Density dependence of the room temperature thermal conductivity of atomic layer deposition-grown amorphous alumina (Al₂O₃)

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We report on the thermal conductivity of atomic layer deposition-grown amorphous alumina thin films as a function of atomic density. Using time domain thermoreflectance, we measure the thermal conductivity of the thin alumina films at room temperature. The thermal conductivities vary ~35% for a nearly 15% change in atomic density and are substrate independent. No density dependence of the longitudinal sound speeds is observed with picosecond acoustics. The density dependence of the thermal conductivity agrees well with a minimum limit to thermal conductivity model that is modified with a differential effective-medium approximation. © 2014 AIP Publishing LLC.

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we only briefly describe the technique here. TDTR is a non-contact optical pump-probe technique that uses a short-pulsed laser to both produce and monitor heating events on a surface of a sample. The laser output from our femtosecond oscillator is separated into “pump” and “probe” paths, in which the relative optical path lengths are adjusted with a mechanical delay stage. This system allows for picosecond temporal resolution of the thermoreflectivity on the sample surface. We frequency double the wavelength of the pump path to 400 nm to assist with optical filtering of the pump light.\textsuperscript{22} The pump path is modulated at 11.39 MHz and a radio-frequency lock-in amplifier is used to detect the change in reflectivity of the probe beam at the modulation frequency of the pump heating event. The sample surface is coated with a thin aluminum film so that the change in reflectivity of the sample surface is an indication of the change in temperature of the Al transducer, which is driven by the thermal properties of the \(a\)-Al\(_2\)O\(_3\) and the substrate. We monitor the ratio of the in-phase to out-of-phase voltage \((V_{\text{in}}/V_{\text{out}})\). An example of a TDTR response on an Al/\(a\)-Al\(_2\)O\(_3\)/quartz sample is shown in Fig. 2.

Analyses accounting for pulse accumulation when using a Ti:sapphire oscillator, and the relationship between this temporal thermal response and the thermophysical properties of the sample, have been previously detailed.\textsuperscript{21,23–25} In our measurements, the thermal response at the surface is related to the thermal conductivities and heat capacities of the Al transducer, the \(a\)-Al\(_2\)O\(_3\) thin film and the substrate, along with the thermal boundary conductances across the Al/\(a\)-Al\(_2\)O\(_3\) and \(a\)-Al\(_2\)O\(_3\)/substrate interfaces. We assume literature values for the heat capacities of each of the layers;\textsuperscript{26,27} the heat capacities of the \(a\)-Al\(_2\)O\(_3\) thin films are then scaled proportional to their reduced atomic densities. We use literature values for the thermal conductivities of the substrates.\textsuperscript{28} Due to our pump and probe spot sizes (pump and probe 1/e\(^2\) radii of 25 \(\mu\)m and 10.5 \(\mu\)m, respectively) and our pump modulation frequency, we are not sensitive to \(\kappa\) of the Al transducer. We therefore have three unknowns in the model: the thermal boundary conductances across each interface and \(\kappa\) of \(a\)-Al\(_2\)O\(_3\). However, we are negligibly sensitive to the thermal boundary conductances at each interface due to a combination of the layer thicknesses, the low thermal conductivity of the \(a\)-Al\(_2\)O\(_3\), and the modulation frequency of the pump beam. Thus, our measurements are most sensitive to \(\kappa\) of the \(a\)-Al\(_2\)O\(_3\) thin films.

We use picosecond acoustic techniques to measure the longitudinal sound speeds in the \(a\)-Al\(_2\)O\(_3\) thin films.\textsuperscript{29,30} The sound speeds provide a relative measure of how the moduli of the \(a\)-Al\(_2\)O\(_3\) thin films change with density. Piezoreflectance provides a signal in the TDTR response during the first few tens of picoseconds when the reflection of a laser-induced strain wave off of the Al/\(a\)-Al\(_2\)O\(_3\) and \(a\)-Al\(_2\)O\(_3\)/substrate interfaces returns to the surface of the Al transducer. The reflection of the strain wave allows for measurement of the longitudinal sound speed of continuum vibrations in the \(a\)-Al\(_2\)O\(_3\). Interpretation of the picosecond acoustic data is based on the acoustic impedances of the materials comprising the interface. As detailed previously,\textsuperscript{31,32} if a strain wave in the metal film is reflected off of an interface of a material with a higher acoustic impedance than that of the metal film, the wave will undergo a \(\pi\) phase shift and will appear as a “dip” in the TDTR data.

As expected based on acoustic impedances for the Al/\(a\)-Al\(_2\)O\(_3\) and \(a\)-Al\(_2\)O\(_3\)/quartz interfaces, we observe a “hump” followed by a “dip” in the picosecond acoustic response. An example of an isolated picosecond acoustic response and the picosecond acoustic residuals are plotted in the left-most and right-most inset of Fig. 2, respectively. From the time difference between the “hump” and “dip,” we notice that the acoustic response and the thermal response are delayed due to the thermal boundary conductances. However, due to the low thermal conductivity of the \(a\)-Al\(_2\)O\(_3\), we observe that the thermal boundary conductances are lower than the acoustic impedances.
along with the measured film thicknesses, we calculate the longitudinal sound speed of the $\alpha$-Al$_2$O$_3$ samples to be $8700 \pm 160$ m s$^{-1}$, with no discernible differences or trends among the samples. The longitudinal sound speed of $\alpha$-Al$_2$O$_3$ has not previously been reported, however, our measured values are within 3% of the longitudinal sound speed of sound in $\alpha$-phase alumina ceramic ($8800$ m s$^{-1}$). The measured longitudinal sound speeds are given in the Supplementary Material; it is noted that, due to the lack of a discernable trend in the measured sound speeds of the samples, the average value of $8700$ m s$^{-1}$ is considered for all samples. Since no density dependence of the longitudinal sound speed is detected within the resolution of our experimental technique, due to the long-range isotropic nature of the amorphous systems, any density dependence of the shear modulus could be considered anomalous. Therefore, we adopt the transverse sound speed of sound in $\alpha$-phase alumina ceramic for all of the samples considered.

Figure 3(a) plots the measured thermal conductivity as a function of atomic density for our ALD $\alpha$-Al$_2$O$_3$ samples. Before discussing the results, we note that the thermal conductivities of the ALD $\alpha$-Al$_2$O$_3$ thin films, presented in the Supplementary Material, are independent of the substrate. We observe an appreciable dependence of the thermal conductivity on density: a $\sim 15\%$ change in density results in a $\sim 35\%$ change in thermal conductivity. A more pronounced density dependence was observed in previous measurements of thermal conductivity of $\alpha$-Al$_2$O$_3$ thin films grown by Lee et al. (also shown in Fig. 3(a)); however, in the study by Lee et al. the variation with density was observed among samples grown by different techniques. Our results elucidate that this density dependence is intrinsic to ALD $\alpha$-Al$_2$O$_3$. Furthermore, the samples measured by Lee et al. were much thicker than the samples studied here and given the relatively close agreement between our measurements and the thermal conductivity of the thicker dc-sputter deposition-grown $\alpha$-Al$_2$O$_3$ we conclude that size effects do not affect $\kappa$ in our ALD-grown $\alpha$-Al$_2$O$_3$ samples at these thicknesses.

As is clear from our measurements, alike other amorphous materials,\textsuperscript{6-10} the thermal conductivity of $\alpha$-Al$_2$O$_3$ decreases upon reduction of atomic density. To investigate the effect of atomic density on $\kappa$, we turn to the minimum limit to thermal conductivity\textsuperscript{12} which has been used as a baseline model to compare to experimental data of amorphous systems for several decades. Within the framework of the minimum limit model, the lifetime of all oscillators is assumed to be one half of the period of vibration, i.e., $\tau = \pi/\omega_0$, where $\omega_0$ is the angular frequency of oscillation. The thermal conductivity in this amorphous-limit approximation, $\kappa_{\text{min}}$, is the sum of three integrals accounting for three sound polarizations (one longitudinal and two transverse) given by

$$\kappa_{\text{min}} = \left(\frac{\pi}{6}\right)^{1/3} k_B R^{2/3} \sum_i c_i \left(\frac{T}{\Theta_i}\right)^2 \int_0^{\Theta_i/(\omega_0)} x^3 e^x \frac{1}{(e^x - 1)^2} dx,$$

where $i$ is the polarization index, $c_i$ is the sound speed, $\Theta_i$ is the Debye temperature, defined as $\Theta_i = c_i/(\hbar/k_B)(\pi^2 n)^{1/3}$, $k_B$ is the Boltzmann constant, $\hbar$ is the reduced Planck constant, and $x = \Theta_i/T$. As evident from Eq. (1), $\kappa_{\text{min}}$ depends on only two material dependent parameters: the polarization-dependent continuum sound speeds and the atomic density of the material. We show calculations of Eq. (1) for $\alpha$-Al$_2$O$_3$, at room temperature, as a function of atomic density as the solid line in Fig. 3(a). For these calculations, we use $c_j$ from our picosecond acoustic measurements and $\Theta_j$ from Ref. 33. We note that our picosecond acoustic analysis confirms that the sound speed in $\alpha$-Al$_2$O$_3$ is independent of atomic density for our samples. To further evaluate this form of the minimum limit to thermal conductivity applied to $\alpha$-Al$_2$O$_3$, we normalize the calculations of Eq. (1) to our data, shown in Fig. 3(b). The density dependent thermal conductivity predictions of Eq. (1) do not capture the trends in our measured data.

In efforts to more closely describe the data over a larger density range, we apply the DEM approximation to the minimum limit model. DEM is an effective-medium approximation derived to account for the effects of multiphase nature on heterogeneous physical systems.\textsuperscript{10,35} The DEM proposes that the thermal conductivity scales with atomic density as

$$\kappa_{\text{DEM}} = \left(\frac{R}{\rho_{\text{bulk}}}\right)^{3/2} \kappa,$$

Figure 3 plots Eq. (2) evaluating $\kappa_{\text{DEM}}$ as a function of atomic density and assuming $\kappa$ as either the measured value for the dc-sputtered film by Lee et al. (dotted line) or $\kappa_{\text{min}}$ explicitly from Eq. (1) (dashed line). For the calculations of Eq. (2) shown in Fig. 3(a), we assume a bulk atomic density of $1.0366 \times 10^{29}$ atoms m$^{-3}$, corresponding to the highest density of $\alpha$-Al$_2$O$_3$ measured by Lee et al.\textsuperscript{11}

Clearly, the density dependence of the thermal conductivity trend in our ALD $\alpha$-Al$_2$O$_3$ samples is steeper than that
predicted by Eq. (1), as is apparent by comparing the normalized data and models in Fig. 3(b). Both of our DEM-based thermal conductivity calculations exhibit much better agreement with our measured data than the traditional minimum limit approach (Eq. (1)). Furthermore, where the DEM calculations of thermal conductivity require the knowledge of the thermal conductivity of the “fully dense” phase of $\alpha$-Al$_2$O$_3$, our approach of using the DEM with Eq. (1) only requires knowledge of atomic density and sound velocities. We have found similar agreement using this DEM-modified minimum limit approach to model low density silica, demonstrating the promise in this modeling approach to predict the thermal conductivity of low density amorphous solids.

In summary, we have measured the room temperature thermal conductivity of ALD-grown $\alpha$-Al$_2$O$_3$ thin films using time-domain thermoelrectance. The thermal conductivities of the thin alumina films at room temperature, which are substrate independent, vary by ~35% for a ~15% change in atomic density. We do not observe any density dependence of the longitudinal sound speeds as measured with picosecond acoustics. From this, we conclude that scaling of the sound speed is not the origin of the density dependence of $\kappa$ over this density regime in amorphous alumina. The density dependence of the thermal conductivity agrees well with a minimum limit to thermal conductivity model that is modified with a differential effective-medium approximation.

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20See supplementary material at http://dx.doi.org/10.1063/1.4885415 for a table of relevant physical properties for the samples studied.