**Title:** Molecular volume and electronic and vibrational polarizibilities for amorphous LaAlO$_3$

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**Subject Terms:** LaAl, Amorphous Films, Dielectric Constant
Molecular volume and electronic and vibrational polarizibilities for amorphous LaAlO$_3$

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Grazing incidence x-ray reflectivity measurements are used to determine the density of sputter-deposited LaAlO$_3$ and anodized LaAl films. Together with refractive index and dielectric constant measurements, it is demonstrated that a coherent picture emerges explaining the low dielectric constant of the amorphous films (~13) as compared to the single-crystal value (~26). The importance of molecular volume dependence of the electronic and vibrational molecular polarizabilities is underlined. © 2004 American Institute of Physics. [DOI: 10.1063/1.1808905]

I. INTRODUCTION

Despite substantial research into high dielectric constant oxides to replace SiO$_2$ as the metal-oxide-semiconductor field-effect transistor (MOSFET) gate insulator, nothing has emerged as a medium to long term solution. Some of the primary requirements for this application are (a) a dielectric constant ($k$) ~25 or greater, (b) high electrical barrier height with respect to the Si substrate and the gate electrode material, (c) thermodynamic stability with respect to Si during process steps such as implanted dopant activation (~1000 °C for short times), (d) low leakage currents, and (e) low density of states at the dielectric/Si interface. Unfortunately, the dielectric constant is, in general, inversely proportional to the insulator band gap so that achieving a high $k$ value to satisfy (a) may be detrimental for (b). A careful study of thermodynamic compatibility of various single and binary oxide systems reveals that there is, in fact, a significant number of oxides which exist that satisfy (c). Together with refractive index and dielectric constant measurements, it is demonstrated that a coherent picture emerges explaining the low dielectric constant of the amorphous films (~13) as compared to the single-crystal value (~26). The importance of molecular volume dependence of the electronic and vibrational molecular polarizabilities is underlined.

![Image](http://jap.aip.org/jap/)

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In the work reported here, we have performed a series of measurements to try to clarify the situation regarding the dielectric constant of amorphous LaAlO$_3$. In particular, we have performed a sequence of measurements which should enable us to clearly demonstrate the consistency between such parameters as film density, dielectric constant, and refractive index. To this avail we have produced thin films of LaAlO$_3$ via three routes, sputtering of a stoichiometric LaAlO$_3$ target, sputtering of stoichiometric LaAl followed by anodic oxidation in an O$_2$ plasma, and sputtering of LaAl followed by a recrystallization annealing then a thermal oxidation at 700°C. The results of measurements on these samples are presented in the following.

II. EXPERIMENT

A. Sputtered LaAlO$_3$

Samples were prepared by radio frequency (rf) sputtering of a stoichiometric LaAlO$_3$ target onto room temperature 3–5 Ω cm Si wafers. The wafers were rinsed in hydrofluoric acid and blown dry prior to installation in the plasma reactor. During deposition, the chamber pressure was 10 mTorr and the gas flow rates were (Ar) 75 (cubic centimeters per minute at STP) SCCM and (O$_2$) 5 SCCM. The 13.56 MHz power used with the TORUS 2 source was typically 60 W, this provided a target bias potential ~−140 V suitable for essentially stoichiometric sputtering of the target material (at least in terms of the La and Al sputtering). The appropriate bias potential was determined by sputtering calculations (TRIM$^{10}$). The use of a partial atmosphere of O$_2$ ensured compensation for any oxygen loss from the target during the sputtering process. Deposition rates were ~1.4 nm min$^{-1}$ and typical final film thicknesses were up to ~112.0 nm, as determined by ellipsometric measurement at a single wavelength (632.8 nm) and confirmed by mechanical stylus measurement (α-step). Some films were obtained using a rf substrate bias to produce an ion-assisted deposition effect, in this case, voltage levels were between ~92 and ~100 V. Larger biases were found to produce simultaneous sputtering/deposition of the films. Film composition was confirmed by using x-ray fluorescence and comparison with a single-crystal standard using correction for beam energy and film thickness effects. One sample was analyzed using profiling x-ray photoelectron spectroscopy to confirm the fluorescence result. The refractive index and thickness of the deposited films was measured using a monochromatic (λ=632.8 nm) ellipsometer, as was the refractive index of a bulk, single crystal LaAlO$_3$ sample. For the as-deposited (without substrate bias) films, we obtained $n = 1.78$ and for the single crystal, $n = 2.01$. The films deposited with substrate bias (i.e., with ion assistance) had a maximum refractive index value of 1.83, slightly larger than the unbiased value.

B. Anodic oxidized LaAl

A stoichiometric LaAl target was used with the TORUS 2 sputtering system mentioned above. Identical substrate preparation steps were used and film thicknesses up to ~0.1 μm were deposited at a rate ~3.3 nm min$^{-1}$ using a chamber pressure of 10 mTorr of Ar. The sputtering power was again adjusted to give a target bias potential ~−140 V, which was calculated to yield stoichiometric sputtering. Following deposition, the O$_2$ plasma was established in the reactor (pressure ~10 mTorr) using a microwave excitation system$^{11}$ and the substrate biased negatively dc. A constant dc mode of anodization was adopted with the total O$^-$ and electronic current density being ~1.2 mA cm$^{-2}$. LaAlO$_3$ films ~80-nm thick were obtained in 8 min. The refractive indices of these films varied slightly from 1.65 to 1.92. In the former case, we confirmed by Fourier transform infrared (FTIR) spectroscopy that the LaAl film had been completely anodized and a thin SiO$_2$ anodic layer had formed at the LaAlO$_3$/Si interface. The higher index value corresponded to samples where no evidence was found for an interfacial oxidation. X-ray diffraction and FTIR were used to confirm that the anodized films were amorphous.

C. Thermal oxidation

Thick LaAl films ~0.5 μm were deposited, as mentioned previously, but this time, the substrates were 4-in. Si wafers coated with a 370-nm-thick film of Si$_3$N$_4$ (plasma-enhanced chemical-vapor deposited). Since the objective of the experiment was to study thermal oxidation, the Si$_3$N$_4$ was used to remove contact between the LaAl and so avoid a possible interaction during the high-temperature oxidation process. The films were subsequently annealed in a tube furnace in flowing N$_2$ at 400°C for 30 min in order to recrystalize the LaAl. The furnace was then heated to 700°C and the polycrystalline film was oxidized for 30 min in flowing O$_2$. The amorphicity of the films was again confirmed by FTIR. However, refractive index measurements were not possible on these films because of the extreme roughness of the structures resulting from the recrystallization of the LaAl film. The roughness resulted in an exaggerated diffusion of light in the ellipsometer, which rendered the measurement meaningless. It is important to note, however, that the oxide of the polycrystalline metal alloy is amorphous even though relatively high temperatures were used.

In order to obtain an estimate of the density of the deposited films, grazing incidence x-ray reflectivity was measured using a Philips X’pert double-crystal diffractometer and Cu K$_{α1}$ radiation together with a 0.45-mm receiving slit. The experimental reflectivity curves were fitted using the WINGIXA software provided by the PANalytical company. Various different samples were analyzed in this manner in order to determine the film density. Measurements were possible for the anodized LaAl films and the sputtered stoichiometric LaAlO$_3$ films but not for the thermal oxide, again, because of the extreme roughness. The dielectric constant of the as-deposited films was obtained by performing capacitance voltage ($C$–$V$) measurements using a Keithley 590 system at a frequency of 100 kHz on MOS capacitors formed by depositing 0.0078 cm$^2$ Al dots on the film surface. Typical accumulation capacitance of the MOS capacitors yielded maximum values of $k$ ~13, consistent with the previous work.$^{4}$ This maximum value was observed for both the sputtered LaAlO$_3$ and the anodized LaAl. Note that great care was taken to reduce the series resistance of the MOS
capacitor structures in order to minimize frequency-dependent corrections to the measured capacitance values. It must be underlined that capacitance-voltage measurements leading to an estimation of the dielectric constant were not possible for the case of the thermally oxidized LaAl films. As for the refractive index measurements, the extreme roughness of the recrystallized then oxidized film yielded a severely distorted curve. Infrared absorption in the films was measured using a Fourier transform infrared spectrometer with a resolution of 4 cm\(^{-1}\). As mentioned previously, with this technique, we were able to confirm the amorphous nature of the LaAlO\(_3\) films and further demonstrate the absence/presence of any significant amount of interfacial SiO\(_2\).

III. RESULTS AND ANALYSIS

A. The dielectric constant, refractive index, and density relationship

We first consider the results of the \(C-V\) measurements. Both as-deposited, zero-substrate bias films, and anodized LaAl films showed significant negative flat-band voltage shifts\(^\text{15}\) consistent with the presence of trapped positive charge. This charge probably resulted from the radiation present during the plasma sputtering of the LaAlO\(_3\) target and in the O\(_2\) plasma used for anodization of the LaAl. Anneals were carried out on both types of samples at 400\(^\circ\)C for 30 min in N\(_2\) postdeposition. (---) subjected an electric of \(-1\) MV cm\(^{-1}\) for 10 min before sweeping from negative to positive voltage (—) subjected to an electric field of 1 MV cm\(^{-1}\) for 10 min before sweeping from positive to negative voltages.

and for the anodized LaAl, 8.7–13. Note also that the samples used to generate the curves of Fig. 1 were not subjected to postmetallization anneals in forming gas, so that some stretch-out and structure is present in the \(C-V\) curves associated with interface states at the film/substrate interface. This stretch-out was also present in the anodized LaAl film, as one would expect. In the case of sputtered LaAlO\(_3\) samples deposited using ion assistance (i.e., using substrate bias), very large negative flat-band voltage shifts were measured. Annealing these samples at 400\(^\circ\)C for 30 min resulted in an evident substrate/film interaction and very distorted \(C-V\) curves. We were unable to use these curves to determine the oxide capacitance in accumulation and hence the dielectric constant. It can be concluded from this that ion-assisted deposition developed damage at the film/substrate interface, which enhanced the probability of intermixing during the annealing process.

In Fig. 2, we show a typical example of the experimental grazing incidence x-ray curve as a function of \(2\theta\) for sputtered LaAlO\(_3\) films deposited without an ion assistance. From the frequency of oscillation of the Kiessig fringes, we deduce that the film thickness is 71.8 nm, acceptably close to the value determined from the ellipsometry measurement. The critical angle, \(\theta_C\), is defined as the angle where the detected number of reflected counts falls to 1/2 the maximum value. This is related to the film density through\(^\text{13}\)

\[ \theta_C/2 = \delta = 4.1516 \times 10^{-4}(\rho ME_\text{f}) \sum c_j f_j, \]

where the sum is over the different concentrations of the elements in the film \((c_j)\) and \(f_j\) are the associated atomic scattering factors, \(\rho\) is the density of the film, \(M\) is the molecular weight, and \(E\) is the energy of the x rays (here, 8.042 keV). From the value of \(\theta_C\) determined from the fit shown in Fig. 2, for example, we ascertain \(\rho = 4.2\) g cm\(^{-3}\), this value is to be compared with the known single-crystal value of \(\rho = 6.51\) g cm\(^{-3}\). Similar values for the density were found for the anodic oxide samples. Note that in Fig. 2, we show the fit curve obtained using the WINGIXA software; this curve is simply displaced to avoid confusion and to enable the reader to clearly see the quality of the fit in terms of the
frequency of the oscillation, slope of the curve, etc. The value of $\theta_c$ is dependent upon the x-ray energy and the accuracy of alignment of the sample.\textsuperscript{3} Although we were unable to measure $\theta_c$ as a function of incident x-ray beam energy, we can use the data presented in Ref. 14 to set some upper limits on the precision of the density value; these are $\pm 0.3$ g cm$^{-3}$. It is possible that our measurements are more precise, but in the absence of the variable energy data, we cannot advance any estimate.

The question arises as to whether or not the sputtered LaAlO$_3$ films may be porous, giving rise to the lower density value. We note first that the film refractive index is directly related to its density [Eq. (2)] and that for our samples deposited with and without a substrate bias, the refractive indices are close. It is generally assumed that one of the roles of substrate bias is to ion-assist the deposition of the film and that this usually leads to a more densified form. Since there is little difference in our case, this may support the hypothesis that our films are already densified, i.e., not porous. Secondly, we have performed measurements on anodized LaAl. Not only are the refractive indices obtained very close to the sputtered LaAlO$_3$ values but so are the dielectric constant and density. It is known from the anodization experiments on Si that anodic oxides are not usually porous and that they are even denser, sometimes, than their thermal counterparts. It is therefore a reasonable assumption that the sputtered LaAlO$_3$ and anodized LaAl films are not porous.

From the density values for the single crystal and for the amorphous films shown in Fig. 2, we can deduce the molecular volumes: $V_m$(crystal) = 54.45 Å$^3$ and $V_m$ (amorph.) = 84.5 ± 6 Å$^3$. The density of the amorphous films is therefore substantially less than that of the single-crystal material and this alone is probably the primary cause for the lower dielectric constant, as will be demonstrated. The increased molecular volume (decreased density) of the amorphous phase of LaAlO$_3$ as compared to the single-crystal value may not be surprising. Magic angle spinning nuclear magnetic-resonance measurements\textsuperscript{16} on amorphous and crystallized bulk LaAlO$_3$ show clear evidence for the fact that in the amorphous phase, the Al atoms are fourfold coordinated with oxygens. In the crystalline phase, coordination increases to 6. Such an increased coordination can lead to more efficient network packing and enhanced density (smaller molecular volume), this has been clearly demonstrated through calculations for the case of Zr$_x$Si$_{1-x}$O$_2$ ternary oxides.\textsuperscript{17} Experimentally, one can appeal to the example of SiO$_2$ polymorphs where for the fourfold coordinated amorphous phase, the density is typically 2.21 g cm$^{-3}$ whilst for the sixfold coordinated stishovite phase, the density increases to 4–4.4 g cm$^{-3}$. Unfortunately, to our knowledge, density measurements on the bulk amorphous phase of LaAlO$_3$ do not exist.

The values of the dielectric constant, refractive index, and molecular volumes are not arbitrary. According to the Lorentz-Lorenz equation\textsuperscript{18}

$$\left( n^2 - 1 \right) / \left( n^2 + 2 \right) = 4 \pi a_{el} / \left( 3 V_m \right),$$

whilst from the Clausius-Mossotti relationship\textsuperscript{19}

$$(k - 1)/(k + 2) = 4 \pi a_{el} / (3 V_m).$$

Here $a_{el}$ is the electronic component of the molecular polarizability and $a_{vib}$ is the polarizability component usually associated with vibrational motion of the network.\textsuperscript{19} The equations presented clearly indicate that the refractive index and dielectric constant are both sensitive to the molecular volume (and hence, the density) and the increased molecular volume (lower density) will result in smaller values of both $n$ and $k$. Therefore, our density, refractive index, and dielectric constant data are consistent with the amorphous films having a much lower density than the crystalline phase, and this is a fundamental result of the present study.

**B. The electronic and vibrational polarizabilities**

From Eqs. (2) and (3), one can produce unique plots of $n$ as a function of $a_{el} / V_m$ and $k$ as a function of $(a_{el} + a_{vib}) / V_m$; these are shown in Figs. 3(a) and 3(b). In Figs. 3(a) and 3(b), we indicate the crystalline and amorphous values of $(a_{el} + a_{vib}) / V_m$ and $a_{el} / V_m$ deduced using the experimental values of $k$ and $n$ for the deposited and anodic films and single crystals. For simplicity, we take the dielectric constant to be 13 for the amorphous films, the maximum value we have measured. It should be noted here that although some high $k$ crystals are relatively anisotropic, this is not the case\textsuperscript{20} for LaAlO$_3$, so we make negligible error in taking a
unique value. Note that in Fig. 3(b), we include a range of $n$ values for the crystalline phase corresponding both to our measurements and those of the others.

Using these known dielectric constants, refractive indices, and molecular volumes, we can deduce the associated polarizabilities; these are given in Table I. One observes, as expected, that $\alpha_{el}$, $\alpha_{vib}$, and the sum $\alpha_{el} + \alpha_{vib}$ are smaller in the crystalline phase than in the amorphous state.

The polarizability data shown in Table I indicate that, in general, both the electronic and vibrational polarizability terms decrease as the molecular volume decreases. The variation of the polarizability with molecular volume has been the subject of various publications. For example, a detailed analysis\textsuperscript{22} of the structure and pressure dependence of the electronic polarizability, $\alpha_{el}$, in four and eight coordinated MgO clearly evidences the fact that this term increases as the molecular volume increases, as indeed we observe for LaAlO$_3$ in Table I. Further evidence for volume-dependent effects comes from the measurements of the dielectric constant as a function of volume in single-crystal LaAlO$_3$. We show the data obtained for the temperature dependence of the molecular volume\textsuperscript{23} and dielectric constant\textsuperscript{24} in Fig. 4. For simplicity, we represent the data in the form of a plot of $\alpha_{el}$ versus $V_m$. Since volume-dependent refractive index data do not exist for this material, we cannot extract the individual molecular volume dependence of $\alpha_{el}$ and $\alpha_{vib}$. However, it is clear from Fig. 4 that the polarizability increases with molecular volume in this material.

Similar analysis and conclusions can be reached by examining the refractive indices of the SiO$_2$ polymorphs,\textsuperscript{25} as shown in Fig. 5. In Fig. 5(a), we show the electronic polarizabilities estimated from the measured refractive indices of various amorphous and crystalline phases. Clearly, $\alpha_{el}$ increases as the molecular volume increases. Similarly, in Fig. 5(b), we show the data for $\alpha_{vib}$ as a function of molecular volume. In this case, experimental values for the dielectric constants were only available for amorphous SiO$_2$ and $\alpha$-quartz. The data used to estimate the value of $\alpha_{el} + \alpha_{vib}$ for stishovite were taken from calculations.

It is clear, therefore, that one should not neglect possible variations in the electronic and/or vibrational components of the overall polarizability as a function of the molecular volume. In the oxide additivity model,\textsuperscript{20} the dielectric constant of a complex oxide can be expressed as a sum of the contributions from the individual molecules through the weighted sum of their polarizabilities

$$\alpha_{el} + \alpha_{vib} = c(\alpha_{el} + \alpha_{vib})_P + (1-c)(\alpha_{el} + \alpha_{vib})_M + c(\alpha_{el} + \alpha_{vib})_{M\alpha O_B},$$

where $c$ is the effective concentration of M$_A$O$_B$ molecules and $(1-c)$ is the concentration of M$_B$O$_B$ molecules. It is a tacit assumption of the additivity model that as the concentration is changed, the only variable is the molecular volume of the composite molecule M$_A$M$_B$O$_{B+P}$. The data presented in Table I for the case of our LaAlO$_3$ oxides clearly show that invariance of $(\alpha_{el} + \alpha_{vib})$ with change in molecular volume cannot be assumed.

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**TABLE I.** The electronic ($\alpha_{el}$) and vibrational molecular ($\alpha_{vib}$) polarizabilities for LaAlO$_3$ films and single crystal deduced from refractive index and dielectric constant measurements. The molecular volume, $V_m$, for the amorphous films was determined by grazing incidence x-ray reflectivity measurement.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\alpha_{el}$ [Å$^3$]</th>
<th>($\alpha_{el} + \alpha_{vib}$) [Å$^3$]</th>
<th>$\alpha_{vib}$ [Å$^3$]</th>
<th>$V_m$ [Å$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>(6.53–6.88)</td>
<td>11.61</td>
<td>5.1–4.73</td>
<td>54.45</td>
</tr>
<tr>
<td>Amorph.</td>
<td>(8.3–8.8)$\pm 0.6$</td>
<td>16.14±1.1</td>
<td>7.59±2.0</td>
<td>84.5±6</td>
</tr>
</tbody>
</table>

---

**FIG. 5.** (a) Variation of the electronic component of the polarizability of polymorphs of SiO$_2$ as a function of molecular volume, as determined from their refractive indices. (b) Variation of the vibrational component of the polarizability of three phases of SiO$_2$, amorphous, $\alpha$-quartz, and stishovite, as determined from their dielectric constants.

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**FIG. 4.** Variation of the total molecular polarizability ($\alpha_{el} + \alpha_{vib}$) with molecular volume, $V_m$, in single crystals of LaAlO$_3$. 

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**FIG. 3.** Variation of the electronic polarizability, $\alpha_{el}$, and the overall polarizability, $\alpha_{el} + \alpha_{vib}$, for stishovite were taken from calculations.
IV. CONCLUSIONS

As demonstrated in Sec. I, there is substantial disparity in the values obtained for the dielectric constant of films of amorphous LaAlO$_3$ deposited on Si. We have endeavored to obtain a coherent explanation of the measured refractive indices and dielectric constant in our deposited and anodic oxidized amorphous films and bulk, single-crystal LaAlO$_3$ samples. It appears that the primary reason for the lower dielectric constant in the amorphous deposited and anodized films, as compared to single-crystal values, is a simple result of the higher molecular volume (lower density) with some associated change in the electronic and vibrational molecular polarizabilities. The origin of this density difference may lie in the coordination of the network since experiments have shown that Al in LaAlO$_3$ is fourfold coordinated in a low-temperature, amorphous material sixfold coordinated in a high-temperature (crystalline) material. Coordination is a dominant factor in the determination of the network density. Using the density measurements one can further analyze refractive index and dielectric constant data in terms of variation of the electronic and vibrational parts of the polarizability. In the absence of significant interfacial interactions between the deposited film and the underlying Si substrate, measuring all these parameters is necessary to achieve a complete physical understanding. The analysis of our measurements suggests a clear variation of the electronic and vibrational parts of the polarizability with molecular volume, and this is consistent with the expectations based upon model calculations. These variations of the polarizability are usually neglected when applying the oxide additivity rule to estimate the dielectric and refractive constants of mixed alloys and this may be a failing of the method.

We are still unable to reconcile the inconsistencies in other published data on the dielectric constant of deposited LaAlO$_3$ films. These inconsistencies could certainly be removed to some degree if optical data, in particular, refractive index measurements, were available for other authors’ films. A survey of the rather limited data sets presented in Sec. I seems to point to the fact that deposition of LaAlO$_3$ on Si, at elevated temperatures, results in a low value of the dielectric constant (as compared to the single-crystal value), at least partially due to film/substrate interaction. One data set, involving deposition onto Pt films indicates that high values of $k$ can be achieved for amorphous films but, perhaps, not on Si. It would therefore be very interesting to see if this indeed results from the nature of the substrate (i.e., Pt), in which case, one would conclude that Si is not a good host for high $k$ LaAlO$_3$ films.

10. The TRIM software is available for free download on: www.srim.gov