Atomic Layer Deposition of Lanthanum-Based Ternary Oxides

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Lanthanum-based ternary oxide LaM_{2−x}O_{3} (M = Sc, Lu, or Y) films were deposited on HF–last Si substrates by atomic layer deposition. Both LaScO_{3} and LaLuO_{3} films are amorphous while the as-deposited LaY_{2}O_{3} 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 LaScO_{3}, LaLuO_{3}, and La_{1.3}Y_{0.7}O_{3} 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 SiO_{2} with the same effective oxide thickness. Conformal coating thickness is demonstrated on holes with aspect ratio ~80:1.

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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 for integrating HfO_{2} into MOSFETs with the physical gate length of 32 nm. The oxide films were deposited in a flow-type 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 (CF_{4} + Ar).

Results and Discussion

The film thickness and the number of ALD cycles have a linear relation with zero intercept (Fig. 1a), showing that growth begins immediately on H-terminated Si surfaces. For m = n = 1 or 2, the ternary oxide growth rate is approximately the summation of m times of the growth rate of La_{2}O_{3} (1.3 Å/cycle) and n times of the growth rate of M_{2}O_{3} (1.1 Å/cycle for Sc_{2}O_{3}, 1.2 Å/cycle for Lu_{2}O_{3}, and 0.8 Å/cycle for Y_{2}O_{3}). The impurity contents, including carbon and nitrogen, are below the detection limit (~1%) of X-ray photoelectron spectroscopy (XPS) (Fig. 1b). The film composition by Rutherford backscattering (not shown) depends on both the ratio m/n and the metal precursors. For m = n = 1, the ternary oxide films were determined to be LaSc_{1.02}O_{2.98}, LaSc_{1.00}Y_{0.00}O_{3}, and La_{1.23}Y_{0.77}O_{3}, respectively. The compositions of La_{Y}_{2−x}O_{3} films for various m and n show a linear relationship between x/m (m = 0.5–0.6) with unit slope, which implies that the growth rate for each material is independent of the composition of the substrate that it is growing on. On this basis of this observation, LaScO_{3} films can be obtained by setting m = 2 and n = 3.

Figure 2a shows a sharp interface between amorphous LaScO_{3} and crystalline Si in a stack of WN/LaScO_{3}/Si. Similar results were found for LaLuO_{3} and La_{Y}_{2−x}O_{3} films [Cross-sectional transmission electron microscopy (XTEM) images not shown]. The step coverage is close to 100% in holes with an aspect ratio of ~80:1. Figure 2b shows that a 12 nm LaLuO_{3} film has a uniform thickness from the top to the bottom of the hole. Despite the fact that all the as-deposited binary oxides (M_{2}O_{3}) are polycrystalline body-centered-cubic phases determined by electron diffraction, both LaScO_{3} and LaLuO_{3} films are amorphous and homogeneous. In contrast, as-deposited La_{Y}_{2−x}O_{3} 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 La_{Y}_{2−x}O_{3}. After the growth of a thin amorphous layer (3–7 nm), the mismatch is relaxed so that a polycrystalline layer of La_{Y}_{2−x}O_{3} 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 LaLuO_{3}, LaScO_{3}, and La_{1.23}Y_{0.77}O_{3} films with no
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 in Fig. 3b, the dielectric constants, extracted from the slopes, are 28 and 17 for LaLuO$_3$ and 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 $\kappa = 3.9 \frac{\text{physical}}{\text{EOT}}$. 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$^{3+}$ (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 soft-

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 µm. 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.
LaScO$_3$ and LaLuO$_3$ films and 2–4 orders of magnitude lower for La$_{1.23}$Y$_{0.77}$O$_3$ films. All ternary oxide films have the same leakage temperature to 200°C. The Poole–Frenkel plots for La$_{1.23}$Y$_{0.77}$O$_3$ films. Effect caused by the relatively larger molar volume in the amorphous phase of the films compared to that of thermal SiO$_2$ films with the same EOT. The current density at 1 V gate bias is up to 6 orders of magnitude lower for LaScO$_3$ films 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 $J = eV \exp[-(\phi_B - \beta \sqrt{V})/k_BT]$, which is exactly the Poole–Frenkel formula. The extracted trap depth $\phi_B$ is 0.3–0.4 eV.

Conclusions

In summary, La$_M$Z$_{2-x}$O$_3$ (M = Sc, Lu, or Y) films were deposited by ALD with metal amidinate precursors and H$_2$O. Both LaScO$_3$ and LaLuO$_3$ films are amorphous and free of interfacial layers. Besides the structural benefits, both oxides have high dielectric constants (~23 for LaScO$_3$ and 28 ± 1 for LaLuO$_3$), low leakage current density, and very few bulk traps, and are scalable to EOT < 1 nm. La$_{1.23}$Y$_{0.77}$O$_3$ films have polycrystalline structures with a moderately high $\kappa = 17$ ± 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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References


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 LaScO$_3$ film (EOT = 0.9 nm) at various temperatures.