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Minimum thermal conductivity considerations in aerogel thin films

Patrick E. Hopkins,[1,a)] Bryan Kaehr,[2,3] Edward S. Piekos,[2] Darren Dunphy,[3] and
C. Jeffrey Brinker[2,3]
[1]*Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia 22904, USA*
[2]*Sandia National Laboratories, Albuquerque, New Mexico 87123, USA*
[3]*Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico 87106, USA*

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We demonstrate the use time domain thermoreflectance (TDTR) to measure the thermal conductivity of the solid silica network of aerogel thin-films. TDTR presents a unique experimental capability for measuring the thermal conductivity of porous media due to the nanosecond time domain aspect of the measurement. In short, TDTR is capable of explicitly measuring the change in temperature with time of the solid portion of porous media independently from the pores or effective media. This makes TDTR ideal for determining the thermal transport through the solid network of the aerogel film. We measure the thermal conductivity of the solid silica networks of an aerogel film that is 10% solid, and the thermal conductivity of the same type of film that has been calcined to remove the terminating methyl groups. We find that for similar densities, the thermal conductivity through the silica in the aerogel thin films is similar to that of bulk aerogels. We theoretically describe the thermal transport in the aerogel films with a modified minimum limit to thermal conductivity that accounts for porosity through a reduction in phonon velocity. Our porous minimum limit agrees well with a wide range of experimental data in addition to sound agreement with differential effective medium theory. This porous minimum limit therefore demonstrates an approach to predict the thermal conductivity of porous disordered materials with no *a priori* knowledge of the corresponding bulk phase, unlike differential effective medium theory. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4729325]

I. INTRODUCTION

The promise of materials in which the electrical, thermal, and mass transport properties are "user-defined" with nanoscale precision has fueled an enormous thrust in the materials science community to develop nanomaterials and fabrication strategies.[1,2] The development of approaches to control nanostructure morphology using self-assembly has drastically simplified nanomaterial synthesis, enabling rapid, low-temperature processing of thin films for use as membranes, dielectric insulator layers, and optical coatings.[3] Despite these advances in thin film processing, characterization of the physical properties in nanostructured thin films remains a considerable challenge due to complex geometries and non-conformal surface areas. For example, measuring heat transport in highly thermally insulating materials such as aerogels, let alone aerogel thin films, has proven to be particularly challenging using standard approaches due to convective and radiative losses.[4–7] Understanding heat transport in thin porous films is critical for low-k dielectric applications in microelectronics as well as optical coatings for solar panels.

In this work, we overcome these challenges and demonstrate the use of time domain thermoreflectance (TDTR) to measure the thermal conductivity, κ, of aerogel thin-films. Where previous works by our group and others have demonstrated the use of TDTR for measuring the heat flow in non-conformal, porous solids as well as liquids,[8–10] we show both experimentally, computationally, and theoretically the advantage of TDTR for measuring highly porous films due to its inherent insensitivity to longer time scale thermal losses. In short, TDTR is capable of explicitly measuring the change in temperature with time of the solid portion of porous media independently from the pores or effective media since the measurement scale of TDTR is on the order of nanoseconds, which is much larger than the time constant of conduction through and losses to the air in the pores. This makes TDTR ideal for determining the thermal transport through the solid network of the highly porous aerogel film. We measure the thermal conductivity of the solid silica networks of an aerogel film that is 10% solid, and the thermal conductivity of the same type of film that has been calcined to remove the terminating methyl groups. We find that the thermal conductivities of these silica aerogels follow similar trends with density as that predicted by differential effective medium (DEM) theory, which is expected as our TDTR measurements are only sensitive to the heat flow through the solid silica network of the aerogel. We theoretically describe the thermal transport in the aerogel films with a modified minimum limit to thermal conductivity that accounts for porosity through a reduction in phonon velocity. Our porous minimum limit agrees well with a wide range of experimental data in addition to sound agreement with DEM theory. Therefore, this porous minimum limit demonstrates an

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[a)]Electronic mail: phopkins@virginia.edu.

approach to predict the thermal conductivity of porous disordered materials with no *a priori* knowledge of the corresponding bulk phase, unlike DEM theory.

II. EXPERIMENTAL DETAILS

Our experimental technique to determine the thermal conductivity of the aerogel films is TDTR, a pump-probe technique in which the change in the thermoreflectance signal from a sample of interest is monitored in the time domain by delaying the probe pulse with respect to the heating event, or pump pulse. Several groups have discussed various experimental configurations to detect the thermoreflectance signal in the time domain.[8,9,11–14] It is important to note that in this work, we use an 80 MHz oscillator which ensures pulse accumulation in our signal, therefore yielding the modulated heat transfer event that is unique to TDTR; this is also necessary for our specific test geometry. We adopt the test geometry similar to the approach discussed by Schmidt *et al.*[9] and Ge *et al.*,[10] as we have described in detail previously.[8] In these works, the samples were fabricated on a transparent substrate coated with a thin metal film. The pump and probe laser pulses were reflected by the metal transducer through the glass, and the change in the TDTR signal was used to deduce the thermal conductivity of the adjacent sample. Only the metal film interacts with the laser radiation, and the thermal energy from the laser pulse is partially absorbed in only the first ∼9 nm of the Al film before the thermal energy propagates through the Al film and then through the adjacent structures. The analysis of the TDTR signal in this geometry is described in detail elsewhere.[8] A schematic of our experimental geometry is shown in Fig. 1. In our experiments, we restrict the laser power incident on the sample to less than ∼15 mW to ensure minimal DC heating.

To prepare the aerogel samples, we evaporate 85 nm of Al on VWR micro cover glass (No. 48368040). We then fabricate the aerogel thin films on the surface of the Al film. The thin aerogel films were prepared using identical procedures as previously described.[15] Briefly, silica sols were prepared from a stock solution (tetraethoxysilane, EtOH, H_2O, HCl in a $1.0{:}3.8{:}1.1{:}7.0 \times 10^{-14}$ molar ratio), refluxed (60 °C, 90 min) and gelled at 50 °C. Surface hydroxyls were partially replaced with methyl groups using hexamethyldisilazane (HMDS) as the derivatizing agent and sonicated to reliquify the solution. The solution was spin coated (2000 rpm, 30 s) onto the Al coated glass. During evaporation, the film gels shrink due to drying stresses and spring back to create a high porosity aerogel film. We refer to these films as "aerogel". After initial TDTR measurements, the aerogel films were calcined (500 °C, 3 h) to remove the methyl groups. We refer to these films as "calcined-aerogel". We also perform TDTR measurements on Al coated glass with no silica film as a calibration. This allows us to accurately determine the thermal conductivity, κ, of the cover glass and the thermal boundary conductance, h_K, between the Al film and cover glass, thereby reducing the number of free parameters in the thermal model needed to determine the thermal conductivity of the aerogel samples. Scanning electron microscopy images of an uncalcined, carbon-coated thin film aerogel are shown in Fig. 1. We note that calcination did not substantially change the thickness of the film.

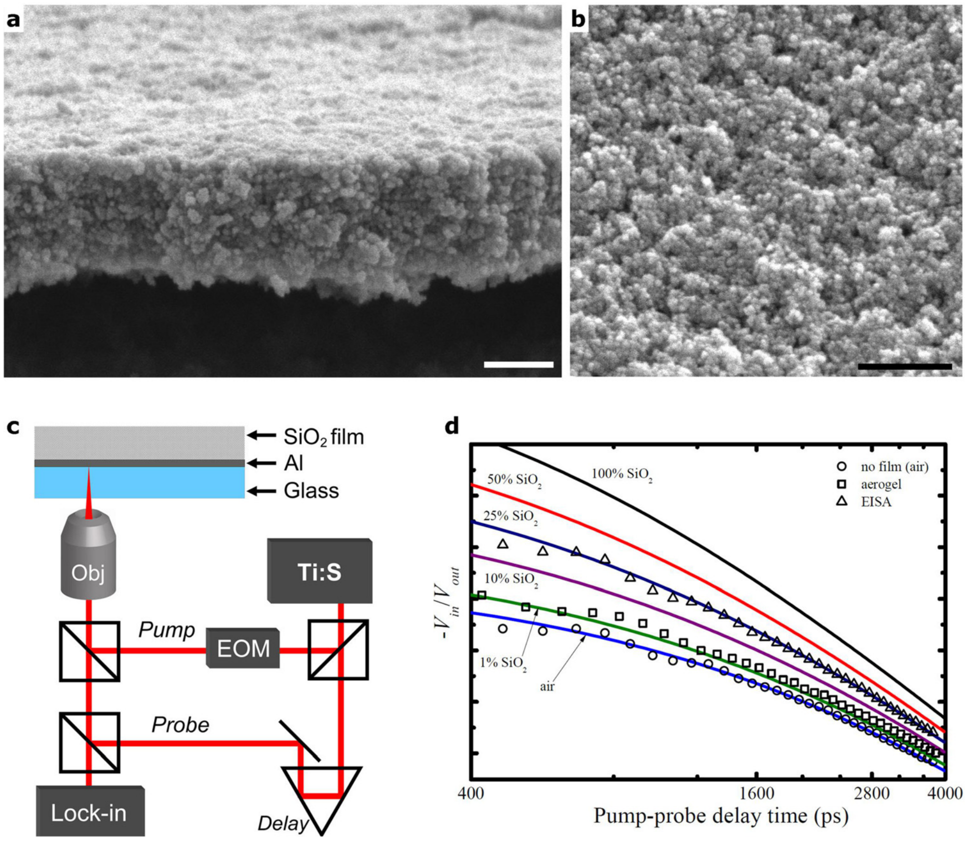

FIG. 1. Scanning electron microsocpy image of the (a) cross section and (b) top view of a thin film aerogel. The scale bars are 500 nm. (c) Schematic of our experimental geometry. (d) TDTR data from the EISA and aerogel films along with data from the sample with no film (i.e., air). The solid lines represent the predictions from the thermal model for various reductions in the SiO_2 sample thermal conductivity.

Figure 1 shows sample TDTR data of the aerogel films along with data from the sample with no film (i.e., air) and data from a previously examined mesoporous silica film evaporation induced self assembly (EISA).[8] Along with the data, we show the predictions from the thermal model for various reductions in SiO_2 sample κ. Since the pump is modulated at 11 MHz, the TDTR data represent measurements of the thermal effusivity of the porous SiO_2 sample, $E = \sqrt{C\kappa}$,[16] where C is the volumetric heat capacity. We fit the data from the sample with no SiO_2 film by adjusting the value for the h_K between the glass slide and the Al film and κ for the glass slide. Due to the low thermal conductivity of the aerogel samples, the TDTR signal is relatively insensitive to the Al/sample thermal boundary conductance.[8,17] The presence of any thermal mass on the free surface of the Al increases the TDTR signal. In fact, TDTR has the sensitivity to be able to measure thermal conductivities of samples with thermal effusivities in the solid matrix of the porous sample as low as 10% of bulk SiO_2, representing a reduction in thermal conductivity to 1% of bulk.

III. THERMAL ANALYSIS

The model calculations and subsequent data analysis in this work (and shown in Fig. 1) require inputs of both κ and C for each layer and h_K for interfaces. As we have previously discussed, our determination of the various values for κ and h_K, we focus now on our assumptions of heat capacity, C, in each layer. For both the glass slide and Al film, we assume a bulk heat capacity, which is typical in TDTR experiments for metal transducers and semi-infinite, bulk substrates. We can also assume that the solid portion of the aerogel film has a heat capacity equivalent to bulk SiO_2 which is valid at temperatures above ~20 K.[18] In TDTR, all the thermal energy is absorbed in the Al transducer and then partially transmitted into the aerogel and glass. We then monitor the thermal decay in the Al film over ~4 ns. This 4 ns of decay is not enough time for any of the thermal energy to conduct into the air from the silica ligaments in the aerogel. For example, typical heat transfer coefficients due to silica/air coupling effects in an aerogel are on the order of 0.1-1.0 W m^{-2} K.[18] For aerogel samples with ligament sizes on the order of 10 nm (similar to those studied in Ref. 18), this corresponds to a silica/air thermal decay time on the order of $0.1 - 1$ s. This is 8–9 orders of magnitude greater than the time frame of TDTR. Therefore, the only media that our measurement detects are the silica ligaments in the aerogel. Therefore, the thermal decay in any porous film (i.e., aerogel) in TDTR is related to the reduced thermal conductivity in the solid ligaments and the bulk heat capacity of the material comprising the ligaments. This is addressed in much more detail in the following discussion.

This assumption, which demonstrates a very powerful aspect of TDTR for easily determining the thermal conductivity of the solid ligaments in porous materials, must be justified further. To ensure that there is no conduction from the aerogel films to the air, we test the samples in ambient and under vacuum at room temperature. We find no change in the measured TDTR signal and subsequent effusivity in any of the samples. This indicates that the air in the pores is not contributing to the thermal effusivity in the time domain of the measurement. Our vacuum pumps the cryostat chamber down to less than 1.0 mTorr, which is sufficient pressure to remove any contribution we would have observed from conduction through the air in the pores of the aerogel samples.[6] Given this observation, we can now theoretically analyze the heat flow in the porous sample (i.e., aerogel film) during TDTR via the "two-fluid" model for heat transfer in porous media.[19] In the most general of experiments in which energy is absorbed in both the solid (silica) and fluid (air) phases, and the two phases are not in equilibrium, the heat conduction is governed by

$$(1-\phi)C_s\frac{\partial T_s}{\partial t} = (1-\phi)\kappa_s\nabla^2 T_s - h(T_s - T_f) + (1-\phi)q \tag{1}$$

for the solid phase and

$$\phi C_f\frac{\partial T_f}{\partial t} = \phi\kappa_f\nabla^2 T_f + h(T_s - T_f) + \phi q \tag{2}$$

for the fluid phase, where ϕ is the porosity of the medium, defined as the volume fraction of the fluid (air), T is the temperature, t is the time, h is the heat transfer coefficient between the solid and fluid, q is the volumetric absorbed power, and the subscripts s and f refer to the solid (silica) and fluid (air), respectively. As we experimentally verified, there is no conduction from the aerogel to the air during our TDTR experiments, so $h = 0$. Therefore, Eqs. (1) and (2) reduce to

$$(1-\phi)C_s\frac{\partial T_s}{\partial t} = (1-\phi)\kappa_s\nabla^2 T_s + (1-\phi)q \tag{3}$$

for the solid phase and

$$\phi C_f\frac{\partial T_f}{\partial t} = \phi\kappa_f\nabla^2 T_f + \phi q \tag{4}$$

for the fluid phase. Let us also assume that all of the heat absorbed in the Al transducer film is transferred to the slica solid, and not to the air, so that $\phi q = 0$ (note, this is further supported by our ambient and vacuum experimental comparison discussed above). Given that there is no heat transferred to the fluid (air) during the time domain in TDTR, there is no temperature gradient and therefore no heat transfer in the fluid (air). Therefore, for our experiments, the two fluid model reduces to simply Eq. (3), which is further reduced to

$$C_s\frac{\partial T_s}{\partial t} = \kappa_s\nabla^2 T_s + q. \tag{5}$$

This means that the transient conduction in the porous film is governed solely by the heat transfer in the solid matrix. Furthermore, since all the heat is absorbed by the solid, the fractional porosity factor $1 - \phi$ cancels out of Eq. (3) to give Eq. (5), and the heat capacity governing the transient decay during TDTR is simply the bulk heat capacity of the solid ligaments. However, we caution that the thermal conductivity determined from this measurement is therefore the thermal conductivity of the solid portion of the porous medium, not the effective medium itself. That is, in our aerogel films, our TDTR measurements are used to extract the thermal conductivity of the solid matrix in the aerogel, not the effective thermal conductivity of the silica/air aerogel effective medium.

To ensure that this theoretical analysis is indeed sound, we turn to a computational validation via finite element analyses. We simulate TDTR experiments on both a porous and nonporous solid and examine the changes in temperature on the surface of the sample. The computational geometry is periodic in its lateral direction and 3 μm tall, with an isothermal boundary condition enforced at the bottom. In the case of the porous simulation, we assume that the silica ligaments are insulated by the air (i.e., $h = 0$ in the two fluid analysis above). We simulate the laser pulses as a spatially uniform heat flux on the top surface with a heating time of 100 fs and a 12.5 ns delay between pulses; we further modulate the pulses at 10 MHz (i.e., 4 pulses "on" followed by 4 pulses "off," closely mimicking the heating during our TDTR experiments). We prescribe the properties of the solid media in our domain to mimic the heat capacity and thermal conductivity of SiO_2. The top 100 nm of the domain we prescribe the properties of Al to mimic the thin film transducer. In the case of the porous media simulation, we describe the pores as 100 nm square and spaced 43 nm apart. A schematic of the simulated domain of the porous structure is shown in Fig. 2 (left).

The modulated pulse series shown was repeated in each case (solid and porous) until the starting and ending temperatures matched to within a milliKelvin. The resulting "steady-state" starting temperature was half a percent lower in the porous media case due to the slightly increased thermal communication with the heat sink provided by transport through the air. This indicates that there could be a very small amount of heat transferring from the Al transducer directly to the air, but this would be negligible and non-observable in our TDTR experiments (as we demonstrated by comparing out TDTR experiments both under vacuum and in ambient). When normalized by this starting temperature, however, the temperature rise due to the pulses is nearly indistinguishable, as shown in Fig. 2 (right). This demonstrates that, due to the vastly lower thermal effusivity of air compared to the parallel heat path presented by the silica, the silica properties dominate the response. That is, the ratio of the thermal effusivity of silica to that of air is $E_{\mathrm{air}}/E_{\mathrm{silica}} \approx 0.004$, which indicates that there is a negligible amount of heat transferring into the air compared to the silica. Consequently, the TDTR procedure is effectively interrogating the properties of only the silica.

This demonstrates the convenience for using TDTR to measure thermal conductivity of porous material; that is, over the time domain interrogated in TDTR measurements (a few nanoseconds), we only observe thermal conduction through the solid matrix of the samples and do not observe any aspect of the air or gas in the porous material. We validated this assumption via experiments under evacuated and ambient conditions, as previously discussed, along with the theoretical and computational analyses described above. Note that this same measurement convenience is applicable to all porous materials assuming there is no heat transfer from the solid to the air.

IV. RESULTS AND DISCUSSION

We plot the thermal conductivity of the samples as a function of measured SiO_2 atomic density for the EISA, aerogel, and calcined-aerogel films in Fig. 3 along with the thermal conductivity of bulk SiO_2,[20] a sputtered SiO_2 thin film,[21] other porous silica materials (XLK and FOx),[21] and

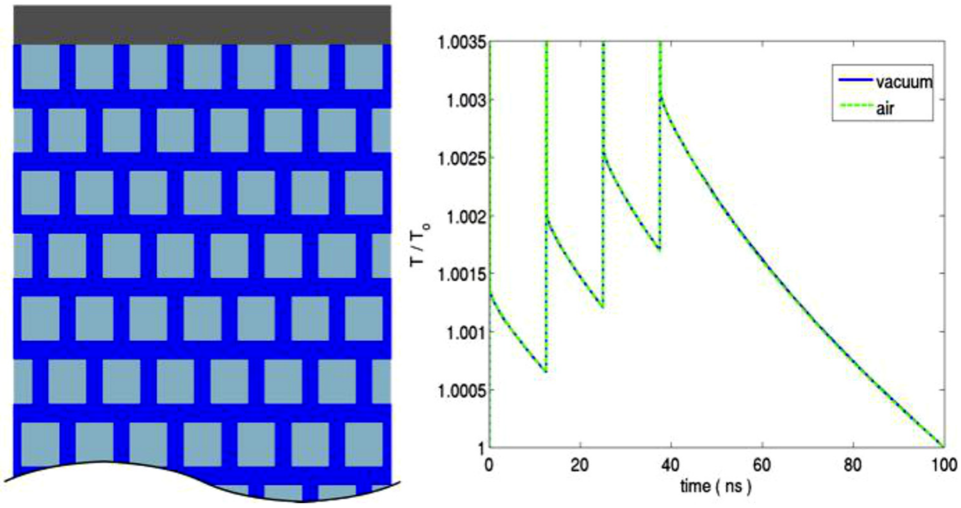

FIG. 2. (left) Schematic of the porous structure used to simulate the TDTR experiment. The top 100 nm of the structure is prescribed the thermal properties of aluminum, the square pores are given the thermal properties of air, and the solid ligaments are assumed to have the thermal properties of SiO_2. (right) Normalized temperature rise on the surface of the aluminum film during the 100 fs pulse heating occuring every 12.5 ns further modulated at 10 MHz on both the porous and nonporous silica domain. This mimics the heating event in our TDTR experiments. The temperature rise due to the pulses is nearly indistinguishable. This demonstrates that, due to the vastly lower thermal effusivity of air compared to the parallel heat path presented by the silica, the silica properties dominate the response.

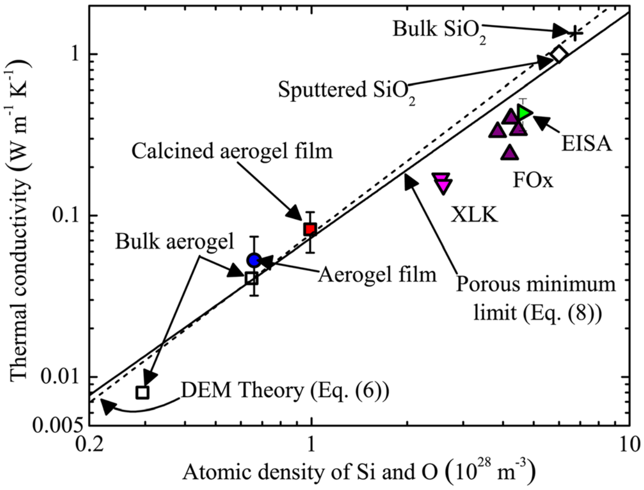

FIG. 3. Thermal conductivity as a function of volumetric SiO$_2$ number density for the aerogel and calcined-aerogel films along with bulk SiO$_2$,[20] a sputtered SiO$_2$ thin film,[21] other porous silica materials (XLK and FOx),[21] and bulk SiO$_2$ aerogels.[6,22] Predictions from the theoretical "porous minimum limit" to the thermal conductivity of SiO$_2$ (solid line – Eq. (8)) that is derived in this work show good agreement with the thermal conductivity of the porous silica structures.

bulk SiO$_2$ aerogels.[6,22] The error bars in our measurements represent the standard deviation about the mean value of κ determined from multiple data sets taken on each sample type (upwards of 10 different TDTR scans taken on each sample and two samples of each type of silica film). We measure the SiO$_2$ compositional percentage[23] and sample porosity in the EISA and aerogel films using ellipsometry and surface acoustic wave techniques[24] and find that the SiO$_2$ molecular densities in the EISA, aerogel, and calcined-aerogel films are 1.54×10^{28}, 2.20×10^{27}, and $3.30 \times 10^{27}\,\mathrm{m}^{-3}$, respectively, assuming a bulk atomic density of SiO$_2$ of $2.28 \times 10^{28}\,\mathrm{m}^{-3}$. This corresponds to an atomic density $4.62 \times 10^{28}\,\mathrm{m}^{-3}$, $6.6 \times 10^{27}\,\mathrm{m}^{-3}$, and $9.9 \times 10^{27}\,\mathrm{m}^{-3}$, respectively. The thermal conductivities of the EISA, aerogel, and calcined-aerogel films are 0.434 ± 0.098 W m^{-1} K^{-1}, 0.053 ± 0.021 W m^{-1} K^{-1}, and 0.082 ± 0.023 W m^{-1} K^{-1}, respectively. We note that burning off the methyl groups from the aerogel skeleton increases the density and thermal conductivity of the film. This is most likely a consequence of silica condensation following exposure to air of free silanol groups which may lead to increased silica network connectivity. In Fig. 3, we compare our data to thermal measurements on silica materials that do not include opacifiers such as carbon soot (thus excluding the data reported in Refs. 5 and 7). We note that the measured values of κ of our aerogel thin films measured with TDTR are in relatively good agreement with the thermal conductivities of aerogel thin films synthesized with a similar technique and measured with the 3ω technique.[25] However, we cannot directly compare our measured values to these data measured by Bauer *et al.*[25] since the density of the aerogels films was not measured.

We compare our results to the DEM theory[26] which relates the thermal conductivity of a porous material to its corresponding bulk phase via

$$\kappa_{\mathrm{porous}} = \left(\frac{n_{\mathrm{porous}}}{n_{\mathrm{bulk}}}\right)^{1.5} \kappa_{\mathrm{bulk}}, \tag{6}$$

where n is the atomic density. The data summarized in Fig. 3 agree well with DEM theory. Although DEM theory proves a powerful tool for predicting the thermal conductivity of porous structures, the downside is that knowledge of the bulk phase must be known for the prediction. For example, in our case, to predict the thermal conductivity of the aerogel films, we must have prior knowledge of the thermal conductivity of bulk silica. Clearly, it would be quite advantageous to have a model that is capable of accurately predicting the thermal conductivity of porous materials without any *a priori* knowledge of the bulk phase thermal conductivity. To develop this model for porous silica structures, we turn to the idea of the lower limit to thermal conductivity.

In amorphous materials such as silica glass, thermal transport is limited by atomic scattering at a distance of the interatomic spacing.[27] This lower limit to thermal conductivity is described by the theoretical minimum thermal conductivity in which the vibrational scattering rate is wavelength limited. This concept has been explored in several works.[28–30] This minimum limit described by Cahill *et al.* is given by[28]

$$\kappa_{\mathrm{min}} = \frac{\pi}{3} \sum_{\mathrm{j}} \int_{\omega_{\mathrm{j}}} \hbar D_{\mathrm{j}} v_{\mathrm{g,j}}^2 \frac{\partial f}{\partial T}\, d\omega, \tag{7}$$

where $\hbar$ is the reduced Planck's constant, D is the density of states, j is an index that refers to the polarization, v_{g} is the group velocity, and f is the Bose-Einstein distribution function. The density of states can be approximated as $D_{\mathrm{j}} = \omega^2/(2\pi^2 v_{\mathrm{p,j}}^2 v_{\mathrm{g,j}})$, where v_{p} is the phase velocity.

The major assumption in applying Eq. (7) to describe thermal conductivity as a function of SiO$_2$ atomic density is that the sound velocity can still be described by the bulk velocities in SiO$_2$. This clearly is not a valid assumption throughout the entire aerogel structure due to the porosity and resulting matrix of overlapping and multidirectional solid silica ligaments that cause a reduction in sound velocity.[21] To address this in the minimum model, we modify the group velocity to scale with the number density in the overall volume of the sample. Note that, as we have previously discussed, we assume that the heat capacity of the solid ligaments in the aerogel can be described as bulk. Therefore, the phase velocities and cutoff frequencies must remain unchanged in our model to predict the thermal conductivity of porous silica, and only the group velocities that represent the velocity of thermal transport must be scaled. The group velocities in porous silica structures scale by $(n/n_{bulk})^{1.4}$ (Refs. 21 and 31). Therefore, Eq. (7) can be recast as a "porous minimum limit" given by

$$\kappa_{\mathrm{min,p}} = \frac{1}{6\pi} \sum_{\mathrm{j}} \int_{\omega_{\mathrm{j}}} \hbar \frac{\omega^2}{v_{\mathrm{p,j}}^2} v_{\mathrm{g,j}} \left(\frac{n}{n_{\mathrm{bulk}}}\right)^{1.4} \frac{\partial f}{\partial T}\, d\omega. \tag{8}$$

We plot Eq. (8) as a function of n in Fig. 3 assuming the longitudinal and transverse sound velocities of SiO$_2$ are 5800 and 3700 m s^{-1}, respectively, $v_p = v_g$ and $n_{\mathrm{bulk}} = 6.74 \times 10^{28}$ m^{-3} (Refs. 32 and 33). In general, the minimum limit given in Eq. (7) over predicts the thermal conductivity of the porous silica and aerogels. However, The predicted κ from our "porous minimum limit" (Eq. (8)) agrees well with our experimental data on the aerogel and calcined aerogel films along with the DEM theory (Eq. (6)), yet we emphasize that no *a priori* knowledge of the bulk phase thermal conductivity is needed in the calculations of Eq. (8), unlike the DEM theory.

We emphasize that our measurements represent the thermal conductivity through the solid silica network in the aerogel (i.e., not the effective thermal conductivity of the aerogel). Therefore, the reduced velocity of thermal transport through the aerogels can be ascribed to the reduction in sound velocity, as per Eq. (8). In Fig. 3, we have compared our data to the EISA film,[8] bulk SiO_2,[20] a sputtered SiO_2 thin film,[21] other porous silica materials (XLK and FOx).[21] These data were taken with the 3ω technique (except for the EISA film which was measured with TDTR). As outlined by Costescu *et al.*,[21] their measurements of the porous silica materials can be treated as a porous silica network with zero thermal conductivity voids. Therefore, these data represent the thermal conductivity of the solid silica matrix in their porous materials, similar to our aerogel measurements. Our porous minimum limit also shows acceptable agreement with these porous silica samples. Finally, we compare our data to bulk SiO_2 aerogels.[6,22] We only compare our data to thermal measurements on silica materials that do not include opacifiers such as carbon soot (thus excluding the data reported in Refs. 5 and 7). We note that these measurements of bulk aerogels were taken under vacuum sufficient enough to suppress the contribution of heat transfer through the gas in the pores. Therefore, outside of any radiative contribution due to the measurement technique of these aerogels, these bulk aerogel data also represent the thermal conductivity through the solid silica network in the samples. We find that for similar densities, the thermal conductivity through the silica in the aerogel thin films is similar to that of bulk aerogels. This is expected as the atomic structure of aerogels is heavily disordered and fractal networks of silica leading to thermal transport through the solid ligaments that are similar to that in amorphous materials, as discussed below. This implies that size effects due to the film thickness will not affect the aerogel thermal conductivity, which is a similar conclusion that was observed in SiO_2 films as thin as 25 nm.[34]

Finally, we note that the DEM theory and velocity scaling based on density are only valid for zone center acoustic modes. Therefore, strictly speaking, the velocity modification that we employ in our porous minimum limit is only valid for the zone-center, non-dispersive modes that are well described in the continuum limit by the elastic moduli in the silica solid backbone. The excellent agreement among DEM theory, our porous minimum limit, and the various experimental data implies that heat transport in porous silica structures could in fact be dominated by low frequency, long wavelength modes. These modes are most likely collective oscillations of silica unit cells comprised of several atomic clusters and pores, since long wavelength phonons (in the traditional sense) will not contribute to heat transfer in these structures due to the nanoscopic pores and geometric scattering sites. This concept is in line with the current theories of oscillations and heat transport in amorphous solids.[28,29,35]

V. SUMMARY

In summary, we have demonstrated the use of TDTR to measure the thermal conductivity of the solid silica network of aerogel thin-films. TDTR is capable of explicitly measuring the change in temperature with time of the solid portion of porous media independently from the pores or effective media. This makes TDTR ideal for determining the thermal transport through the solid network of the aerogel film. We measured the thermal conductivity of the solid silica networks of an aerogel film that is 10% solid, and the thermal conductivity of the same type of film that has been calcined to remove the terminating methyl groups (resulting in an atomic density increase to 15% solid). We find that the thermal conductivities of these silica aerogels follow similar trends with density as that predicted by DEM theory, which is expected as our TDTR measurements are only sensitive to the heat flow through the solid silica network of the aerogel. We theoretically describe the thermal transport in the aerogel films with a modified minimum limit to thermal conductivity that accounts for porosity through a reduction in phonon velocity. Our porous minimum limit agrees well with a wide range of experimental data in addition to sound agreement with DEM theory. Therefore, this porous minimum limit demonstrates an approach to predict the thermal conductivity of porous disordered materials with no *a priori* knowledge of the corresponding bulk phase, unlike DEM theory.

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