becker, E. Kim, and R. G. Gordon, *Chem. Mater.*, **16**, 3497 (2004).
8. C. Zhao, T. Witters, B. Brijs, H. Bender, O. Richard, M. Caymax, T. Heeg, J. Schubert, V. V. Afanas'ev, and A. Stesmans, *Appl. Phys. Lett.*, **86**, 132903 (2005).
9. J. Schubert, T. Heeg, O. Trithaveesak, G. Herber, L. Edge, Y. Jia, and D. G. Schlom, Paper presented at the MRS Spring Meeting, San Francisco, CA, April 2004.
10. K. A. Fleeting, H. O. Davies, A. C. Jones, P. O'Brien, T. J. Leedham, M. J. Crosbie, P. J. Wright, and D. J. Williams, *Chem. Vap. Deposition*, **5**, 261 (1999).
11. M. Putkonen, M. Nieminen, J. Niinisto, L. Niinisto, and T. Sajavaara, *Chem. Mater.*, **13**, 4701 (2001).
12. P. Myllymäki, M. Nieminen, J. Niinistö, M. Putkonen, K. Kukli, and L. Niinistö, *J. Mater. Chem.*, **16**, 573 (2006).

13. B. S. Lim, A. Rahtu, J. S. Park, and R. G. Gordon, *Inorg. Chem.*, **42**, 7951 (2003).
14. D. Hausmann, P. de Rouffignac, A. Smith, R. Gordon, and D. Monsma, *Thin Solid Films*, **443**, 1 (2003).
15. B. S. Lim, A. Rahtu, P. de Rouffignac, and R. G. Gordon, *Appl. Phys. Lett.*, **84**, 3957 (2004).
16. C. Musgrave and R. G. Gordon, *Future Fab Int.*, 18, 126 (2005).
17. C. Mui and C. B. Musgrave, *J. Phys. Chem. B*, **108**, 15150 (2004).
18. M. M. Frank, Y. J. Chabal, M. L. Green, A. Delabie, B. Brijs, G. D. Wilk, M. Y. Ho, E. B. O. da Rosa, I. J. R. Baumvol, and F. C. Stedile, *Appl. Phys. Lett.*, **83**, 740 (2003).
19. J. Päiväsaari, C. L. Dezelah, D. Back, H. M. El-Kaderi, M. J. Heeg, M. Putkonen, L. Niinistö, and C. H. Winter, *J. Mater. Chem.*, **15**, 4224 (2005).
20. D. M. Hausmann and R. G. Gordon, *J. Cryst. Growth*, **249**, 251 (2003).
21. Z. Wang, V. Kugler, U. Helmersson, E. K. Evangelou, N. Konofaos, S. Nakao, and P. Jin, *Philos. Mag. B*, **82**, 891 (2002).
22. J. R. Hauser and K. Ahmed, in *Characterization and Metrology for ULSI Technology*, D. Seiler, Editor, p. 235, AIP, Woodbury, NY (1998).
23. W. Tsai, R. J. Carter, H. Nohira, M. Caymax, T. Conard, V. Cosnier, S. DeGendt, M. Heyns, J. Petry, O. Richard, W. Vandervorst, E. Young, C. Zhao, J. Maes, M. Tuominen, W. H. Schulte, E. Garfunkel, and T. Gustafsson, *Microelectron. Eng.*, **65**, 259 (2003).