Atomic Layer Deposition of Lanthanum-Based Ternary Oxides

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Published Version</td>
<td>doi:10.1149/1.3074314</td>
</tr>
<tr>
<td>Citable link</td>
<td><a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:9310888">http://nrs.harvard.edu/urn-3:HUL.InstRepos:9310888</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at <a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA">http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA</a></td>
</tr>
</tbody>
</table>
Atomic Layer Deposition of Lanthanum-Based Ternary Oxides

Hongtao Wang,* Jun-Jieh Wang,* Roy Gordon,b,∗,z Jean-Sébastien M. Leman,c Huazhi Li,c Daewon Hong,c and Deo V. Shenai†

*Lanthanum-based ternary oxide La$_{1-m}$M$_m$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$_{1.23}$Y$_{0.77}$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$_{1.23}$Y$_{0.77}$O$_3$ films are $\epsilon_{31} \sim 22$, $\epsilon_{31} \sim 23$, and $17 \pm 1.3$, 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 $\sim$80:1.

© 2009 The Electrochemical Society. [DOI: 10.1149/1.3074314] All rights reserved.

Manuscript submitted November 30, 2008; revised manuscript received January 5, 2009. Published January 29, 2009.

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$500°C. Amorphous dielectrics with high thermal stability are still preferred because they have no intrinsic defects, such as grain boundaries, and show homogeneous electrical properties, provided they still have the advantages of HfO$_2$, such as high dielectric constant ($\kappa \sim 22$ to 23), wide bandgap ($E_g \sim 5.5$ 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 effective oxide thickness was posited on Si substrates, which made it impossible to scale the EOT down to the subnanometer range. The step coverage of $\sim$100% in holes with an aspect ratio of $\sim$80:1.

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 $n = 1$ 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 ($\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 LaSc$_{1.00}$Sc$_{0.00}$O$_{3.00}$, LaLu$_{0.77}$Lu$_{0.23}$O$_{3.00}$, and La$_{1.23}$Y$_{0.77}$O$_{3.00}$, respectively. The compositions of La$_{1-2x}$Y$_{2x}$O$_3$ films for various $x$ and $n$ show a linear relationship between $x$ and $m/n = 0.63x$ with unit slope, which implies that the growth rate of each material is independent of the composition of the substrate that it is growing on. On the basis of this observation, La$_{1-x}$Y$_x$O$_3$ 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$_{1-x}$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 $\sim$80:1. Figure 2b shows that a 12 nm LaLuO$_3$ film has a uniform thickness from the top to the bottom of the hole. Despite the fact that all the as-deposited binary oxide films (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$_{1-2x}$Y$_{2x}$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$_{1-2x}$Y$_{2x}$O$_3$. After the growth of a thin amorphous layer (3–7 nm), the mismatch is relaxed so that a polycrystalline layer of La$_{1-2x}$Y$_{2x}$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

* Electrochemical Society Active Member.
† E-mail: gordon@chemistry.harvard.edu
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 ± 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 $\kappa = 3.9 \frac{\text{physical}}{\text{EOT}}$. Both LaScO3 and LaLuO3 films have higher dielectric constants than those of their binary oxide components, i.e., La2O3 (κ ~ 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 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 LaLuO3.

Figure 2. (a) XTEM image of a WN/LaScO3 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 LaLuO3 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 of LaScO$_3$ and LaLuO$_3$ films. 12

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 $J = eV \exp[-(\phi_B - \beta_{PF}V^{1/2})/k_BT]$, which is exactly the Poole–Frenkel formula. The extracted trap depth $\phi_B$ is 0.3–0.4 eV.

**Conclusions**

In summary, La$_M$$_2$O$_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 $\pm$ 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.

**Acknowledgments**

This work was supported in part by Rohm and Haas Electronic Materials and performed, in part, at Harvard University’s Center for Nanoscale Systems, a member of the National Nanotechnology Infrastructure Network, supported by the U.S. National Science Foundation under award no. ECS-0335765. We also thank Professor Ramanathan for helping in the leakage current measurement.

Harvard University assisted in meeting the publication costs of this article.

**References**


