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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-etched Si substrates by atomic layer deposition (ALD). The ternary oxide films (LaLuO_{3}) are amorphous and homogeneous. In transmission electron microscopy and electrical analysis, the absence of interfacial layers is confirmed. The dielectric constants for LaScO_{3}, LaLuO_{3}, and La_{1.23}Y_{0.77}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 ~10:1.

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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 the growth rate of LaO (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}O_{3}, La_{1.20}Y_{0.80}O_{3}, and La_{1.23}Y_{0.77}O_{3}, respectively. The compositions of La_{2−x}Y_{x}O_{3} films for various m and n show a linear relationship between x/m and (m = 0.63x) 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 the basis of this observation, LaYO_{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_{2−x}Y_{x}O_{3} 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 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_{2−x}Y_{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 the nucleation of crystalline phases adjacent to Si, resulting in an amorphous lower layer of La_{2−x}Y_{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_{2−x}Y_{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_{1.2}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-Insulator-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±1 and 17±1.3 for LaLuO₃ and La₁.23Y₀.77O₃ films, respectively. The nearly zero intercept for LaLuO₃ films indicate the absence of any interfacial layer, consistent with the sharp interfaces observed by high-resolution XTEM. The dielectric constant for LaScO₃ is 23, which is estimated by $\kappa = \frac{3.9\gamma_{\text{physical}}}{\text{EOT}}$. Both LaScO₃ and LaLuO₃ films have higher dielectric constants than those of their binary oxide components, i.e., La₂O₃ ($\kappa = 19$), La₂O₃ (16), and Sc₂O₃ (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– (La³⁺ radius 103 pm) develops frames of polyhedrons with the smaller ions (Sc³⁺ radius 75 pm or Lu³⁺ 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-
LaScO₃ and LaLuO₃ films and 2–4 orders of magnitude lower for the effect caused by the relatively larger molar volume in the amorphous film. 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 $J = eV \exp(-[(\phi_B - \beta_{\text{PF}} V^{1/2})/k_B T])$, which is exactly the Poole–Frenkel formula. The extracted trap depth $\phi_B$ is 0.3–0.4 eV.

Conclusions

In summary, LaₓMₓ₋ₓO₃ (M = Sc, Lu, or Y) films were deposited by ALD with metal amidoine 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. Laₓ₁₋ₓYₓO₃ films have polycrystalline structures with 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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