Atomic Layer Deposition of Lanthanum-Based Ternary Oxides

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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 as low as $\sim 500^\circ$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 ($\kappa \sim 22$ 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, pulsed laser 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 deposited on Si substrates, which made it impossible to scale the effective oxide thickness (EOT) to the subnanometer range. All rights reserved.

**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 $m = 1$ 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 ($\sim 1\%$) 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 La$_{1.02}$Sc$_{0.98}$O$_3$, La$_{1.01}$Lu$_{0.99}$O$_3$, and La$_{1.23}$Y$_{0.77}$O$_3$, respectively. The compositions of La$_2$Y$_2$O$_5$, La$_2$Sc$_2$O$_5$, and La$_2$Lu$_2$O$_5$ films 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$_2$Y$_2$O$_5$ 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$_2$Y$_2$O$_5$. After the growth of a thin amorphous layer (3–7 nm), the mismatch is relaxed so that a polycrystalline layer of La$_2$Y$_2$O$_5$ can grow on the top. MOS capacitors were made to measure the electrical properties. However, pure HfO$_2$ is readily crystallized at temperatures as low as $\sim 500^\circ$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 ($\kappa \sim 22$ to 23), wide bandgap ($E_g = 5.5$ eV), and low leakage.

**Experimental**

The oxide films were deposited in a flow-type ALD reactor with water vapor alternating with vapors of metal aminate precursors: lanthanum tris(N,N’-di-iso-propylformamidinate), scandium tris(N,N’-diethyldiaminomethanate), lutetium tris(N,N’-diethyldiaminomethanate), and yttrium tris(N,N’-di-isopropylacetamidinate). The ternary oxide films La$_{1.5}$M$_2$O$_3$ (M = Sc, Lu, or Y) were deposited by repeatedly growing n-layers of La$_2$O$_3$ followed by n-layers of M$_2$O$_3$ with $m = 1$ or 2. The deposition temperature was 300°C for LaScO$_3$ and LaLuO$_3$, and 280°C for La$_{1.2}$Y$_2$O$_3$ thin films were grown by molecular beam deposition, pulsed laser 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 deposited on Si substrates, which made it impossible to scale the effective oxide thickness (EOT) to the subnanometer range. All rights reserved.
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 and 17 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 \( \kappa = 3.9 \frac{\text{physical}}{\text{EOT}} \). Both LaScO₃ and LaLuO₃ films have higher dielectric constants than those of their binary oxide components, i.e., La₂O₃ (\( \kappa \approx 19 \)), 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⁺ 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 $T_{\text{H₂O}}$ to 200°C. The Poole–Frenkel plots for these films. The effect caused by the relatively larger molar volume in the amorphous films, which can be more than enough to make up for an adverse temperature dependence of the leakage current. Frenkel mechanism is verified in the ternary oxide films by studying 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₋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.

Conclusions

In summary, LaₓMₓ₋ₓO₃ (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₋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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