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Atomic Layer Deposition of Lanthanum Oxide Films for High-κ Gate Dielectrics

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Lanthanum-containing oxide films are emerging candidates for gate-oxide films, due to expected high dielectric constants as well as promising crystal and electronic band structure. We have used tris(bistrimethylsilylamido)-lanthanum $La[N(SiMe_3)_2]_3$ to achieve atomic layer deposition of La_2O_3 on a (100) Si wafer. Crystalline and electrical properties of the resulting films have been characterized. Dielectric constant values in the range of 20-23, and a dielectric breakdown field of about 4.2 MV/cm were observed. The electrical properties of our structures remain consistent even after prolonged ambient exposure.
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To meet the requirements of Moore's Law of increasing density of functions on semiconductor chips, extrapolation of transistor dimensions is now severely limited by the excessive tunneling currents of gate oxides of thickness 10 Å and below. The generally accepted solution is to substitute higher-dielectric constant (κ) films for the currently used SiO_2. Initial attempts using Ta_2O_5 and $(Ba,Sr)TiO_3$ (BST) were unsuccessful due to silicide formation. Thermodynamic calculations provided a ready explanation for this observation,[1] shifting attention toward zirconium and hafnium oxides. However, zirconium oxides have been found to be vulnerable to interdiffusion between the gate oxide and the silicon substrate, decreasing carrier mobility.[2] Current attention is focused on hafnium oxides and silicates, but recent indications are that hafnium may again diffuse into the silicon substrate.[3]

Several lanthanum compounds are expected to be stable on the silicon substrate. The dielectric polarizability[4] of La^{3+} is almost twice that of Hf^{4+}, so lanthanum can generally be expected to yield films of relatively high κ. In particular, $LaAlO_3$ films[5] are promising, exhibiting κ of ~24,[6] a small lattice mismatch with Si,[7] and predicted band offsets of 2.1 and 1.9 eV, respectively with the conduction and valence bands of silicon.[8] La_2O_3 itself (κ of the polycrystalline material measured at 21[9]) is not overly interesting as a gate oxide dielectric, partly because, like all binary oxides, it is relatively difficult to form amorphous films which are expected to be required to minimize oxygen diffusion through the gate dielectric. An even more serious objection to La_2O_3 is its reported reactivity with ambient CO_2 and H_2O.[10,11] Surprisingly, we have found that our atomic layer deposition (ALD) derived films appear quite resistant to air exposure. We have studied deposition of La_2O_3 primarily as a first step in the development of other La-containing films having potential as future high-κ dielectrics.

ALD is an attractive deposition technique for this application because it enables precise control of the dielectric composition, including the formation of nanolaminates which may prove useful as a means of minimizing diffusion from the gate stack to the substrate. ALD of La_2O_3 has been reported by Niemenem *et al.*[12] using the β-diketonate precursor $La(thd)_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) and ozone. However, the resulting films had a high carbon-content at low deposition temperatures, probably resulting from inefficient ligand cracking of the volatile metal organic. Therefore, we have investigated the ALD of La_2O_3 using the La precursor, $La[N(SiMe_3)_2]_3$. This reaction was briefly mentioned in a previous report by Gordon *et al.*[13] The labile lanthanide nitrogen bonds are expected to react more completely in the ALD process than oxygen bonds. This precursor has been used by others for the formation of La-silicate (La Si_xO_y) films by MOCVD,[14] in the absence of a separate silicate source. While it may appear attractive to prepare a complex film using a single source, we are of the opinion that it is preferable to control the delivery of each film component individually.

In this paper, we describe the deposition of La_2O_3 by ALD, briefly summarize the characterization of these films, and report their electrical characteristics. Our precursor, $La[N(SiMe_3)_2]_3$, was synthesized using a novel route which eliminates halide contamination. The precursor synthesis and characterization will be described elsewhere.

Experimental

La_2O_3 films were deposited using the self-limiting growth process of ALD. In this process one reactant is injected into the growth area, and after surface reaction, excess species and by-products are purged with an inert gas. As a result, films are grown by sequential surface half-reactions. Ideally, this method enables precise control of film composition and thickness since the growth proceeds one monolayer at a time on an atomic scale.

The substrates for this investigation consisted of standard p-type silicon wafers cleaved into 5 × 5 cm squares. These substrates were dipped into 10% HF before they were loaded into the ALD reactor. The metal oxide precursors were $La[N(SiMe_3)_2]_3$ and water vapor, which served as the oxygen source. A typical ALD sequence proceeded by repeating a growth cycle several times, once the process parameters such as source and growth temperatures and pulse widths were optimized. One deposition cycle consisted of 0.8 s pulse of $La[N(SiMe_3)_2]_3$, followed by 1 s N_2 purge pulse (to remove excess precursor molecules and by-products), then a 0.8 s water pulse, and finally another 1 s N_2 purge pulse. Nitrogen (300 sccm) also served as the carrier gas for the $La[N(SiMe_3)_2]_3$. Growth temperature was 250°C, chamber pressure<100 mTorr, and the La source crucible was at 110°C. Under these conditions, the growth rate was 0.43 nm/cycle. Following deposition, thicknesses and refractive indices of the films were measured with a spectroscopic ellipsometer (SOPRA, Bois-Colombes, France). For electrical characterization, platinum dots were sputtered on these films to define metal oxide semiconductor (MOS) capacitor structures. Capacitance was measured (at 1 MHz) with an HP4275 LCR meter and the current-voltage (I-V) leakage characteristics of the films were analyzed using HP4145B parameter analyzer. Whenever stated, the post-deposition annealed samples were treated to 400°C for 60 s in forming gas.

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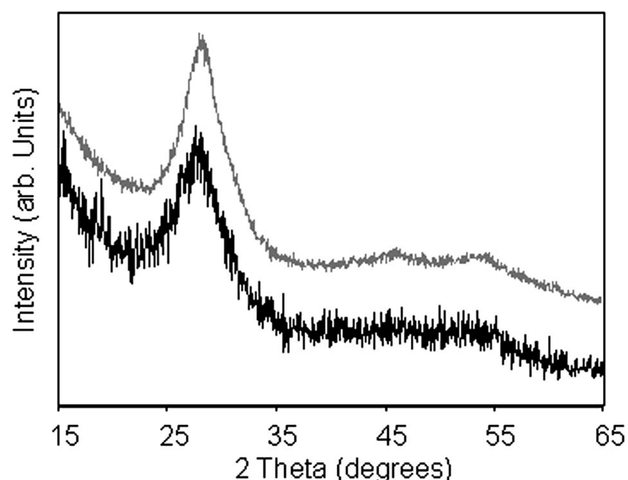

Figure 1. XRD spectra of as-deposited and annealed La_2O_3 film. Traces are shown displaced for clarity. The smoother trace corresponds to the annealed film.

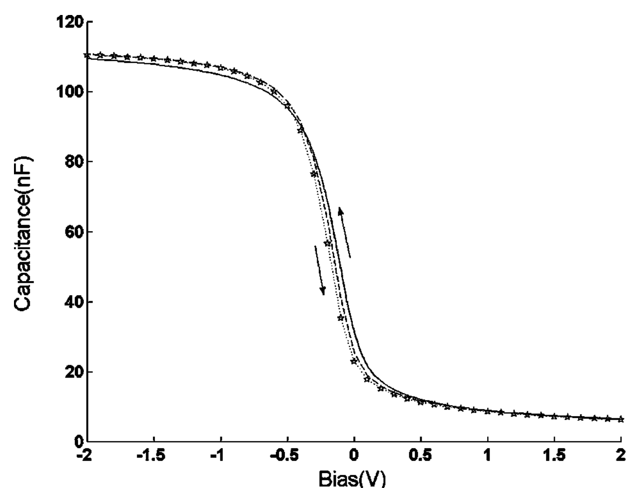

Figure 3. C-V profile of a lanthanum oxide capacitor showing hysterisis (dotted lines) measured 16 months ago. The solid line shows the C-V response obtained recently.

Results and Discussion

The film thickness was determined using the spectroscopic ellipsometer (SE). The SE modeling indicated the refractive index of the as deposited films to be 1.836, with an extinction coefficient value of 0 at 632.8 nm. The fact that modeling fit well with the extinction coefficient value of 0 indicated transparent films. Post-deposition anneal increased the refractive index to 1.97. Energy-dispersive X-ray analysis confirmed that the film composition was approximately La_2O_3. Si contamination could not be quantified due to the background Si signal from the underlying film. C contamination was about 1%.

The morphology of the deposited films was determined using X-ray diffraction (XRD). Pre-and post-annealed XRD spectra of a 93 nm thick La_2O_3 film are shown in Fig. 1. The spectra appear almost amorphous, with a weak (222) cubic reflection. Note that the anneal does not change the phase of the film. The surface roughness was evaluated using X-ray reflectivity (XRR) as shown in Fig. 2. For this annealed sample, XRR analysis was used to extract a film thickness of 89.0 $\pm$ 0.5 nm, 0.59 nm surface roughness, and 0.55 nm roughness at the Si/La_2O_3 interface.

Electrical characterization included evaluation of the capacitive and breakdown properties of the oxide films. The C-V profile of an annealed 130 nm thick film is shown as dotted lines in Fig. 3. The hysteresis offset is about 30 mV, on the order of kT (where k is the Boltzmann constant and T the absolute temperature) suggesting very little charge trapping and de-trapping in the dielectric. From the accumulation region of this plot, a relative dielectric constant κ of 21 was calculated. The variation of κ over various samples ranged from 20 to 23. From our previous work on ALD of other high-κ thin films grown using water as the oxidizing agent, we have observed formation of a thin SiO_2 film at the film/Si substrate interface.[15] It is most likely that the presence of such an interfacial layer limits the overall dielectric constant of the stack.

Flat-band voltage shift gives an indication of the trapped charge in the dielectric. A flat-band voltage of -0.27 V was determined from Fig. 3. This value is for a $Pt/La_2O_3/Si$ stack. Considering the work functions of Pt and p-type Si, this indicates a negative ionic charge in the dielectric. At this time we do not know the source of the negative charge. However, positive trapped charge has been reported in lanthana films deposited by other means which has been attributed to oxygen vacancies or presence of $(OH)^-$ ions at O^{2-} sites.[16,17] The leakage current in a 15 nm thick La_2O_3 film is shown in the I-V curve is presented in Fig. 4. The leakage current starts with a soft breakdown at about -4 V, followed by a hard dielectric breakdown at a field of 4.2 MV/cm.

The ambient instability of La_2O_3 films was mentioned above.[10,11] It has been reported that these films degrade when exposed to

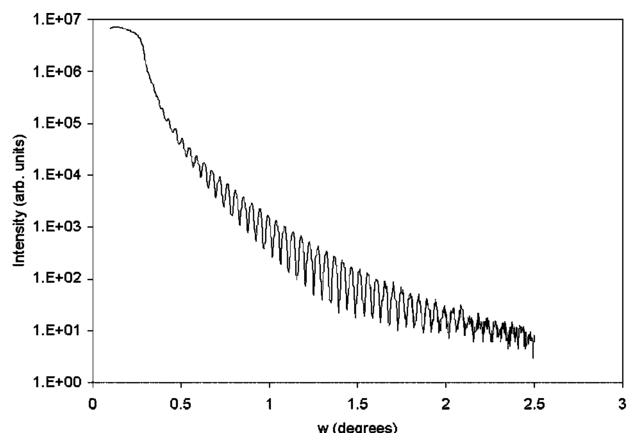

Figure 2. XRR spectrum of a lanthanum oxide film.

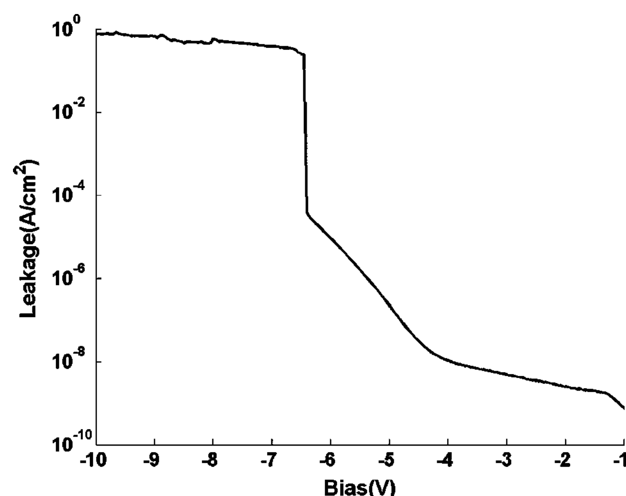

Figure 4. I-V plot showing the leakage current and hard breakdown.

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air by reacting with moisture and/or CO_2. While we have not looked carefully for ambient effects on the atomic structure of our films, the electrical properties of our capacitors remain constant after air exposure. The C-V curve shown in Fig. 3 with the dotted line was measured 16 months before the solid line. The two data sets were collected for different devices on the same substrate. This sample was stored in a nitrogen box that was opened frequently, exposing it to air. As can be seen, there is no significant difference in the C-V profile, implying very little change in the electrical properties of the material. A comparison of Auger analysis of a sample deposited 16 months ago and another produced recently showed little difference. The stability of freshly deposited films was further tested as follows. C-V profiles of MOS capacitors were first measured and then these devices were left in the probe station, exposed to ambient for a week. The C-V curves were again examined and compared to the earlier results. No significant difference in the two sets of data was found. The previously reported instability was for uncapped films, while our capacitors include a polycrystalline platinum electrode deposited prior to electrical characterization. The electrode may provide protection from ambient species, and the deposition chemistry may also contribute to the robustness of the film.

In summary, atomic layer deposition of La_2O_3 has been demonstrated using $La[N(SiMe_3)_2]_3$ as a La precursor. Electrical characterization of the films deposited on Si shown κ values in the range of 20-23, and a dielectric breakdown field of about 4.2 MV/cm. The electrical properties of capacitors formed with these films show no apparent change even after prolonged ambient exposure.

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