

Electrical characterization of amorphous lanthanum aluminate thin films grown by molecular-beam deposition on silicon

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(Received 28 November 2005; accepted 9 February 2006; published online 16 March 2006)

Amorphous LaAlO₃ thin films were deposited at room temperature directly on *n*-type and *p*-type Si (001) by molecular beam deposition. The dielectric properties of the stoichiometric amorphous LaAlO₃ thin films deposited on silicon were determined through capacitance-voltage and current-voltage measurements. The electrical measurements indicate that the amorphous LaAlO₃ thin films have a dielectric constant (*K*) of $K=16\pm 2$. This is significantly lower than the $K=24$ of crystalline LaAlO₃. The equivalent oxide thickness values range between 9.8 and 15.5 Å for films deposited on *n*-type silicon with physical thicknesses of 45–75 Å. © 2006 American Institute of Physics. [DOI: [10.1063/1.2182019](https://doi.org/10.1063/1.2182019)]

The scaling of SiO₂ in metal-oxide-semiconductor field-effect transistors (MOSFETs) is approaching its fundamental limit, which has been estimated to be 7 Å.^{1,2} To transcend this limit, new gate dielectric materials must be developed to replace SiO₂. The 2005 edition of the *International Technology Roadmap for Semiconductors* anticipates the use of higher dielectric constant (high-*K*) gate dielectrics in production as early as 2007.³ The first high-*K* MOSFETs to enter the market will have gate dielectrics with *K* ranging between 10 and 20 and will later be replaced with materials having *K* greater than 20. One of these higher *K* candidate materials is LaAlO₃.^{3–6} LaAlO₃ is a promising high-*K* gate dielectric due to its good thermal stability,^{7,8} high optical band gap (5.6 eV for crystalline LaAlO₃ and 6.2 eV for amorphous LaAlO₃),^{9–11} and high band offsets (1.8 eV for electrons and 3.2 eV for holes for amorphous LaAlO₃).¹¹

In crystalline form, the dielectric constant of LaAlO₃ is 24.1 ± 0.1 (measured at 145 GHz).¹² There is a significant discrepancy, however, in the literature for the dielectric constant of amorphous LaAlO₃ thin films. Part of this discrepancy could be due to the films being off composition, as α -Al₂O₃ has a *K* ranging from 9.4 to 11.6 as a function of direction.¹³ If we restrict our consideration to only La_{*x*}Al_{2–*x*}O₃ films with $0.8\leq x\leq 1.2$, the reported values vary from $K=13$ to 27 depending on the deposition technique. La_{0.9}Al_{1.1}O₃ films deposited by atomic layer deposition (ALD) have a reported $K=13$,¹⁴ sputtered LaAlO₃ films have a $K=14$,¹⁵ electron-beam deposited LaAlO₃ films have an estimated $K=21–25$,^{16,17} metalorganic chemical vapor deposition deposited La_{0.8}Al_{1.2}O₃ films have a $K=25$,^{18,19} and pulsed-laser deposited La_{1.04}Al_{0.96}O₃ films have a $K=25–27$.²⁰

In this letter, we report the dielectric properties of amorphous LaAlO₃ thin films deposited on silicon by molecular-

beam deposition (MBD) using elemental lanthanum, aluminum, and O₂ sources. The LaAlO₃ thin films are stoichiometric and have no detectable interfacial layer between the LaAlO₃ and the silicon.^{8,21} The dielectric properties were extracted through capacitance-voltage (*C-V*) and current-voltage (*I-V*) characterization.

Amorphous LaAlO₃ thin films (45, 60, and 75 Å thick) were grown by MBD in an EPI 930 MBD chamber modified for the growth of oxides.²² The thickness of the films was determined from x-ray reflectivity (XRR) measurements using a Bede 300 mm system. The Bede REFS software was used to fit the XRR data. The films were grown on both *n*-type (phosphorous doped, $0.2–1\times 10^{15}$ P/cm³) and *p*-type (boron doped, $1–2\times 10^{19}$ B/cm³) Si (001) wafers. The silicon wafers were cleaned using a 50:1 solution of de-ionized (DI) water: concentrated hydrofluoric acid (HF). (The amorphous LaAlO₃ films were formed by codepositing lanthanum, aluminum, and molecular oxygen at a background pressure of 6×10^{-6} Torr onto unheated silicon wafers. The lanthanum and aluminum fluxes were each 2×10^{13} atoms/cm² s. This deposition process has been shown to produce an abrupt amorphous LaAlO₃/Si interface free of any detectable interfacial SiO₂.^{8,21} The films were capped *in situ* with a 1000-Å-thick aluminum film that served as the top electrode. The aluminum was patterned and wet etched using the Transene-type A aluminum etch²³ to produce 50 μm × 50 μm squares.

Several 1500-Å-thick amorphous LaAlO₃ films have been analyzed by Rutherford backscattering spectrometry (RBS) (1.4 MeV He⁺, 170° scattering angle). RBS indicates that the films are stoichiometric with a ratio of La:Al = 1 ± 0.05 (not shown).

The *C-V* measurements were performed in a probe station using a HP 4284A. The electrical measurements were made on the as-deposited films and the results presented here are from *C-V* measurements made on virgin devices. The *I-V* measurements were made using a HP 4158A.

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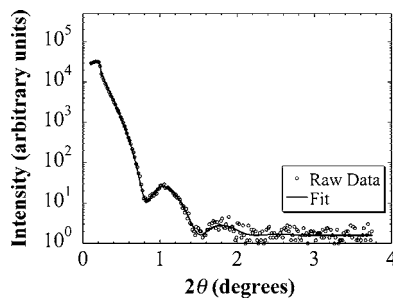


FIG. 1. X-ray reflectivity measurements and modeled data for an amorphous LaAlO_3 film with a physical thickness of $60 \pm 2 \text{ \AA}$.

The thickness of the LaAlO_3 thin films was determined using XRR. Figure 1 shows the XRR measurement and the model for the $60 \pm 2 \text{ \AA}$ thin film. The physical thickness of the LaAlO_3 thin films extracted by XRR is in agreement with high-resolution transmission electron microscopy measurements on similar films.²¹

Figure 2 shows the C - V measurements of films deposited on n -type and p -type silicon, respectively. The equivalent oxide thickness (EOT) indicated in the figures was determined using the Hauser CVC modeling program.²⁴ The EOT values range between 9.8 and 15.5 \AA for films deposited on n -type silicon with physical thicknesses of 45–75 \AA . The EOT values range between 12.2 and 20.1 \AA for films deposited on p -type silicon with physical thicknesses of 45–75 \AA .

Figure 3 shows the I - V measurements on n -type and p -type silicon, respectively, for the same films measured in Fig. 2. The leakage current densities are significantly lower for the films deposited on the n -type wafers and range between 1×10^{-3} and $6 \times 10^{-7} \text{ A/cm}^2$ at $V_{\text{fb}} + 1 \text{ V}$ for films with physical thicknesses of 45 and 75 \AA . The leakage current densities for the films deposited on p -type wafers range

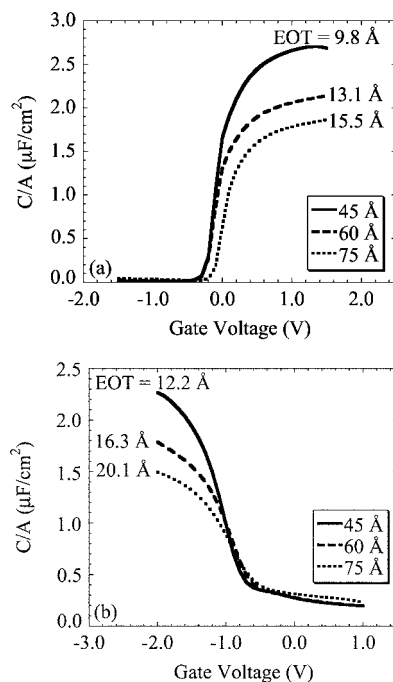


FIG. 2. (a) C - V curves as a function of amorphous LaAlO_3 film thickness on n -type wafers. (b) C - V measurements as a function of thickness on p -type wafers. The measurements were made at 100 kHz on $50 \mu\text{m} \times 50 \mu\text{m}$ capacitors.

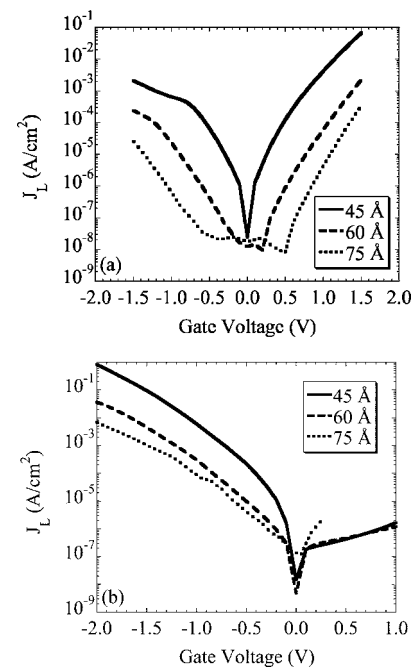


FIG. 3. (a) I - V measurements as a function of amorphous LaAlO_3 film thickness on the same n -type wafers shown in Fig. 2(a). (b) I - V measurements as a function of thickness on the same p -type wafers shown in Fig. 2(b).

between 0.8 and $8.5 \times 10^{-3} \text{ A/cm}^2$ at $V_{\text{fb}} - 1 \text{ V}$ for films with physical thicknesses of 45–75 \AA .

Figure 4 shows the forward and reverse bias sweeps for 45 \AA LaAlO_3 thin films deposited on n -type and p -type silicon, respectively. The n -type wafers showed significantly lower hysteresis than the p -type wafers. Several postdeposition anneals have also been performed to try to reduce the

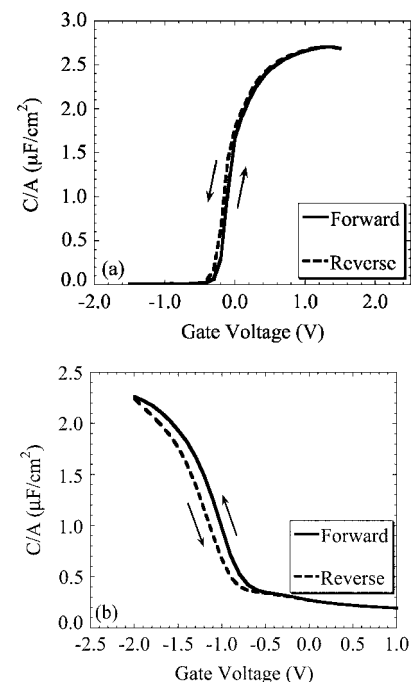


FIG. 4. (a) Forward and reverse bias C - V measurements on a 45- \AA -thick amorphous LaAlO_3 thin film deposited on n -type silicon. The hysteresis was 66.1 mV. (b) Forward and reverse bias C - V measurements on a 45- \AA -thick amorphous LaAlO_3 film deposited on p -type silicon. The hysteresis was 272 mV.

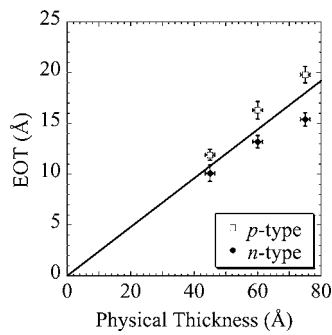


FIG. 5. EOT as a function of physical thickness for amorphous LaAlO₃ films deposited on both *n*-type and *p*-type silicon.

hysteresis on *p*-type wafers. For example, samples annealed *in situ* in UHV directly after MBD at temperatures ranging between 400 and 600 °C for 30 min exhibited no improvement in the hysteresis. Subsequent *ex situ* annealing in forming gas (4% hydrogen and 96% nitrogen) at 350 °C for 30 min also did not improve the hysteresis of the LaAlO₃ thin films deposited on *p*-type silicon. The as-deposited films were also *ex situ* annealed in N₂ for 30 min at 750 °C, but this resulted in breaking down the films.

It was possible to eliminate the hysteresis by making multiple voltage sweeps on the same device. This indicates that there are traps in the LaAlO₃ thin films deposited on *p*-type silicon. It is suspected that there might be a defect level in the band structure in the LaAlO₃ near the valance band that causes the trapped states.

Figure 5 shows the EOT as a function of physical thickness for the films deposited on *n*-type and *p*-type silicon. The lack of a detectable interfacial layer²¹ results in the intersection with the plot origin. From the slope of this plot, the dielectric constant of the amorphous LaAlO₃ thin films deposited by MBD was extracted to be 16±2. This dielectric constant is significantly lower than the dielectric constant of crystalline LaAlO₃, which is $K=24$.¹² The relatively low K value is, however, in good agreement with other LaAlO₃ thin films deposited by ALD¹⁴ and sputtering.¹⁵

Busani and Devine²⁵ proposed that the reduced dielectric constant of amorphous LaAlO₃ thin films was caused by an increase in the molecular volume of the amorphous films that was caused by a lower density in sputtered amorphous LaAlO₃ thin films compared to the density of single crystalline LaAlO₃. Using the thickness determined from XRR measurements and the areal density of cations deposited based on quartz crystal microbalance flux measurements calibrated by RBS measurements on thicker films, the density of our amorphous MBD LaAlO₃ thin films was calculated to be 4.3 g/cm³. This density is in good agreement with Busani and Devine's²⁵ sputtered LaAlO₃ thin films and is significantly lower than the density of crystalline LaAlO₃, which is 6.5 g/cm³. The dielectric constant of an isotropic and homogeneous amorphous material²⁶ (as well as certain cubic structures²⁷) is related to its molecular volume by the Clausius–Mossotti equation^{28,29}

$$K = \frac{3V_m + 8\pi\alpha_D^T}{3V_m - 4\pi\alpha_D^T}, \quad (1)$$

where V_m is the molar volume and α_D^T is the total dielectric polarizability of the material.¹³ Therefore, as the molecular

volume increases, the dielectric constant decreases. The increased molecular volume of our films resulting from their low density could be the reason for the reduced dielectric constant of amorphous LaAlO₃ thin films deposited by MBD compared to crystalline LaAlO₃.

The authors L.F.E., D.G.S, P.S., and R.M.W. gratefully acknowledge the financial support of the Semiconductor Research Corporation (SRC) and SEMATECH through the SRC/SEMATECH FEP Center. L.F.E. gratefully acknowledges an AMD/SRC fellowship.

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