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Atomic Layer Deposition of Lanthanum-Based Ternary Oxides

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ternary rare earth oxide

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Abstract

Lanthanum-based ternary oxide La2M2−O3 (M = Sc, Lu, or Y) films were deposited on HF-last Si substrates by atomic layer deposition. Both LaScO3 and LaLuO3 films are amorphous while the as-deposited La2Y2−O3 films form a polycrystalline layer/ amorphous layer structure on Si. Transmission electron microscopy and electrical analysis show the absence of interfacial layers. The dielectric constants for LaScO3, LaLuO3, and La2Y2−O3 films are ~23, 28 ± 1, and 17 ± 1.3, respectively, with leakage current density up to 6 orders of magnitude lower than that of thermal SiO2 with the same effective oxide thickness. Conformal coating thickness is demonstrated on holes with aspect ratio ~80:1.


Hafnium oxide has been widely studied as an alternative gate dielectric to replace silicon dioxide for metal-oxide-semiconductor field-effect transistors (MOSFETs) and dynamic random access memories. In 2007, Intel Corporation announced its accomplishment of integrating HfO2 into MOSFETs with the physical gate length of 22 nm. In 2007, Metal-oxide-semiconductor (MOS) capacitors were made to measure the electrical properties. Tungsten nitride (WN) was deposited in the same ALD reactor as a top metal electrode. Platinum dots were finally deposited by evaporation and liftoff and used as hard masks during the removal of exposed WN by reactive ion etching (CF4 + Ar).

Results and Discussion

Figure 1a shows a sharp interface between amorphous LaScO3 and crystalline Si in a stack of WN/LaScO3/Si. Similar results were found for LaLuO3 and La2Y2−O3 films [Cross-sectional transmission electron microscope (XTEM) images not shown]. The step coverage is close to 100% in holes with an aspect ratio of ~80:1. Figure 2a shows that a 12 nm LaLuO3 film has a uniform thickness from the top to the bottom of the hole. Despite the fact that the as-deposited binary oxides (M2O3) are polycrystalline body-centered-cubic phases determined by electron diffraction, both LaScO3 and LaLuO3 films are amorphous and homogeneous. In contrast, as-deposited La2Y2−O3 films show a polycrystalline layer over an amorphous layer on Si by XTEM. The lattice incompatibility between these oxides and Si increases the activation energy barrier for nucleating crystalline phases adjacent to Si, resulting in an amorphous lower layer of La2Y2−O3. After the growth of a thin amorphous layer (3–7 nm), the mismatch is relaxed so that a polycrystalline layer of La2Y2−O3 can grow on the top.

MOS capacitors were made to measure the electrical properties. Figure 3a shows the high-frequency (1 MHz) capacitance-voltage (C–V) curves of LaLuO3, LaScO3, and La2Y2−O3 films with no

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noticeable stretching or shoulders. The small hysteresis (0–10 mV) indicates very few bulk traps in the films. The 10 and 100 kHz $C-V$ curves not shown are closely aligned to 1 MHz ones with frequency dispersion less than 2–3% of the accumulation capacitance. Small shoulders appear in the weak inversion region of $C-V$ curves measured at 10 and 100 kHz, which indicate the existence of some slowly responding interface states. The EOT was obtained by fitting the $C-V$ data to ideal simulation curves using the Metal-Insulation-Semiconductor CV Fitting (MISFIT) program with charge quantization effect. By linearly fitting the EOT vs physical thickness plot shown in Fig. 3b, the dielectric constants, extracted from the slopes, are 28 for LaLuO$_3$ and 17 for La$_{1.23}$Y$_{0.77}$O$_3$ films, respectively. The nearly zero intercept for LaLuO$_3$ films indicate the absence of any interfacial layer, consistent with the sharp interfaces observed by high-resolution XTEM. The dielectric constant for LaScO$_3$ is 23, which is estimated by $\kappa = \frac{3.9}{\text{physical EOT}}$. Both LaScO$_3$ and LaLuO$_3$ films have higher dielectric constants than those of their binary oxide components, i.e., La$_2$O$_3$ ($\kappa \sim 19$), Lu$_2$O$_3$ (16), and Sc$_2$O$_3$ (17). These results imply that the amorphous ternary oxides form new microscopic structures, rather than simple mixtures of the two binary oxides. In view of the continuous random network theory, it is possible that locally –O–La–O– (La$^{3+}$ radius 103 pm) develops frames of polyhedrons with the smaller ions (Sc$^{3+}$ radius 75 pm or Lu$^{3+}$ 86 pm) caged inside. The Sc–O or Lu–O bonds are softened due to their smaller metal ion sizes, and the polarizability is therefore enhanced by the bond softening.

Figure 1. (Color online) (a) The thickness vs ALD cycle plot. The thickness was measured by both X-ray reflectivity (XRR) and variable angle scanning ellipsometer (VASE). (b) The XPS spectrum for LaLuO$_3$.

Figure 2. (a) XTEM image of a WN/LaScO$_3$ stack on Si substrate. The white line along the interface is caused by transmission electron microscope aberration. It consists of discrete spots, which are an extension of the Si lattice. (b) A 12 nm LaLuO$_3$ film deposited in holes with aspect ratio ~80:1. The hole has an elliptical cross section with semi-long axes 75 nm and semi-short axes 35 nm. Its depth is 7.2 $\mu$m. On the right-hand side are three higher magnification images for comparing the film thickness in the top, middle, and bottom parts of the trench.

Figure 3. (Color online) (a) $C-V$ curves measured at 1 MHz. The lines are simulated curves with MISFIT by assuming no interface traps. (b) The EOT plots as a function of the physical thickness.
LaScO₃ and LaLuO₃ films and 2–4 orders of magnitude lower for La₁.2₃Y₀.7₇O₃ films. All ternary oxide films have the same leakage temperature to 200°C. The Poole–Frenkel plots films.12

Figure 4. (Color online) (a) Leakage current density at \(|V_g - V_{FB}| = 1\) V and (b) Poole–Frenkel plot of the leakage current density of a LaScO₃ film (EOT = 0.9 nm) at various temperatures.

...ening, which can be more than enough to make up for an adverse effect caused by the relatively larger molar volume in the amorphous films.12

Figure 4a shows the leakage current density scaling of our ALD films compared to that of thermal SiO₂ films with the same EOT. The current density at 1 V gate bias \(|V_g - V_{FB}| = 1\) V is up to 6 orders of magnitude lower than that of thermal SiO₂ for both LaScO₃ and LaLuO₃ films and 2–4 orders of magnitude lower for La₁.2₃Y₀.7₇O₃ films. All ternary oxide films have the same leakage current-voltage (J-V) behaviors. Figure 4b shows the J-V curves of a LaScO₃ film with 0.9 nm EOT at temperatures from room temperature to 200°C. The Poole–Frenkel plots (Fig. 3b) of this J-V measurement show linear behaviors in the range of 0.3–1.5 V. The dynamic refraction index calculated from the slopes is ~1.9 to 2.0, which is comparable to the optical refraction index measured at wavelength of 630 nm. The leakage currents also obey the Arrhenius law at different fixed voltages (not shown). Combining these two observations, we conclude that

\[ J = eV \exp\left(-\frac{\phi_B - \beta_V V^{1/2}}{k_BT}\right) \]

which is exactly the Poole–Frenkel formula. The extracted trap depth \(\phi_B\) is 0.3–0.4 eV.

Conclusions

In summary, La₉₂₋ₓMₓO₃ (M = Sc, Lu, or Y) films were deposited by ALD with metal amidinate precursors and H₂O. Both LaScO₃ and LaLuO₃ films are amorphous and free of interfacial layers. Besides the structural benefits, both oxides have high dielectric constants (~23 for LaScO₃ and 28 ± 1 for LaLuO₃), low leakage current density, and very few bulk traps, and are scalable to EOT < 1 nm. La₁.2₃Y₀.7₇O₃ films have polycrystalline structures with moderately high \(k = 17 \pm 1.3\) and low leakage current. The Poole–Frenkel mechanism is verified in the ternary oxide films by studying temperature dependence of the leakage current.

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