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Effects of Low Temperature O$_2$ Treatment on the Electrical Properties of Amorphous LaAlO$_3$ Films Made by Atomic Layer Deposition

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Amorphous LaAlO$_3$ films were deposited on hydrogen-terminated silicon substrates by atomic layer deposition (ALD) at 300 °C. The precursors were lanthanum tris(N,N'-diisopropylformamidinate), trimethylaluminum (TMA) and water. Capacitance-voltage measurements made on ALD MoN/LaAlO$_3$/Si stacks showed humps especially at low frequencies. They were effectively removed by O$_2$ treatment at 300 °C without affecting the dielectric constant ($\kappa \sim 15$). The O$_2$ treatment can be carried out either after deposition of a LaAlO$_3$ film, or after each ALD cycle. The O$_2$ treatment also lowered the leakage current from 80 mA cm$^{-2}$ to 1 mA cm$^{-2}$ for EOT = 1.3 nm. This indicates that oxygen vacancies are the main defects in as-deposited LaAlO$_3$. Oxygen treated LaAlO$_3$ is one of the best candidates for future high-$\kappa$ dielectric material due to its low leakage, low defect density and abrupt interface with silicon.

Introduction

Since the introduction of metal oxide semiconductor (MOS) field-effect transistors (FETs) as the centerpiece of microelectronic devices, scaling down of transistor size has continued to improve transistor performance. Therefore, the thickness of SiO$_2$-based gate dielectrics has been scaled down to keep the transistor drive current high enough to sustain speed enhancement. The thickness for gate dielectric layers specified in the ITRS roadmap has become so small that the leakage current density would be too high if SiO$_2$-based films were used as gate dielectrics (1). One solution for this problem is the integration of high-$\kappa$ dielectrics into gate stacks. Recent developments in employing high-$\kappa$ dielectric layers have focused on hafnium-based dielectrics. However the requirement of a significantly thick (>0.5 nm) SiO$_2$ interlayer or a formation of low-dielectric-constant silicate alloys with SiO$_2$ limits future scalability of Hf-based dielectrics (2).

LaAlO$_3$ has been considered as a potential high-$\kappa$ dielectric. It has a high dielectric constant ($\kappa_{\text{bulk}}$ is 20-25) (3, 4) as compared to SiO$_2$ ($\kappa \sim 3.9$), wide band gap ($E_g=5.8$ eV), high band offsets with respect to silicon (>2 eV) (5, 6) and abrupt interfaces when grown on silicon (7, 8). Many studies have shown that it is thermally stable in contact with silicon up to ~800 °C (9-12). Amorphous LaAlO$_3$ films have been grown using several physical and chemical deposition methods such as molecular beam deposition (MBD) (9, 13), sputtering (10, 11), electron-beam evaporation (14), chemical vapor deposition (CVD) (15) and atomic layer deposition (ALD) (16). ALD is a very attractive method for depositing DRAM insulators and advanced gate oxides for 3-D transistors, because the film thickness is easy to control, and the uniformity across the wafer and deep trenches is
better than with other deposition methods. Many issues, including high leakage current and high densities of bulk traps, remain to be resolved. Thus, in this letter, we suggest O₂ annealing during or after LaAlO₃ deposition to decrease the leakage current and reduce the trap density in the film.

**Experimental**

LaAlO₃ thin films were deposited in a horizontal gas flow reactor at 300 °C with the precursors lanthanum tris(N,N'-diisopropylformamidinate), trimethylaluminum (TMA) and H₂O. The lanthanum precursor was synthesized by methods similar to those described previously (17). It is the most volatile lanthanum compound known, with a vapor pressure of 82 mTorr at 120 °C. During the depositions, the lanthanum precursor was heated to 120 °C in an oven, while TMA and H₂O were kept at ambient temperature. The substrates were n-type Si (100) with resistivity 0.5-1 Ω cm. Before deposition, the substrates were dipped in a 5% aqueous HF solution for 5 sec. to achieve a hydrogen-terminated surface. Each cycle of LaAlO₃ consisted of two sub-cycles of La₂O₃ and one sub-cycle of Al₂O₃. A sub-cycle was the sequential dosing of the metal precursor and H₂O with a nitrogen purge following each dose. The pulse ratio of the lanthanum precursor to TMA was 2:1 to obtain a stoichiometry close to LaAlO₃. The growth rate was measured to be 2.8 Å/cycle based on thickness measurements from spectroscopic ellipsometry and x-ray reflectivity (XRR). The refractive index of the films was determined by spectroscopic ellipsometry to be between 1.84 and 1.88. To obtain film composition and impurity content, Rutherford backscattering spectroscopy (RBS) was performed on the films deposited on amorphous carbon substrates or Si₃N₄ membrane to increase sensitivity to light elements. The composition was found to be La₁.1Al₀.9O₃. Carbon and nitrogen concentrations were below the detection limit (<1 at. %).

ALD MoN was deposited on the LaAlO₃ layers in the same reactor, serving as a capping layer and a gate metal (18). The precursors for the ALD MoN were bis(tert-butylimido)bis(dimethylamido)molybdenum and ammonia gas (19). The Mo precursor was kept at 70 °C in an oven. The deposition temperature for MoN was 300 °C, at which temperature the growth rate was 0.5 Å/cycle according to thickness measurements by XRR. The stoichiometry is Mo₁N₁ according to RBS and the film was mostly amorphous as deposited (19). The resistivity of MoN was approximately 3000 µΩ cm, measured by a FPP5000 4-point probe.

For electrical analysis, multiple MOS capacitors were made out of MoN/ LaAlO₃ stacks on Si. The thickness of the MoN layers was fixed at 20 nm, while the LaAlO₃ layers varied in thickness from 5 to 10 nm. Au/Cr was patterned by a lift-off process on the sample to serve as an etch mask and to enhance the conductivity of the top contact for electrical measurement. MoN was then etched by CF₄/Ar reactive ion etching (RIE) through the etch mask to form MOS capacitor structures. The pad area was 10⁻⁴ cm². Backside oxide was etched off by dilute HF, and then Pt/Pd alloy was sputtered on the back to minimize the contact resistance. All of the capacitors then underwent rapid thermal annealing (RTA) at 400 °C for 4 min in forming gas (5% H₂ + 95% N₂). The leakage current was measured with a Keithley 2400 meter and the C–V curves were taken with a HP 4275A meter in a shielded probe station at room temperature.
Results and Discussion

The $C-V$ curves measured from MOS capacitors with an 8.3 nm thick as-deposited LaAlO$_3$ layer at different frequencies (10 kHz, 100 kHz, 1 MHz) are shown Figure 1 (a).

![Figure 1](image_url)

Figure 1. Comparison of $C-V$ curves at different frequencies between (a) the as-deposited sample and (b) PDA O$_2$ treated sample. A simulation curve is at 1 MHz is shown in (b); (c) as-deposited and simulated at 10 kHz; (d) PDA O$_2$ treated sample and simulated at 10 kHz.

The dielectric constant calculated from the $C-V$ curve is around 15, which is lower than the dielectric constant of the bulk material. This may be attributed to the lower density (14) of the LaAlO$_3$ amorphous phase (4.9 g/cm$^3$ according to the RBS and XRR data) as compared to its crystalline phase (6.5 g/cm$^3$). Experiments (20) have shown that in the crystalline phase the Al atoms are six-fold coordinated with oxygen, while in the amorphous phase, the coordination number decreases to 4. This decrease of the coordination number may lead to the lower density found in the amorphous phase. The dielectric constant should be lower in the less-dense amorphous phase according to the Clausius-Mossotti relationship (21).

Small humps were found in the midgap region of the $C-V$ curves measured at frequencies lower than 100 kHz (Fig. 1a and 1c). In order to find the origin of the humps and try to remove them, we tried in-situ post deposition anneal (PDA) at the deposition temperature 300 °C in O$_2$ with pressure 1 Torr for 10 min ($6 \times 10^8$ Langmuir exposure).
PDA was conducted before the MoN deposition to prevent the oxidation of MoN. As is shown in Figure 1(b), not only are the humps effectively removed at lower frequencies, but also the curve at 1 MHz is less stretched, indicating that fewer traps exist in the film. An equivalent oxide thickness (EOT) of 2.2 nm and flatband voltage of 0.65 V were determined by fitting the measured data by the MISFIT (22) simulation program (including quantum mechanical effects). The measured $C-V$ curves showed good agreement with simulation assuming a uniform distribution of electron traps. The estimated trap density in the as-deposited film is $3.5 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ by fitting the curve including humps at 10 kHz, while the estimated value for the O$_2$ treated film is lowered to $6 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$, as shown in Figure 1d.

Figure 2. The effect of oxygen exposure on (a) $C-V$ curves at 10 kHz and (c) $I-V$ curves. The midgap region is zoomed in (b). The middle electrical-field region is zoomed in (d).

Because PDA in O$_2$ ambient at the deposition temperature was effective, we grew other films that incorporated O$_2$ exposure during the growth of LaAlO$_3$, rather than after the films were completed. After each complete cycle of LaAlO$_3$, O$_2$ gas was exposed for various time periods and then purged. Comparing the $C-V$ curves measured at 10 kHz, shown in Figure 2 (a), humps were gradually removed as the total exposure of O$_2$ increased from $2 \times 10^5$ Langmuir (L) (by a measured dose of O$_2$ injected into a continuous flow of N$_2$) to $1 \times 10^8$ L (by O$_2$ enclosed in the reactor for 5 s without flow). The $I-V$ curves in Figure 2(c) also showed gradual improvement. The leakage at $2 \times 10^5$ L was similar to the as-deposited sample, but the leakage decreased to that of PDA at an O$_2$ exposure of $1 \times 10^8$ L. None of these treatments decreased the capacitance in the accumulation region, showing that there is no interfacial layer formed after the O$_2$ treatments.
$I-V$ curves in Figure 2 (c) and (d) confirmed that PDA in O$_2$ effectively reduced the leakage current density from $1.1 \times 10^{-4}$ A/cm$^2$ to $1.6 \times 10^{-5}$ A/cm$^2$ at 1V bias voltage ($|V_{G-V_{FB}}|$) at EOT = 2.2 nm. For films with EOT = 1.3 nm, the PDA in O$_2$ reduced the leakage current by a factor of 80, from 80 mA cm$^{-2}$ to 1 mA cm$^{-2}$.

Figure 3. High resolution TEM micrographs of a MoN/LaAlO$_3$ stack on Si. After deposition, the LaAlO$_3$/Si was treated in O$_2$ at 300 °C for 10 min, and then the whole stack underwent RTA at 400 °C for 4 min in forming gas prior to imaging. Both MoN/LaAlO$_3$ and LaAlO$_3$/Si interfaces are sharp and smooth.

Figure 3 shows high resolution cross-sectional transmission electron microscopy (TEM) micrographs of a MoN/LaAlO$_3$ stack on (100) Si. The thicknesses of LaAlO$_3$ and MoN were 12 nm and 20 nm, respectively. LaAlO$_3$/Si was under PDA O$_2$ treatment at 300 °C for 10 min, and then the whole stack underwent RTA at 400 °C for 4 min in forming gas prior to imaging. The images demonstrate that both LaAlO$_3$ and MoN films are uniform. The absence of lattice fringes in the LaAlO$_3$ film is in contrast to the distinct lattice of the Si, confirming that the LaAlO$_3$ film is amorphous. The MoN/LaAlO$_3$ and LaAlO$_3$/Si interfaces are smooth and abrupt. Most importantly, the transition from Si to LaAlO$_3$ is lacking any amorphous low-$\kappa$ SiO$_x$ interlayer after O$_2$ annealing which is consistent with the results above from the electrical measurements.

Figure 4. EOT plotted as a function of physical thicknesses of LaAlO$_3$. The intercept from the linear fit is 0.05 ± 0.09 nm and the dielectric constant is 15 ± 1.
The EOT versus physical thickness \((t_{\text{phy}})\) plot is shown in Figure 4. The y-intercept of the linear fit provides an estimate of the interfacial layer thickness \((t_{\text{IL}})\), and the slope is used to extract the dielectric constant \(\varepsilon_{\text{LaAlO}_3}\), as is seen from Eq. (1):

\[
EOT = t_{\text{IL}} + \frac{\varepsilon_{\text{SiO}_2}}{\varepsilon_{\text{LaAlO}_3}} \times t_{\text{phy}}
\]  

[1]

The estimated \(t_{\text{IL}}\) is zero within the experimental error, which provides additional electrical evidence for the idea that there is no low-\(\kappa\) interlayer. The extracted dielectric constant is 15, which agrees with the previous reported value. The results indicate very good scalability of O₂ treated ALD LaAlO₃ films.

The effectiveness of O₂ treatments in removing the humps indicates that they are due to oxygen vacancies in the bulk LaAlO₃. Guha et. al. (23) showed the origin of humps in the \(C-V\) curve in HfO₂ is positively charged oxygen vacancies. LaAlO₃ is also expected to have shallow oxygen vacancies (24). The Frenkel-Poole (FP) conduction mechanism usually fits well with defect-rich ALD HfO₂ films. During FP conduction, trapped charge carriers hop between potential wells that define the trap states, and an applied electric field enhances the hopping state because of the barrier-lowering effect. The current density and the electric field (J-E) characteristics follow the relationship (25):

\[
J \sim E \exp\left[\frac{-q(\Phi_b - \sqrt{qE/\kappa_d \pi})}{kT}\right]
\]  

[2]

where \(\kappa_d\) is the dynamic dielectric constant and is the FP trap energy. The electric field in the dielectric was calculated by

\[
E = \frac{V_G - V_{FB} - \Phi_s}{t}
\]  

[3]

where \(t\) is the physical thickness of the dielectric, \(V_G\) is the voltage being applied to the gate, and \(\Phi_s\) is the silicon substrate band bending. It can be seen from Eq. (2) that the field dependence of the J-E characteristics \(\ln(J/E)\) vs \(E^{1/2}\) should be linear, provided the conduction is dominated by FP hopping.

Figure 5. Frenkel-Poole (FP) fitting of the J-E curves measured from (a) as deposited (b) post-deposition-annealed sample at room temperature.
Figure 5 shows that our data fitted very well using a FP hopping formula from mid- to high field region for both as deposited and post annealed samples. The deviation from the fitted curve in the low-field and high-field regions is believed to result from trap-assisted tunneling and Fowler-Nordheim tunneling (26) respectively, which are excluded from the trap energy calculation. The trap depths of $\Phi_t$ and the dynamic dielectric constant $\kappa_{dy}$ are then extracted from the slopes and the intercepts of the linear fits. The trap depth of $\Phi_t$ is 0.69 eV and $\kappa_{dy}$ is around 2.1 for the PDA sample, while the values for the as deposited one are 0.59 eV and $\kappa_{dy}$ around 2.6. The extracted values are close to the energy levels of the oxygen vacancies in LaAlO$_3$ calculated in the literature (24). The trap depth of $\Phi_t$ is increased from 0.59 eV to 0.69 eV after the O$_2$ treatment, which might be one of the main reasons why the hump is removed and the leakage current is decreased.

![Figure 6. Leakage current density at 1 V of $|V_G-V_{FB}|$ with respect to EOT for LaAlO$_3$ (both as-deposited and samples treated with O$_2$ after deposition), SiO$_2$ and HfO$_2$.](image)

Another important aspect to consider when discussing scalability of a dielectric is how its leakage current density increases with respect to decreasing EOT. Figure 6 shows the leakage current density scaling of both the as-deposited and post annealed LaAlO$_3$ films, compared with that of thermal SiO$_2$ films (27) and of HfO$_2$ films (28). The leakage current density of the oxygen post annealed capacitors is about four orders magnitude lower than that of thermal SiO$_2$ films, and one order magnitude higher than that of HfO$_2$ films. Lower leakage can be expected if the deposition process is conducted also in the clean room.

In conclusion, we demonstrated that O$_2$ treatments during deposition or after deposition at 300 $^\circ$C can improve the electrical characteristics of ALD LaAlO$_3$ film. By fitting the J-E curve into the FP formula and comparing the extracted parameters, we proposed a possible reason for the improvement by O$_2$ treatments.

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