Atomic Layer Deposition of Lanthanum-Based Ternary Oxides

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Lanthanum-based ternary oxide La$_{2}$M$_{2}$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 La$_{y}$Y$_{2-x}$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$_{0.23}$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 ~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 of integrating HfO$_{2}$ into MOSFETs with the physical gate length of 45 nm. However, pure HfO$_{2}$ is readily crystallized at temperatures of 450 to 500°C. Amorphous dielectrics with high thermal stability are still preferred because they have no intrinsic defects, such as grain boundaries, and show homogeneous electrical properties, provided they still have the advantages of HfO$_{2}$, such as high dielectric constant (κ ~ 22 to 23), wide bandgap ($E_g = 5.5$ eV), and low leakage. Recent reports show that lanthanum-based ternary oxides, such as lanthanum scandate (LaScO$_{3}$) and lanthanum lutetium oxide (LaLuO$_{3}$), can meet all these requirements. These materials were grown by molecular beam deposition, or atomic layer deposition (ALD). However, these lanthanide oxide films had nanometer-thick interfacial layers when deposited on Si substrates, which made it impossible to scale the effective oxide thickness (EOT) to the subnanometer range. Previously, we found that interfacial layers could be avoided when atomic layer deposition, both as-deposited La$_{y}$Y$_{2-x}$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$_{0.23}$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 ~80:1.

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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-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 for LaLuO₃ and La₂₋ₓY₂ₓO₃ 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 $\kappa = 3.9 \frac{\text{physical}}{\text{EOT}}$. Both LaScO₃ and LaLuO₃ films have higher dielectric constants than those of their binary oxide components, i.e., La₂O₃ ($\kappa \sim 19$), Lu₂O₃ (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–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-
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 effect caused by the relatively larger molar volume in the amorphous films.

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.

Figure 4 shows the leakage current density scaling of our ALD films compared to that of thermal SiO$_2$ 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 SiO$_2$ for both 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 current-voltage ($J$-$V$) behaviors. Figure 4b shows the $J$-$V$ curves of a LaScO$_3$ 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 $\sim 1.9$ 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 $J = eV \exp[-(\phi_B - \beta F V^{1/2})/k_B T]$, which is exactly the Poole–Frenkel formula. The extracted trap depth $\phi_B$ is 0.3–0.4 eV.

Conclusions

In summary, La$_x$M$_{2-x}$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 ($\sim 23$ 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 moderately high $\kappa = 17 \pm 1.3$ 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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