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Molecular volume and electronic and vibrational polarizabilities 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) dielectric constant ($k \sim 25$ 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 ($\sim 1000^\circ\text{C}$ 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 gap¹ so that achieving a high k value to satisfy (a) may be detrimental for (b). A careful study² 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). The use of non-Si-based dielectrics implies either a direct film deposition or oxidation of a deposited metal, both of these techniques are well known to result in films having defect-related conductivities (primarily via the Poole-Frenkel mechanism), which are usually substantially higher than one observes in thermally grown SiO_2 on Si. Finally, if crystallization of the film occurs during postdeposition, high-temperature processing sequence substantial electrical leakage along grain boundaries may occur. Both defect-related conductivity and grain-boundary leakage³ may be critical.

Of all the oxide systems studied so far, LaAlO_3 appears very promising. It is predicted that there is thermodynamic stability² with respect to Si and the dielectric constant, for single crystals, is ~ 26 . Furthermore, it is anticipated that deposited films may remain amorphous even in the presence of a relatively high-temperature processing (in fact, probably to $800\text{--}850^\circ\text{C}$) so that potential sources of leakage current

via grain boundaries³ should be absent. Preliminary measurements on amorphous deposited films^{4–6} suggest that direct leakage currents are, in fact, extremely low (at least for amorphous films) at typical operational electric fields ($\sim 1\text{ MV cm}^{-1}$) and electrical barrier heights are large enough to minimize carrier injection from the valence or conduction bands of the Si substrate. There is, however, significant confusion over the value of the dielectric constant of these films. LaAlO_3 and LaAlO_xN_y amorphous films have been deposited by pulsed laser deposition^{7,8} (laser ablation) onto Si substrates^{7,8} and Pt films.⁷ In the case of Si substrates, film/substrate interaction was evidenced, leading to dielectric constants⁷ ~ 4.9 , in the Pt case, $k \sim 25\text{--}27$ is quoted.⁷ Electron-beam evaporation methods have also been used,⁶ in which the films were deposited onto heated Si substrates (temperatures up to 800°C) and values of $k \sim 21\text{--}25$ quoted. This result is surprising since for the same range of substrate temperatures, the data in Refs. 7 and 8 show clear evidence for significant film/substrate interaction under these conditions in the form of an unidentified interfacial layer and, correspondingly, a reduced dielectric constant. Similar conclusions are arrived at from annealing studies presented in Ref. 4. Furthermore, attempts⁴ to reproduce the electron-beam-evaporated film experiments of Refs. 5 and 6 resulted in low dielectric constant values and evidence in the remnant target material (single-crystal LaAlO_3) of preferential evaporation in the form of blackened areas, where the electron beam had impacted. Such preferential evaporation is not unusual in mixed oxides since one cannot assume that all the components evaporate at the same rate from the molten target.

Finally, films deposited by sputtering from stoichiometric LaAlO_3 targets at room temperature⁴ onto Si substrates resulted in dielectric constants in the range 11–13. Other sputtering results⁹ yield a value of $k \sim 8.1$ although in this case, a 750°C annealing was performed and, again, this has been demonstrated to result in a measurable film/substrate interaction.⁴

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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 $3\text{--}5\ \Omega\ \text{cm}$ 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 $\sim -140\ \text{V}$ 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 (TRIM¹⁰). 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 $\sim 1.4\ \text{nm min}^{-1}$ and typical final film thicknesses were up to $\sim 112.0\ \text{nm}$, 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 $-100\ \text{V}$. 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 ($\lambda = 632.8\ \text{nm}$) ellipsometer, as was the refractive index of a bulk, single crystal LaAlO_3 sample. For the as-deposited (without substrate bias) films, we obtained $n \sim 1.78$ and for the single crystal, $n \sim 2.01$. 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 $\sim 0.1\ \mu\text{m}$ were deposited at a rate $\sim 3.3\ \text{nm min}^{-1}$ using a chamber pressure of 10 mTorr of Ar. The sputtering power

was again adjusted to give a target bias potential $\sim -140\ \text{V}$, which was calculated to yield stoichiometric sputtering. Following deposition, the O_2 plasma was established in the reactor (pressure $\sim 10\ \text{mTorr}$) using a microwave excitation system¹¹ and the substrate biased negatively dc. A constant dc mode of anodization was adopted with the total O^- and electronic current density being $\sim 1.2\ \text{mA cm}^{-2}$. LaAlO_3 films $\sim 80\text{-nm}$ 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 $\sim 0.5\ \mu\text{m}$ were deposited, as mentioned previously, but this time, the substrates were 4-in. Si wafers coated with a 370-nm-thick film of Si_3N_4 (plasma-enhanced chemical-vapor deposited). Since the objective of the experiment was to study thermal oxidation, the Si_3N_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 recrystallize 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 $\text{Cu K}_{\alpha 1}$ 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 ($C\text{--}V$) measurements using a Keithley 590 system at a frequency of 100 kHz on MOS capacitors formed by depositing $0.0078\ \text{cm}^2$ Al dots on the film surface. Typical accumulation capacitance of the MOS capacitors yielded maximum values of $k \sim 13$, 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

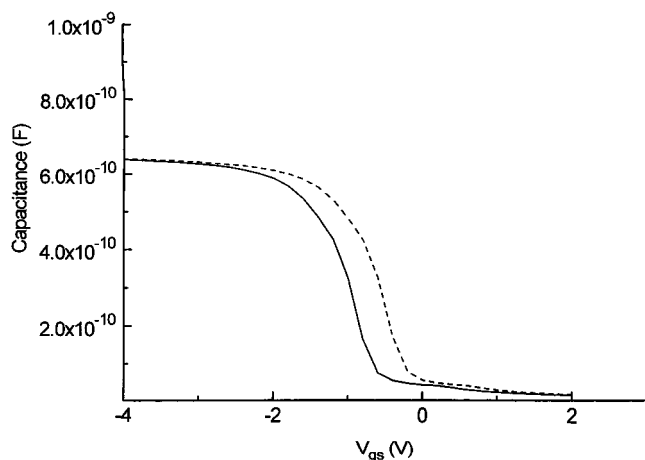


FIG. 1. Capacitance/gate electrode to substrate voltage (V_{gs}) curves measured at 100 kHz on MOS capacitors formed on 115-nm-thick films of amorphous LaAlO_3 deposited by sputtering. The films were annealed at 400°C for 30 min in N_2 postdeposition. (---) subjected to an electric field of -1 MV cm^{-1} 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.

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 shifts¹² 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°C for 30 min in flowing N_2 to reduce the level of trapped charge. Typical C - V curves resulting from annealed, sputtered LaAlO_3 samples are presented in Fig. 1. They were generated by first applying a bias electric field of 1 MV cm^{-1} (-1 MV cm^{-1}) for a period of 10 min then sweeping the voltage from positive (negative) to negative (positive). A hysteresis $\sim -0.74 \text{ V}$ is evident, which is consistent with the presence of some mobile, positively charged species in the annealed film. We underline the fact that the dielectric constant of the sputtered LaAlO_3 films was in the range 11–13

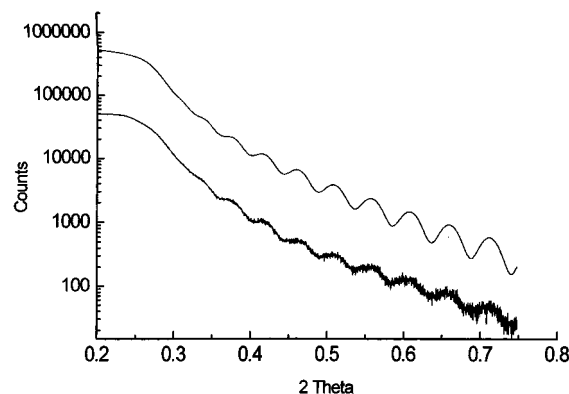


FIG. 2. Grazing incidence x-ray reflectivity signal (in counts) as a function of twice the angle of beam incidence (2θ) in nominally 71.8-nm-thick, sputtered, amorphous LaAlO_3 films. The density of the film determined from these measurements is $4.2 \pm 0.5 \text{ g cm}^{-3}$. The upper displaced curve is the fit obtained using the WINGIXA software package.

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°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 2θ 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, θ_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 through¹³

$$\theta_C^2/2 = \delta = 4.1516 \times 10^{-4} (\rho/ME^2) \sum c_j f_{1j}, \quad (1)$$

where the sum is over the different concentrations of the elements in the film (c_j) and f_{1j} are the associated atomic scattering factors, ρ 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 θ_C determined from the fit shown in Fig. 2, for example, we ascertain $\rho = 4.2 \text{ g cm}^{-3}$, this value is to be compared with the known single-crystal value of $\rho = 6.51 \text{ g cm}^{-3}$. 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 θ_C is dependent upon the x-ray energy and the accuracy of alignment of the sample.⁴ Although we were unable to measure θ_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 $\pm 0.3 \text{ g cm}^{-3}$. 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 experiments¹⁵ 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: $V_m(\text{crystal}) = 54.45 \text{ \AA}^3$ and $V_m(\text{amorph.}) = 84.5 \pm 6 \text{ \AA}^3$. 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 measurements¹⁶ 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 $\text{Zr}_x\text{Si}_{1-x}\text{O}_2$ ternary oxides.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 $4\text{--}4.4 \text{ g cm}^{-3}$. 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 equation¹⁸

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

whilst from the Clausius-Mossotti relationship¹⁹

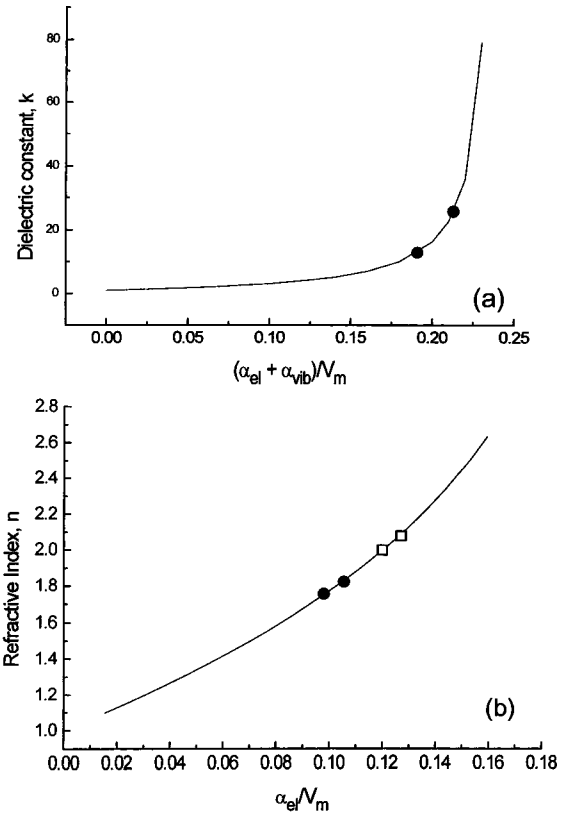


FIG. 3. (a) Variation of the dielectric constant, k , with $(\alpha_{el} + \alpha_{vib})/V_m$ from the Clausius-Mossotti equation. The filled circles indicate the experimental points corresponding to $k=13$ and $k=26$. (b) Variation of the refractive index, n , with α_{el}/V_m from the Lorentz-Lorenz equation. The filled circles represent the experimental points for the refractive index determined at a wavelength of 632.8 nm in the sputtered films and the open squares are the points corresponding to the range of single-crystal values.

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

Here α_{el} is the electronic component of the molecular polarizability and α_{vib} is the polarizability component usually associated with vibrational motion of the network.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 α_{el}/V_m and k as a function of $(\alpha_{el} + \alpha_{vib})/V_m$; 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 $(\alpha_{el} + \alpha_{vib})/V_m$ and α_{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 case²⁰ for LaAlO_3 , so we make negligible error in taking a

TABLE I. The electronic (α_{el}) and vibrational molecular (α_{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.

Structure	α_{el} [$\text{\AA}^3$]	$(\alpha_{el} + \alpha_{vib})$ [$\text{\AA}^3$]	α_{vib} [$\text{\AA}^3$]	V_m [$\text{\AA}^3$]
Crystal	(6.53–6.88)	11.61	(5.1–4.73)	54.45
Amorph.	$(8.3\text{--}8.8) \pm 0.6$	16.14 ± 1.1	7.59 ± 2.0	84.5 ± 6

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.²¹ 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 $\alpha_{el} < (\alpha_{el} + \alpha_{vib})$ and that, in general, α_{el} and $(\alpha_{el} + \alpha_{vib})$ 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 analysis²² of the structure and pressure dependence of the electronic polarizability, α_{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 volume²³ and dielectric constant²⁴ in Fig. 4. For simplicity, we represent the data in the form of a plot of $(\alpha_{el} + \alpha_{vib})$ versus V_m . Since volume-dependent refractive index data do not exist for this material, we cannot extract the individual molecular volume dependence of α_{el} and α_{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,²⁵ as shown in Fig. 5. In Fig. 5(a), we show the electronic polarizabilities estimated from the measured refractive indices of

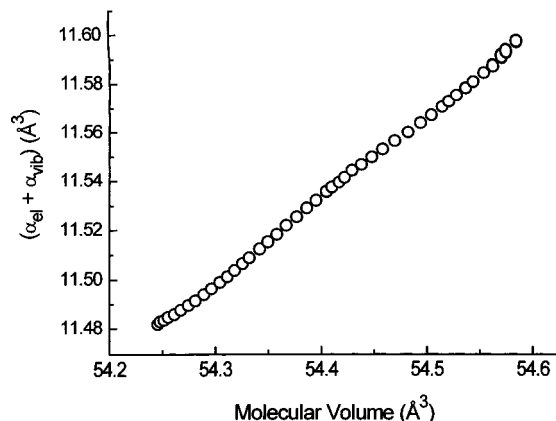


FIG. 4. Variation of the total molecular polarizability ($\alpha_{el} + \alpha_{vib}$) with molecular volume, V_m , in single crystals of LaAlO_3 .

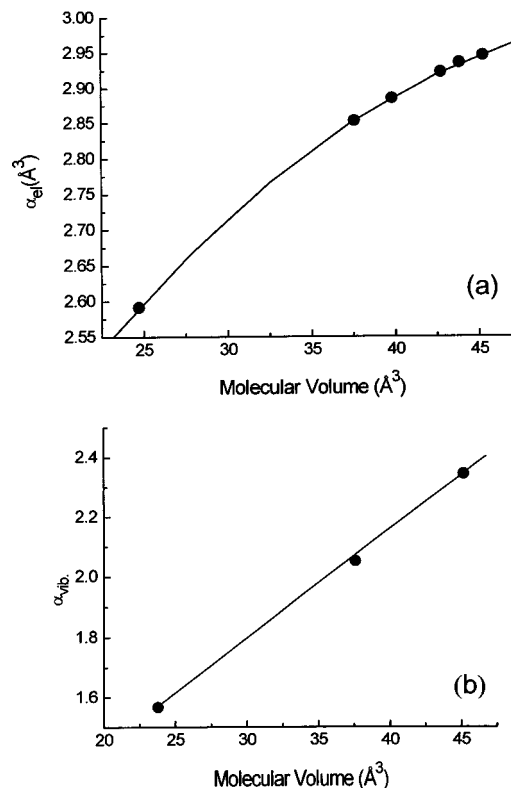


FIG. 5. (a) Variation of the electronic component of the polarizability of polymorphs of SiO_2 as a function of molecular volume, as determined from their refractive indices. (b) Variation of the vibrational component of the polarizability of three phases of SiO_2 , amorphous, α -quartz, and stishovite, as determined from their dielectric constants.

various amorphous and crystalline phases. Clearly, α_{el} increases as the molecular volume increases. Similarly, in Fig. 5(b), we show the data for $(\alpha_{el} + \alpha_{vib})$ as a function of molecular volume. In this case, experimental values for the dielectric constants were only available for amorphous SiO_2 and α -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,²⁶ 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

$$(\alpha_{el} + \alpha_{vib})_{M_A M_Q O_{B+P}} = c(\alpha_{el} + \alpha_{vib})_{M_A O_B} + (1 - c)(\alpha_{el} + \alpha_{vib})_{M_Q O_P}, \quad (4)$$

where c is the effective concentration of $M_A O_B$ molecules and $(1 - c)$ is the concentration of $M_Q O_P$ 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 $M_A M_Q O_{B+P}$. 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.

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.²² 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.

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