Vibrational properties of bulk LaAlO$_3$ from Fourier-transform infrared ellipsometry

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ABSTRACT

We used Fourier-transform infrared spectroscopic ellipsometry to determine the dielectric function of twinned single-crystalline bulk lanthanum aluminate at 300 K in the region of lattice vibrations from 250 to 1000 cm^{-1}. We fit the experimental data using a classical sum of Lorentz oscillators as well as a factorized model. We were able to determine the parameters of five infrared-active optical phonons within our spectral range. Transverse phonons appear as peaks in the imaginary part of the dielectric function which are clearly visible without fitting. By transforming the data to obtain the loss function, we are able to observe the longitudinal phonons as peaks in the imaginary part. The polar nature of LaAlO$_3$ causes a strong splitting between the transverse optical (TO) and longitudinal optical (LO) phonon energies. We report energies, amplitudes and broadenings of five TO/LO phonon pairs and compare the two models used to describe the data.

1. Introduction

Lanthanum aluminate (LaAlO$_3$) is widely used as a substrate material in oxide epitaxy [1]. Recently, thin films of LaAlO$_3$ have drawn considerable attention owing to the discovery of a two-dimensional electron gas in LaAlO$_3$/SrTiO$_3$ heterostructures [2–4]. During the early development of high-k gate dielectrics, the semiconductor industry considered LaAlO$_3$ as a replacement for SiO$_2$ as a gate dielectric, mostly because of its close lattice match with Si [5–7].

LaAlO$_3$ is a polar perovskite with a distorted cubic crystal structure. It can be viewed as an alternating stack of positively charged LaO and negatively charged AlO$_2$ planes. The distortions lead to a rhombohedral structure with space group R$\bar{3}$c or D_{3d}^6 (space group 167) at room temperature [8–12]. The rhombohedral lattice constants of LaAlO$_3$ are found to be $a = b = 5.365$ Å and $c = 13.111$ Å using neutron powder diffraction [9,10]. The long-wavelength optical phonon modes expected for this crystal structure are given by the factor group [12–14]

$$\Gamma\left(D_{3d}^6\right) = 2A_{1u} + 3A_{2g} + A_{1g} + 3A_{2u} + 4E_g + 5E_u. \tag{1}$$

The relationship between the cubic $Pm\bar{3}m$ or O_h^1 perovskite phonons and the crystal field splittings due to the rhombohedral distortions are summarized in Table 1 [12–14].

Near 800 K, LaAlO$_3$ transforms from the rhombohedral to the cubic crystal structure [9,10,12,15]. Raman measurements of low-energy phonons with energy below 200 cm^{-1} have revealed that there is a soft phonon [9,12] associated with this transition. The energy splitting of

the lowest-energy E_g/A_{1g} phonon pair (representing the rotation of an AlO$_6$ octahedron) decreases with increasing temperature. At 800 K, they merge into a zero-frequency phonon with F_{2u} symmetry [9,12].

The vibrational structure of LaAlO$_3$ has been studied both theoretically and experimentally. Abrashev et al. [14] calculated the long-wavelength optical phonon frequencies using a semi-empirical shell model and plotted diagrams showing the displacement patterns of the atoms involved in the vibration. They also included the splittings between transverse (TO) and longitudinal (LO) optical phonons due to the long-range polar interactions. More recently, Delugas et al. [16] presented an ab initio density-functional and self-interaction-corrected calculation of the optical phonon frequencies, in which the TO/LO splittings were ignored. None of these calculations are sufficiently accurate for comparison with experimental results for the phonon frequencies.

The factor group analysis in Eq. (1) describes the symmetry of the optical phonons and how they can be observed experimentally. The results are summarized in Table 1: One A_{1g} mode and four E_g modes are Raman active. Three A_{2u} and five E_u modes are infrared active and can be observed with Fourier-transform infrared (FTIR) ellipsometry. Finally, two A_{1u} modes and three A_{2g} modes are silent and not accessible experimentally using first-order Raman or infrared measurements.

While most Raman spectroscopy studies have focused on the temperature dependence of the A_{1g} and E_g soft modes and their implications about the phase transition from the rhombohedral to the cubic crystal structure [9,12,14], the higher-energy Raman modes have also been investigated [12,14]. Four Raman modes have clearly been identified, while the assignment of the fifth mode is controversial. See Table 1 for a summary of experimental results.

The IR-active modes have been investigated by infrared reflectance or transmittance measurements, usually followed by fitting of the dielectric function as a sum of Lorentz oscillators [13,17–19]. Three pairs

Table 1
Summary of transverse optical phonon modes for LaAlO$_3$ at 300 K. All energies are listed in units of cm^{-1}.

R$\bar{3}$c symmetry	Pm$\bar{3}$m symmetry	Activity	Pattern	Energy (exp)
E$_g$	F$_{2u}$(R)	Raman	AlO$_6$	33[a]
A$_{1g}$	F$_{2u}$(R)	Raman	AlO$_6$	123[b]
E$_g$	F$_{1u}$(R)	Raman	La	152[b]
E$_g$	F$_{1u}$(R)?	Raman	O	470[b] (?)
E$_g$	E$_u$(R)?	Raman	O	487[b]
A$_{2u}$	F$_{1u}$(Γ)	IR	AlO-La	188(1)[c]
A$_{2u}$	F$_{1u}$(Γ)	IR	O bend	427.0(1)[c]
A$_{2u}$	F$_{1u}$(Γ)	IR	O stretch	650.79(5)[c]
E$_u$	F$_{1u}$(Γ)	IR	AlO-La	188(1)[c]
E$_u$	F$_{2u}$(Γ)	IR	O	weak
E$_u$	F$_{1u}$(Γ)	IR	O bend	427(1)[c]
E$_u$	F$_{2g}$(R)	IR	Al	495.72(1)[c]
E$_u$	F$_{1u}$(Γ)	IR	O stretch	708.2(9)[c]
A$_{1u}$	F$_{2u}$(Γ)	silent		NA
A$_{1u}$	F$_{2g}$(R)	silent	Al	NA
A$_{2g}$	F$_{1u}$(R)	silent	La	NA
A$_{2g}$	F$_{1u}$(R)	silent	O	NA
A$_{2g}$	A$_{2u}$(R)	silent		NA

[a] Ref. [12].
[b] Ref. [14].
[c] This work using Eq. (4).

of A_{2u}/E_u modes, arising from the crystal field splitting of the three cubic F$_{1u}$(Γ) modes, lead to strong features in the spectra [14]. One weak zone-folded E_u mode is also seen clearly, while the second E_u mode (derived from F_{2u}, which is silent in the cubic parent structure) has been considered too weak to be observable [14]. There is considerable disagreement in the literature about the exact phonon energies, amplitudes, and broadenings used to fit experimental spectra.

In this work, we determined the energies, broadenings, and amplitudes of the infrared-active optical phonons with very high accuracy using Fourier-transform infrared ellipsometry. We also describe the symmetries of all phonons and their relationships, such as rhombohedral splittings and the relationship to their cubic phonon counterparts.

2. Experiment and models

Two single-sided polished, 2-inch LaAlO$_3$ wafers with 0.5 mm thickness and (100) surface orientation were obtained commercially [20]. To reduce the reflections from the backside, one wafer was roughened further using a bead blaster. Our substrates are twinned and the surface orientation refers to the pseudo-cubic structure. Additional information about the samples and their properties are given in our earlier work [21], where we also report the dielectric function of LaAlO$_3$ from 0.8 to 6.6 eV between 77 and 700 K. Most importantly for the present work, our earlier research found $\epsilon_\infty = 4.12 \pm 0.01$ at 300 K.

Infrared ellipsometry measurements were performed on a J.A. Woollam FTIR-VASE variable angle of incidence ellipsometer at the Center for Integrated Nanotechnologies user facility. This instrument is based on a fixed analyzer (at 0° and 180°), a fixed polarizer (at ± 45°), and a rotating compensator. To increase accuracy, two fixed positions for the analyzer and polarizer were chosen (four-zone measurements), as this cancels experimental errors to first order in the analyzer and polarizer position. We measured at four angles of incidence: 60°, 65°, 70°, and 75°. Nominally, the instrument reports data between 250 and 8000 cm^{-1} but we restrict our analysis to the region of the lattice vibrations between 250 and 1000 cm^{-1}. We did not observe features in the spectra above 1000 cm^{-1} other than normal dispersion. In the spectral range around 6000 cm^{-1}, our FTIR ellipsometry results are consistent with our earlier near-IR work [21].

For various reasons, FTIR ellipsometry measurements on a bulk LaAlO$_3$ wafer are quite challenging. On one hand, the reflectance of LaAlO$_3$ is quite low (about 11% at normal incidence in the mid-IR), much lower than for a bulk semiconductor or for a thin film on Si. In

the region of the lattice vibrations, the reflectance becomes very small [18,22] near 300, 620, and 800 cm^{-1}. On the other hand, the phonon broadenings in LaAlO$_3$ are very low (near 4 cm^{-1} or less). We therefore select a resolution of 2 cm^{-1} for the FTIR spectrometer. These conditions create noise below 350 and near 800 cm^{-1}. We are thus forced to select a data acquisition time of eight hours to improve the signal to noise ratio, using 20 FTIR scans per spectrum and 15 spectra for each revolution of the rotating compensator.

Spectroscopic ellipsometry measures the ellipsometric angles ψ and Δ as a function of photon energy. These ellipsometric angles and the Fresnel reflectance ratio $\rho = e^{i\Delta}\tan\psi$ are related to the pseudo-refractive index $\hat{n}$ and the pseudo-dielectric function $\hat{\epsilon} = \hat{n}^2$ of the sample through [23,24]

$$\rho = \frac{(\hat{n}\ cos\ \phi_0 - cos\ \phi_1)\ (cos\ \phi_0 + \hat{n}\ cos\ \phi_1)}{(\hat{n}\ cos\ \phi_0 + cos\ \phi_1)\ (cos\ \phi_0 - \hat{n}\ cos\ \phi_1)}, \tag{2}$$

where ϕ_0 is the angle of incidence and ϕ_1 the angle of refraction. For an ideal sample without surface overlayers, $\hat{n}$ and $\hat{\epsilon}$ are equal to the refractive index n and the dielectric function $\epsilon = n^2$. Δ equals zero or π for an ideal transparent substrate (for an insulator outside of the region of lattice vibrations), because all quantities in Eq. (2) are real. For our LaAlO$_3$ substrates, the surface overlayers are very thin (see Table I in Ref. [21]). The surface roughness is between 15 and 20 Å for our samples.

Normally, spectroscopic ellipsometry requires extensive data analysis to determine the optical constants (the complex dielectric function $\epsilon = n^2$) from the ellipsometric angles. This is not the case for our analysis. We can simply convert the measured ellipsometric angles into the dielectric function using Eq. (2), because the effect of surface roughness is negligible. The transverse optical (TO) phonons appear as peaks in the dielectric function [25,26]. Longitudinal optical (LO) vibrations are possible at energies where $\epsilon(\omega) = 0$. LO phonons therefore appear as peaks in the loss function Im$(-1/\epsilon)$.

To determine accurate phonon energies, amplitudes, and broadenings, we write the dielectric function ϵ as a function of photon energy ω as a sum of uncoupled damped harmonic oscillators [25–27]

$$\epsilon(\omega) = \epsilon_\infty + \sum_i \frac{A_i\omega_i^2}{\omega_i^2 - \omega^2 - i\gamma_i\omega}. \tag{3}$$

The first term $\epsilon_\infty = 4.12 \pm 0.01$ (see Ref. [21]) describes the contributions of electronic transitions to the dielectric function. In principle, we expect eight terms in the sum, one for each infrared active phonon. In practice, some of these phonons may be very weak, while others may be degenerate. Normally, we use five oscillators as described below.

The Lorentz model (3) is derived for charges oscillating in an electric field. This model is classical and it assumes that the frictional force acting on the charge is proportional to their velocity [25]. This results in harmonic damping and a constant broadening term. (The LO broadening parameter is generally different from the TO broadening, most often larger, but not independent.)

The anharmonic coupling of phonons causes the decay of optical phonons into acoustic or other optical phonons with lower energy. Usually, the decay products are zone-edge phonons with a high density of states. If the splitting between the TO and LO phonons is large, then they will have different decay paths and their damping constants γ_{TO} and γ_{LO} may differ. Therefore, the uncoupled Lorentz oscillator model (3) often gives a good description of experimental data, which can be improved by assigning different damping parameters to LO and TO phonons yielding [26–29]

$$\epsilon(\omega) = \epsilon_\infty \prod_i \frac{\omega_{i,LO}^2 - \omega^2 - i\gamma_{i,LO}\omega}{\omega_{i,TO}^2 - \omega^2 - i\gamma_{i,TO}\omega} \tag{4}$$

as the functional form for the infrared dielectric function of insulators. If we set $\gamma_{i,TO} = \gamma_{i,LO} = \gamma_i$, then both descriptions (3) and (4) become