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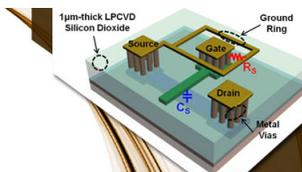
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Systematically controlling Kapitza conductance via chemical etching

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We measure the thermal interface conductance between thin aluminum films and silicon substrates via time-domain thermoreflectance from 100 to 300 K. The substrates are chemically etched prior to aluminum deposition, thereby offering a means of controlling interface roughness. We find that conductance can be systematically varied by manipulating roughness. In addition, transmission electron microscopy confirms the presence of a conformal oxide for all roughnesses, which is then taken into account via a thermal resistor network. This etching process provides a robust technique for tuning the efficiency of thermal transport while alleviating the need for laborious materials growth and/or processing. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3695058>]

Advances in micro- and nano-technology have led to the development of a wide array of devices, all of which share one common feature: characteristic length scales on the order of a few to hundreds of nanometers. At the same time, this ongoing trend of miniaturization has had a significant auxiliary impact on the thermal transport properties of modern devices as well, insofar as they are now dictated more so by the interfaces between constituent materials than by the materials themselves.¹ As a result, a significant effort has been put forth to both investigate and explain the behavior of thermal transport across solid-solid interfaces, the efficiency of which can be described by the thermal interface conductance, or Kapitza conductance, h_K .² Prior works have demonstrated how the mismatch of phonon spectra,^{3–7} interfacial chemistry and bonding,^{8–15} crystallographic orientation,^{16–21} and interfacial roughness^{5,22–28} can each influence Kapitza conductance.

Generally speaking, the expression “interfacial roughness” can include one or a combination of several unique structural features, including compositional mixing, dislocations, interstitials, deviations from crystallinity, or nanometer-scale geometric facets. When compared to that at a nominally “smooth” interface, certain combinations of these features have been found to enhance Kapitza conductance,^{5,28} while others have been shown to reduce it.^{5,22,24–26} Furthermore, it has been shown that thermal transport efficiency can be effectively tuned if precise control over interfacial roughness is possible. For example, Pernot *et al.*²⁹ and Hopkins *et al.*²⁵ demonstrated that controlling interface roughness through quantum-dot patterning can reduce the effective thermal conductivity of silicon-based superlattices and the Kapitza conductance at aluminum-silicon interfaces, respectively. However, other methods of interface roughening, including chemical treatments²⁶ and back-sputtering,²² have not yet been shown to provide precise enough control over roughness to systematically and repeatably alter interface conductance.

In this letter, we demonstrate that chemically etching substrates prior to thin-film deposition can, in fact, provide the precise control over interfacial roughness required to systematically tune Kapitza conductance without the need for laborious materials growth and/or processing, e.g., quantum-dot patterning. Cross-section transmission electron microscopy (TEM) confirms that the roughness induced by chemical etching does not lead to compositional mixing between aluminum and silicon due to the presence of a thin and conformal native oxide (<2 nm), nor a deviation from crystallinity in either the film or the substrate. The Kapitza conductances at four aluminum-silicon interfaces of varying roughness are measured by time-domain thermoreflectance (TDTR) and are correlated to the root-mean-square (RMS) surface roughness of the interface. It is found that Kapitza conductance exhibits an exponential dependence on interface roughness consistent with prior experimental data and as described by previous models.^{24,25} In addition, it is found that as roughness increases, the temperature dependence of Kapitza conductance is substantially suppressed.

We prepared four different aluminum-silicon interfaces by evaporating 80 nm of aluminum (vacuum pressure < 10×10^{-7} Torr) on silicon substrates. The silicon wafers are each 500 μm thick, phosphorus doped (*n*-type), and single crystalline (100). Prior to deposition, all substrates were first cleaned with methanol and acetone and then rinsed in de-ionized water. Sample I received no further processing, whereas samples II through IV were treated in buffered oxide etch (BOE) to remove the native oxide and then submersed in tetramethyl ammonium hydroxide (TMAH) at 80 °C in order to roughen the substrates in a fashion similar to Ref. 26. After surface pretreatment, all samples were left exposed to ambient for 24 h to allow a native oxide to reform on the surface. The RMS surface roughnesses, δ , of the samples were determined prior to aluminum thin film deposition via atomic force microscopy (AFM). Substrate surface roughness increased with the time submersed in the TMAH solution. The measured RMS surface roughnesses and room-temperature Kapitza conductances of the four samples, along with the repeatability of the measurements, are listed in Table I.

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TABLE I. Root-mean-square roughnesses and room-temperature Kapitza conductances of the four Al:Si interfaces studied within this work. The reported standard deviations represent the repeatability of the measurement, i.e., the deviation about the mean value of several measurements made on a single sample.

Sample	δ (nm)	h_K @ 300 K ($\text{W m}^{-2} \text{K}^{-1}$)
I	$<0.1 \pm 0.0$	193 ± 18
II	0.6 ± 0.3	182 ± 15
III	6.5 ± 2.3	131 ± 13
IV	11.4 ± 3.1	90 ± 13

Cross-sectional TEM was implemented to further characterize the roughnesses and quality of the interfaces post aluminum thin film deposition. Micrographs of samples I and IV at two different magnifications are shown in Fig. 1. The micrographs indicate that regardless of roughness, an approximately 1.75 nm thick conformal oxide layer covers the silicon substrates after 24-h exposure to ambient. This oxide layer prohibits any apparent interdiffusion or compositional mixing of aluminum and silicon at the interface, as opposed to earlier studies of chromium-silicon interfaces where Auger electron spectroscopy confirmed a significant mixing of species within roughly 10 nm of the interface.²² In addition, the micrographs indicate that the aluminum thin films exhibit a columnar crystal structure regardless of substrate roughness, and that the crystallinity of the substrate is undisturbed by the etch. Again, this is contrary to the aforementioned chromium-silicon study, where TEM indicated the chromium films were amorphous.²²

We measured the Kapitza conductance across the four aluminum-silicon interfaces with TDTR.^{30,31} TDTR is a non-contact, pump-probe technique in which a modulated short pulse laser (full-width half max ≈ 100 fs) is used to create a heating event (pump) on the surface of a sample. This heating event is monitored with a time-delayed probe pulse. The change in the reflectivity of the probe at the modulation frequency of the pump is detected through a lock-in amplifier; the change in reflectivity is related to the change in temperature at the sample surface. This temporal thermal response is then related to the thermophysical properties of the sample of interest. We monitor the thermoreflectance signal over 4.5 ns of probe delay time. The deposited energy takes approximately 100 ps to propagate through the aluminum film, after which the response is related to the heat flow across the aluminum-silicon interface and the thermal effusivity of the silicon substrate. Our specific experimental setup is described in detail elsewhere.³²

We monitor is the ratio of the in-phase to the out-of-phase voltage recorded by the lock-in amplifier ($-V_{\text{in}}/V_{\text{out}}$), which is related to the temperature change on the surface of the sample. The thermal model and analysis used to predict the temperature change and subsequent lock-in ratio are described in detail in references 30, 32, and 33. In short, the model accounts for heat transfer in composite slabs³⁴ from a periodic, Gaussian source (pump) convoluted with a Gaussian sampling spot (probe).^{30,34} The pump is modulated at 11 MHz and the pump and probe $1/e^2$ radii are $7.5 \mu\text{m}$. The temperature change at the surface is related to the thermal conductivity and heat capacity of the composite slabs, as

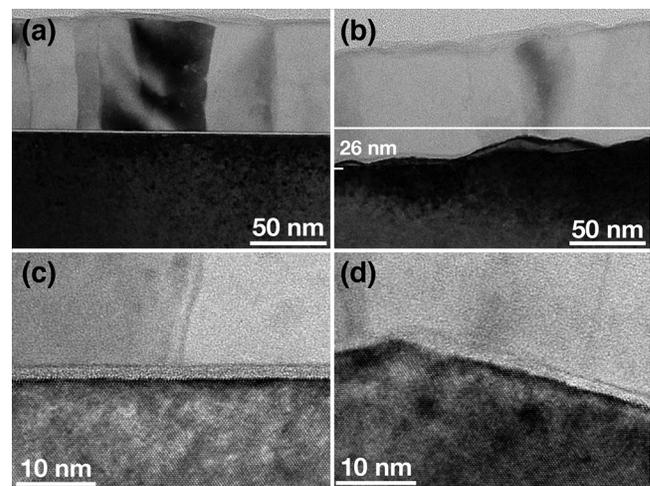


FIG. 1. Cross sectional TEM micrographs of samples I (a and c) and IV (b and d) Al:Si interfaces at two different magnifications. The micrographs indicate show that regardless of roughness, a ≈ 1.75 nm conformal oxide layer covers the Si substrates after 24h exposure to ambient. This oxide layer prohibits any noticeable interdiffusion or compositional mixing of species near the interface. Lastly, the evaporated Al thin film exhibits a columnar crystal structure regardless of substrate surface roughness, while the crystallinity of the substrate is undisturbed.

well as the Kapitza conductance between each slab. Although dominated by the aluminum-silicon Kapitza conductance,³² the TDTR signal is also related to the heat capacity and thickness of the Al film and the thermal properties of the silicon substrate (which, due to time delay and modulation frequency can be taken as semi-infinite in this work). We first assume bulk values for the properties of the film and substrate³⁵ and we verify the aluminum film thickness via picosecond acoustics.^{36,37} We then adjust the thermal conductivity of the substrate during our analysis to achieve a better fit between the model and the data.³

Figure 2 shows the measured Kapitza conductance across the four aluminum-silicon interfaces as a function of temperature (filled symbols). In addition, we plot the Kapitza conductance at a nominally flat and oxide-free aluminum-silicon interface as reported in Ref. 38 (open circles). As the data indicate, even a thin oxide layer at the interface substantially reduces the effective Kapitza conductance ($>50\%$ reduction at room temperature). In addition, these two data sets demonstrate significantly different temperature dependencies, suggesting that the oxide layer inhibits multiple-phonon scattering events which would otherwise contribute to Kapitza conductance.^{6,7} Similarly, comparing the four data sets of the present study, increased interface roughness both reduces the magnitude of Kapitza conductance as well as suppresses its temperature dependence, i.e., Kapitza conductance is less temperature dependent as interface roughness increases.

In addition to the data, several different predictive models are plotted as well. All models are calculated assuming that elastic phonon-phonon interactions dominate Kapitza conductance, i.e., phonons in silicon at frequencies higher than the maximum phonon frequency of aluminum do not participate in transport. The diffuse mismatch model³⁹ (DMM) is calculated using an approach we outlined previously in Ref. 40, where the vibrational properties of film and

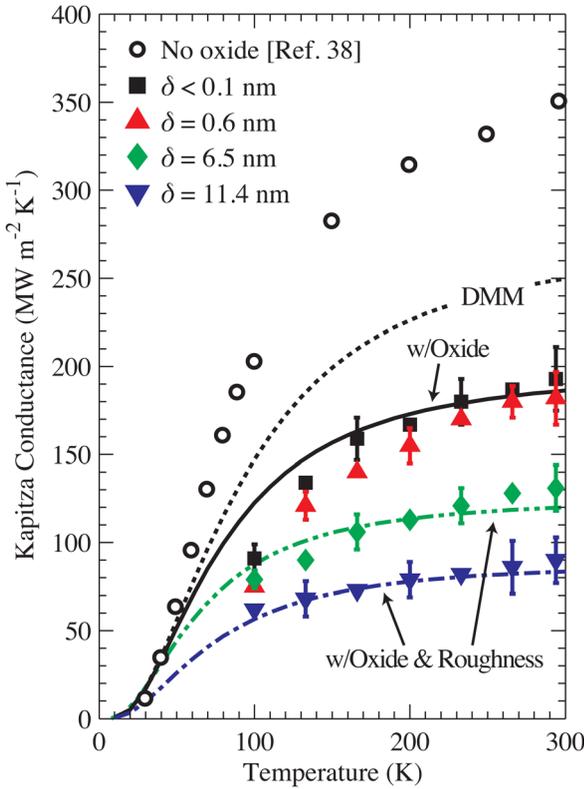


FIG. 2. (Color online) Predicted and measured values of Kapitza conductance at Al:Si interfaces plotted as a function of temperature. The open circles are the measured values at oxide-free Al:Si interfaces from Ref. 38, and the filled symbols are the data measured in the present study. It is evident that both the presence of a native oxide layer and interface roughness can have a significant effect on Kapitza conductance. Not only does roughness decrease Kapitza conductance, but it suppresses the temperature dependence as well. The agreement between the dash-dot lines and the data suggest that the DMM can be adjusted to take into account both the presence of an oxide layer and interface roughness.

substrate are approximated by fitting polynomials to the phonon dispersion curves of aluminum⁴¹ and silicon⁴² along the [100] crystallographic direction; assumed spherical Brillouin zones are then constructed via an isotropic revolution of these polynomial fits in wavevector space. As seen in Fig. 2, the prediction of the DMM falls between the data of Ref. 38 and that at the smoothest interface presently considered. This suggests that without an oxide layer, inelastic phonon-phonon scattering could play a role in thermal transport across aluminum-silicon interfaces.^{6,7} On the other hand, we attribute the difference between the predicted and measured values at the smoothest interface considered (black squares) to the native oxide layer. The conductance of this oxide layer is described by its thermal conductivity divided by its thickness,

$$h_{\text{oxide}} = \kappa_{\text{oxide}}/t_{\text{oxide}}. \tag{1}$$

When evaluating Eq. (1), we use the temperature-dependent bulk thermal conductivity of α :SiO₂, as it has been shown that the thermal conductivity of thin-film α :SiO₂ does not substantially differ from that of bulk.^{16,43} A series-resistor approach then yields

$$h_K = (h_{K,\text{DMM}}^{-1} + h_{\text{oxide}}^{-1})^{-1}. \tag{2}$$

This prediction is represented by the solid black line in Fig. 2 and agrees well with our experimental data.

In order to take interfacial roughness into account, we introduce a spectral attenuation coefficient previously proposed by the authors,^{24,25} and insert this coefficient into the integral expression of the DMM. This coefficient, γ , is unity when the phonon wavelength, λ , is greater than the RMS roughness, δ . On the other hand, $\gamma = \exp[-(4\pi\beta/\lambda)\delta]$ when $\lambda < \delta$. That is, phonons with wavelengths greater than δ are unaffected by the roughness of the interface, whereas those with wavelengths less than δ are affected in a fashion similar to that of photons in an absorptive media, e.g., the Beer-Lambert law. Qualitatively speaking, this approach suggests that as the "absorptivity" of the interface increases, so too does the temperature drop across it. With the spectral attenuation coefficient implemented, the DMM is once again plotted in Fig. 2 for roughnesses of 6.5 nm and 11.4 nm. We find that a value of $\beta = 0.04$ works well across all data sets. As is evident in the plot, this approach not only captures the reduction in Kapitza conductance due to interface roughening, but captures the reduction in temperature-dependence as well. Finally, we plot room-temperature Kapitza conductance as a function of RMS roughness in Fig. 3, comparing the present data, the aforementioned roughness model calculated at 300 K, and two prior sets of experimental data. Generally speaking, the present data demonstrates the same systematic control over both roughness and Kapitza conductance previously demonstrated only by quantum-dot roughening.²⁵

To summarize, we have measured Kapitza conductance at aluminum-silicon interfaces with time-domain thermoreflectance. The root-mean-square roughness of each interface was controlled by submersing the silicon substrates in tetramethyl ammonium hydroxide prior to aluminum deposition. It was shown that this technique can provide an inexpensive

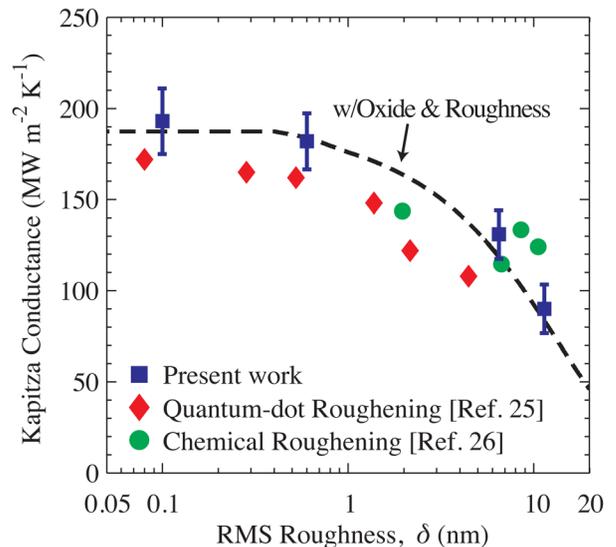


FIG. 3. (Color online) Room-temperature predicted (dashed line) and measured (blue squares) Kapitza conductance at Al:Si interfaces plotted as a function of interface roughness. In addition, the quantum-dot roughened Al:Si interfaces of Ref. 25 (red diamonds) and the chemically roughened Al:Si interfaces of Ref. 26 (green circles) are plotted for comparison. The present data demonstrates the same systematic control over both roughness and Kapitza conductance previously demonstrated only by quantum-dot roughening.

and scalable process for tuning Kapitza conductance at solid-solid interfaces by more than a factor of two at room temperature.

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