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Evidence of aluminum silicate formation during chemical vapor deposition of amorphous Al_2O_3 thin films on Si(100)

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Using narrow nuclear reaction resonance profiling, aluminum profiles are obtained in ~ 3.5 nm Al_2O_3 films deposited by low temperature ($< 400^\circ\text{C}$) chemical vapor deposition on Si(100). Narrow nuclear resonance and Auger depth profiles show similar Al profiles for thicker (~ 18 nm) films. The Al profile obtained on the thin film is consistent with a thin aluminum silicate layer, consisting of Al–O–Si bond units, between the silicon and Al_2O_3 layer. Transmission electron microscopy shows evidence for a two-layer structure in Si/ Al_2O_3 /Al stacks, and x-ray photoelectron spectroscopy shows a peak in the Si $2p$ region near 102 eV, consistent with Al–O–Si units. The silicate layer is speculated to result from reactions between silicon and hydroxyl groups formed on the surface during oxidation of the adsorbed precursor. © 1999 American Institute of Physics.

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The Semiconductor Industry Association road map indicates that a sub-1-nm oxide will be required for complementary metal–oxide–semiconductor (CMOS) devices with 50 nm gate widths. However, significant leakage and reliability issues occur with thermal SiO_2 at this thickness, and new high dielectric constant (high- k) materials are being explored. An important factor for any new high- k dielectric is its stability in contact with silicon. Annealing of tantalum oxide thin films¹ on silicon, for example, results in an interfacial SiO_2 layer due to reduction of the Ta_2O_5 .^{2,3} An interface layer between the high- k and the silicon can be included to minimize oxidation, but this contributes additional undesired capacitance in the gate stack. Gibbs free energy and ternary phase diagrams can predict oxide compositions that are stable in contact with silicon at elevated temperatures. For example, BeO, MgO, and ZrO_2 , are predicted to be stable with silicon at 700°C , consistent with experiments.^{4,5}

Al_2O_3 is an attractive dielectric because it has a large (9 eV) band gap and large band offsets with silicon, and it is a good barrier to ionic transport. Crystalline Si can be formed on Al_2O_3 without significant reaction between the Si and Al_2O_3 ,⁶ and epitaxial Al_2O_3 films have been deposited on silicon by chemical vapor deposition (CVD)⁷ and molecular-beam epitaxy (MBE).⁸ A low temperature route to stable high- k /Si interfaces is desired for CMOS devices, but transmission electron microscopy (TEM) analysis of low temperature amorphous Al_2O_3 on Si typically shows a relatively

thick intermediate layer.⁹ The composition of this layer has not previously been determined. Based on available free energy data for aluminum silicates, including mullite, kyanite, sillimanite, and andalousite,¹⁰ the Al_2O_3 /Si interface is expected to be stable to silicate formation. However, kinetics of deposition and interface formation reactions must be considered and analyzed, especially in low temperature processes, to understand interface reactions and achieve optimum material structure.

Advances in ultrathin high- k /Si interfaces require improved techniques to better understand Si/oxide interface reactions. Depth profiling techniques such as secondary ion mass spectroscopy (SIMS) and sputtered Auger depth profiling give spatial resolution of 5–10 nm, which is not sufficient for ultrathin dielectrics. Ion scattering techniques such as Rutherford backscattering spectroscopy and medium energy ion scattering cannot easily distinguish between Al and Si because of their similar atomic mass. This letter reports the use of a narrow nuclear reaction resonance profiling (NRP) technique to attain subnanometer Al concentration depth profiles in thin Al_2O_3 films deposited on silicon.

Thin Al_2O_3 films were grown by low pressure CVD using triethylaluminum tri-sec-butoxide (TEDA-TSB) as the Al source.¹¹ The metal organic was introduced in the reactor by flowing 30 standard cubic centimeters per minute (sccm) of Ar carrier gas through a bubbler heated to 150°C . The reactor pressure was maintained at 0.5 Torr, while 100 sccm O_2 was used as the oxidizing species. The substrates were $1\text{--}2 \Omega\text{ cm } n\text{-type Si}(100)$, cleaned with a J. T. Baker clean

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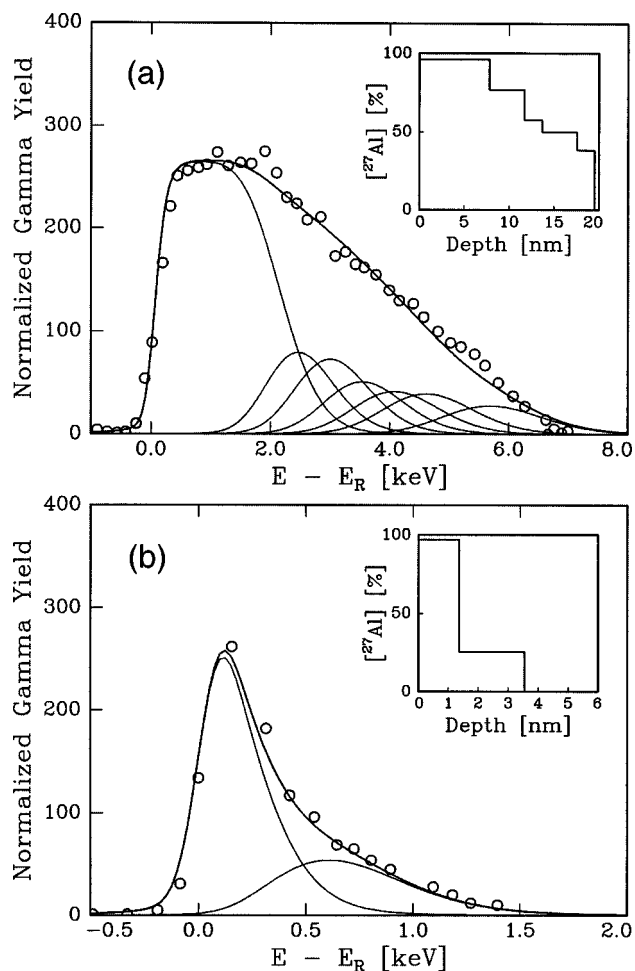


FIG. 1. (a) Narrow resonance nuclear reaction profile (NRP) of 18 nm Al_2O_3 on Si. Model of results (shown in inset) show two layers with the first layer having an Al concentration corresponding to Al_2O_3 . (b) NRP data for a thin 3.5 nm Al_2O_3 film.

solution and dipped in 10:1 buffered HF solution to remove the native oxide prior to deposition. The substrate temperature was 400 °C, which resulted in a growth rate of approximately 1 nm/min. The depth distribution of ^{27}Al concentration was obtained using the narrow and isolated resonance in the cross sections of the nuclear reaction $^{27}\text{Al}(p, \gamma)^{28}\text{Si}$ at 405 keV.¹² The measured excitation curves (i.e., γ ray yields versus incident proton energy) around the resonance energy (E_R) can be converted into concentration versus depth using the SPACES program,¹³ assuming a density of 3.8 g/cm³ for the stoichiometric Al_2O_3 film. The width of the nuclear reaction resonance at 405 keV was determined here as being smaller than 40 eV, by measuring the excitation curves for thin and thick aluminum films. For the ^{27}Al profiling in aluminum oxide thin film on Si, a tilted sample geometry ($\Psi = 55^\circ - 65^\circ$) was used to increase the depth resolution. Owing to the combination of an extremely narrow nuclear reaction resonance ($\Gamma \cong 40$ eV), a proton-beam energy stability of 80 eV at 405 keV, and an apparent thickness magnification due to tilting by a factor of 1.7–2.4, a maximum depth resolution of about 0.5 nm near the film surface was obtained.¹⁴

Figure 1(a) shows the excitation curve of the $^{27}\text{Al}(p, \gamma)^{28}\text{Si}$ nuclear reaction around the resonance at 405 keV for a thick (18 nm) Al_2O_3 film on Si(100). The inset

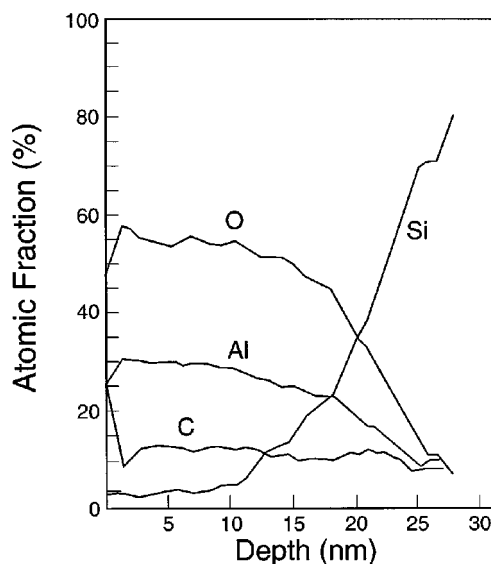


FIG. 2. Auger depth profile of a $\text{AlO}/\text{AlSi}_x\text{O}_y$ film showing the appearance of Si at approximately 100 Å.

shows the corresponding aluminum concentration profile with respect to stoichiometric Al_2O_3 , determined by SPACES simulation. A decreasing Al concentration toward the oxide/Si interface is observed, with an average Al concentration less than 50% of the first layer. Figure 1(b) shows the sensitivity and depth resolution of the nuclear resonance technique for a thin (~ 3.5 nm) Al_2O_3 film on silicon. The fit to the gamma yield indicates a two-layer Al profile. Figure 2 is a sputtered Auger depth profile of the same sample shown in Fig. 1(a), showing results similar to the NRP data. Figure 3 is a TEM image of the same film, demonstrating contrast between bulk and interface layers. Interface roughness suggests a reaction has occurred at the silicon surface. TEM data of the thin film (not shown) are consistent with the NRP results, indicating a total film thickness of 3.5 nm, made up of two sublayers of approximately equal thickness.

The near-surface region (6–10 nm) of the thick film was characterized using x-ray photoelectron spectroscopy (XPS), resulting in an O/Al atomic ratio of 1.64. For the thin film, the position and shape of the Si $2p$ peaks shown in Fig. 4 are used to probe the composition and structure the Si/ Al_2O_3 interface. The peak near 99 and the shoulder near 103.5 eV are assigned to Si^0 substrate and Si–O bonding in the film,



FIG. 3. TEM image Al_2O_3 deposited on silicon at ~ 400 °C in the as-deposited state. The total film thickness is approximately 18 nm. Two distinct layers are observed with approximately equal thickness.

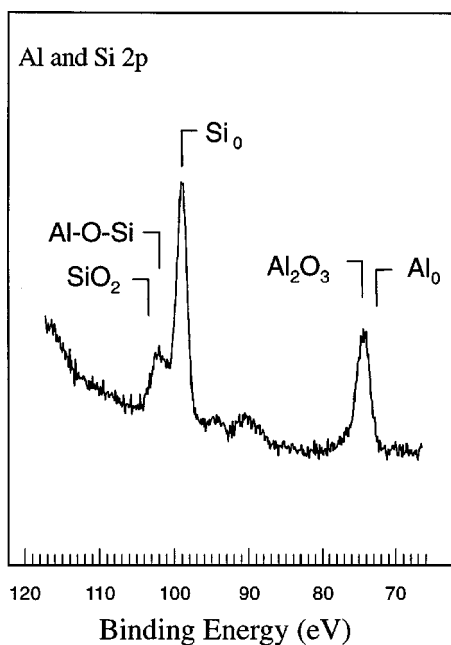


FIG. 4. XPS spectrum of Al and Si region of a 3.5 nm aluminum oxide film deposited on silicon, showing evidence for Al–O–Si silicate bonding.

respectively. The peak near 102 eV is assigned to Al–O–Si bonds, confirming that the thin intermediate layer consists of Al–O–Si (silicate) bonding units. The position of the Al 2p peak at 74.7 eV indicates that the Al present in the near-surface region is bound as Al₂O₃. No signal from Al metal is observed. The XPS survey spectrum shows the presence of approximately 20 at. % carbon. While some carbon is likely residual from the metalorganic deposition process, carbon contamination is also expected from the in-air sample transfer to the analysis chamber. This is consistent with the Auger data in Fig. 2, where carbon contamination is primarily on the surface. Silicates of Hf and Zr have been shown to have lower dielectric constants than their corresponding Si free oxides,^{15,16} and electrical analysis of our layers shows similar results for aluminum silicate.

We can speculate on the mechanism for the thin silicate layer formation in the low temperature CVD process. XPS and NRP show excess oxygen in the oxide layer, and infrared indicates OH density is near the detection limit (<0.5 at. %). When as-deposited films are annealed, XPS shows an increase in the silicate peak at 102 eV, indicating some post-deposition silicate formation. However, substantial silicate formation also occurs during deposition. Excess oxygen available during deposition will tend to oxidize silicon, but the layer is thicker than expected from silicon oxidation ki-

netics (and from oxidation experiments) at this temperature, suggesting an additional kinetic pathway for oxidation is present during the deposition. Moreover, when the Al₂O₃ deposition is performed on silicon pre-coated with silicon nitride, no silicate interface layer is observed. The metal-organic precursor, physisorbed or dissociated chemisorbed on silicon, may present a low temperature kinetic route to oxidation that is not available with only O₂, possibly involving OH formed on the surface during precursor oxidation. Such pathways will be suppressed at higher temperature or low H conditions, consistent with the sharp interface observed using high temperature CVD and MBE. Kinetic processes for interface layer formation are also likely important during low temperature metalorganic deposition of other material heterostructures. For example, TiO₂ deposition on silicon using H-free precursors at 280 °C shows formation of an interface layer¹⁷ (presumed to be SiO₂) suggesting that hydrogen elimination is not necessarily sufficient to limit low temperature silicon oxidation.

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