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Anisotropic and inhomogeneous thermal conduction in suspended thin-film polycrystalline diamond

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While there is a great wealth of data for thermal transport in synthetic diamond, there remains much to be learned about the impacts of grain structure and associated defects and impurities within a few microns of the nucleation region in films grown using chemical vapor deposition. Measurements of the inhomogeneous and anisotropic thermal conductivity in films thinner than 10 μm have previously been complicated by the presence of the substrate thermal boundary resistance. Here, we study thermal conduction in suspended films of polycrystalline diamond, with thicknesses ranging between 0.5 and 5.6 μm , using time-domain thermoreflectance. Measurements on both sides of the films facilitate extraction of the thickness-dependent in-plane (κ_r) and through-plane (κ_z) thermal conductivities in the vicinity of the coalescence and high-quality regions. The columnar grain structure makes the conductivity highly anisotropic, with κ_z being nearly three to five times as large as κ_r , a contrast higher than that reported previously for thicker films. In the vicinity of the high-quality region, κ_r and κ_z range from 77 ± 10 W/m-K and 210 ± 50 W/m-K for the 1 μm thick film to 130 ± 20 W/m-K and 710 ± 120 W/m-K for the 5.6 μm thick film, respectively. The data are interpreted using a model relating the anisotropy to the scattering on the boundaries of columnar grains and the evolution of the grain size considering their nucleation density and spatial rate of growth. This study aids in the reduction in the near-interfacial resistance of diamond films and efforts to fabricate diamond composites with silicon and GaN for power electronics. *Published by AIP Publishing.*

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I. INTRODUCTION

Diamond is a promising candidate as heat-spreader in high heat-flux applications such as high electron mobility transistors and quantum cascade lasers.^{1,2} The single-crystalline, defect-free form is the most highly conducting three-dimensional material at room temperature. Thin film diamond is typically grown in polycrystalline form using chemical vapor deposition (CVD), yielding a thermal conductivity that is lower than that of the bulk single-crystal due to strong phonon scattering at grain boundaries, except when film thickness exceeds a few hundred μm .³ The problem of heat conduction within substantially thinner films has received some attention, but there are many unresolved questions about phonon scattering on various defects in polycrystalline films of thickness below a few micrometers.

The complex microstructural characteristics of polycrystalline diamond films affect their thermal transport properties in important ways. First, nucleation and coalescence create a region of small grains within tens of nm of the growth interface. The high density of grain boundaries and other defects

and impurities causes this region to have a low thermal conductivity, and therefore increases the effective thermal boundary resistance (TBR) at the diamond/substrate interface.⁴ Second, as grains grow, the lateral grain size increases with distance from the growth interface. This inhomogeneity results in a thermal conductivity that increases with film thickness.^{5,6} Third, competition and survival of grains during the growth process leads to the formation of a columnar grain structure with the long axis of grains oriented normal to the growth interface. A higher density of grain boundaries in the lateral compared to the film-normal direction causes the in-plane conductivity κ_r to be lower than the through-plane conductivity κ_z .³

Prior work on measuring intrinsic properties of polycrystalline diamond has focused mostly on films ranging from tens of μm to few mm in thickness.⁵ Although measurements on thinner films have been performed, they were unable to separate the intrinsic thermal resistance of the diamond layer from the TBR of the diamond/substrate interface.⁴ Further, the measurement of anisotropy is an important ingredient in the development of an accurate device-level thermal physics model. Previous measurements of anisotropy have largely been on films thicker than ~ 30 μm .^{3,7–10} These authors used different experimental techniques to measure thermal conduction in the

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two orthogonal directions, such as the transient thermal grating and steady state electrothermal methods for κ_r , and nanosecond laser flash for κ_z . The use of separate techniques complicates sample preparation and potentially makes a one-to-one comparison between data sets challenging.

This paper aims to contribute through a focused study on thermal conductivity in films thinner than 6 μm , with an emphasis on anisotropy and inhomogeneity. We isolate intrinsic diamond properties by removing the growth substrate and creating suspended regions. The suspended film structure allows the measurement of both κ_r and κ_z . Time-domain thermoreflectance (TDTR), an optical pump-probe technique, is used to measure thermal conductivity, with the relative measurement sensitivity to conduction in the lateral and vertical directions tuned by varying the thermal penetration length-scale in TDTR. Inhomogeneity in thermal conductivity over film thickness is directly probed by performing measurements from both sides of the suspended membranes.^{11,12} By measuring films of different thicknesses from 0.5 to 5.6 μm grown under identical conditions, we show how the evolving grain structure impacts thermal conductivity at different distances from the growth interface, effectively providing thermal cross-sectioning information. A theoretical model based on the geometrical growth and fractional survival of grains, and phonon scattering at grain boundaries, provides predictions that are in good agreement with the experimental data.

II. SAMPLE FABRICATION AND CHARACTERIZATION

Nanocrystalline diamond films with thicknesses 0.5, 1.0, and 5.6 μm were deposited on crystalline silicon substrates using microwave plasma CVD, using purified methane and hydrogen as reactant gases. Prior to growth, the silicon substrates were seeded with ITC (International Technology Center, North Carolina, USA) grade I-6 (detonation) nanodiamond powder. This material has a high degree of grain size homogeneity, with an average particle size of 4.0 nm, and a chemical purity in excess of 98%, as reported by the manufacturer. The seeding process consisted of an ultrasonic treatment of the substrate submerged in an ethanol-based nanodiamond suspension, followed by an ultrasonic rinse and immediate spin-dry, yielding a uniform seeding density greater than 10^{12} nuclei/cm². This was determined by counting the grains in the coalesced layer using scanning electron microscopy (SEM) from the back side, on samples similar to the ones studied here.

Chemical vapor deposition was carried out in an ASTEX 1.5 KW microwave plasma CVD system operating at 15 Torr, 750 °C, at a power of 800 W. The methane to hydrogen ratio varied from 0.7% during the initial film coalescence stage to 0.3% during the remaining diamond film deposition, without the presence of an inert carrier gas.

Silicon substrates were selectively etched using an HNA (HF/HNO₃/CH₃COOH) isotropic silicon etch process to produce suspended diamond membranes spanning ~ 5 mm in diameter, on each sample (see Figure 5(a)). For the purposes of TDTR measurements, aluminum transducer films with a nominal thickness of 50 nm were deposited on the top and

bottom sides of each sample using electron-beam evaporation. The exact thickness of Al was measured using cross-sectional transmission electron microscopy (TEM) [see Figure 2(d)].

The diamond films are nucleated through the growth of small grained crystals from the dispersed nanodiamond seeds. Individual grains coalesce into a continuous film within 20 nm of the growth interface, and this region is called the coalescence region. Subsequent growth and survival of competing grains leads to the formation of a columnar grain structure, with the long axes of crystals oriented perpendicular to the growth surface, and whose lateral grain size increases with distance from the substrate.

Figure 1(a) shows a cross sectional SEM image of the 5.6 μm thick film. Diamond grain boundaries are oriented normally to the diamond/silicon growth interface, with a columnar morphology. Figures 1(c)–1(e) show plan-view SEM images of the three films taken at the same magnification. The average in-plane grain size $\langle d_r \rangle$ is measured from these images using the planimetric method (see supplementary material for details¹³) and is plotted in Figure 1(b). A linear correlation is observed between $\langle d_r \rangle$ and the film thickness h_{Diam} . This relationship is well represented by the equation: $\langle d_r \rangle = 0.066 h_{\text{Diam}} + 130$ nm. Atomic force microscopy (AFM) is used to determine the root mean square (RMS) roughness δ_{RMS} on the top-side of each film, giving $\delta_{\text{RMS}} = 16$ nm, 24 nm, and 72 nm for the 0.5 μm , 1.0 μm , and 5.6 μm films, respectively [Figure 1(i)], measured over 50×50 μm scan areas. Representative AFM images are shown in Figures 1(f)–1(h).

In addition to SEM and AFM, TEM was used to obtain further information about the diamond microstructure and its evolution with thickness, as well as image the interfaces of diamond with the Al transducer and Si growth substrate. The sample was prepared using the *in-situ* focused ion beam (FIB) technique and imaged with a FEI Tecnai TF-20 FEG/TEM operated at 200 kV in TEM and high-angle annular dark-field (HAADF) STEM mode. Figures 2(a) and 2(b) show low magnification bright-field TEM and HAADF STEM images, respectively, of the 0.5 μm thick diamond sample on top of the Si substrate, capped by the ~ 50 nm Al layer. The evolving columnar microstructure of diamond is clearly visible in Figure 2(c), which shows a montage of zoomed-in images of different regions of the film. High magnification TEM images shown in Figures 2(d) and 2(e) provide detail of the Al/diamond and diamond/Si interfaces, respectively. Additionally, as mentioned above, a measurement of the Al thickness is made from Figure 2(d), giving a value 50 ± 3 nm.

III. EXPERIMENTAL METHODOLOGY

A. TDTR Setup

TDTR is a well-established optical pump-probe technique that is used to measure the thermal conductivity of bulk materials, thin films, and thermal conductance of interfaces.^{14–16} We use a 1064 nm Nd:YVO₄ laser emitting 9 ps wide pulses at a repetition rate of 82 MHz. The output of the laser is split into pump and probe components. Pump pulses

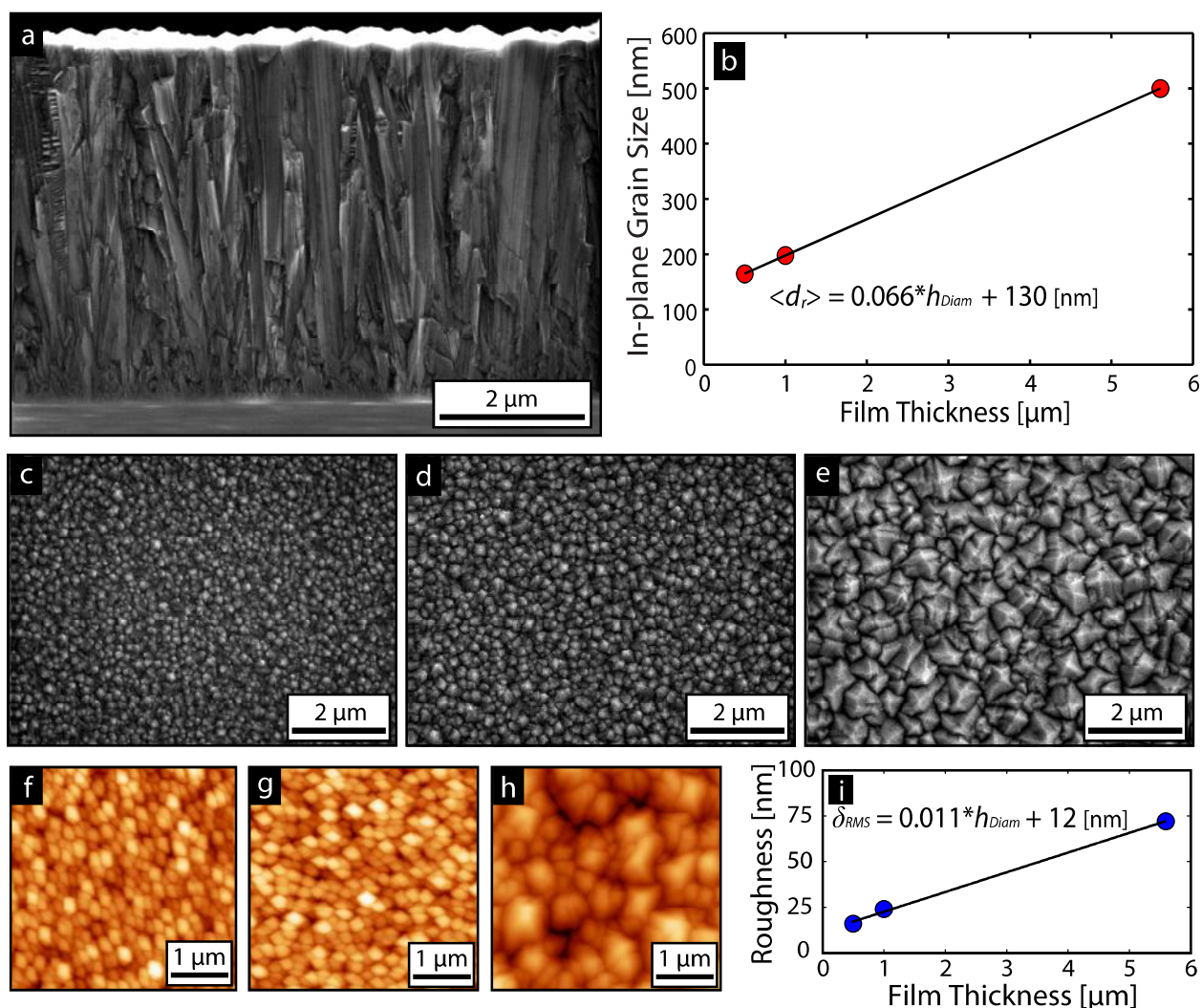


FIG. 1. Morphological characterization of nanocrystalline diamond films. (a) Cross-sectional SEM image of the 5.6 μm thick film showing a columnar grain structure. (b) Average in-plane grain size plotted against film thickness. (c)–(e) Plan-view SEM images of the 0.5, 1.0, and 5.6 μm films. (f)–(h) Top-side AFM images of the 0.5, 1.0, and 5.6 μm films. (i) Top-side RMS surface roughness.

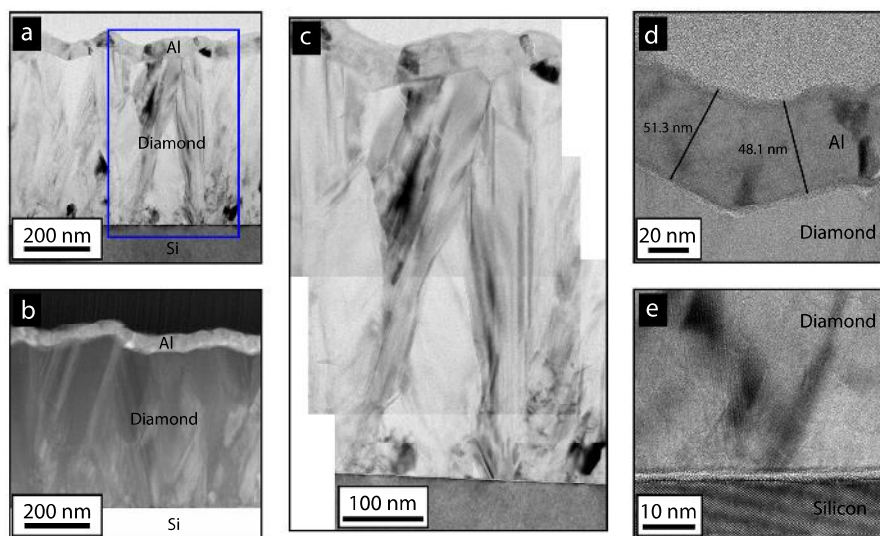


FIG. 2. Cross-sectional transmission electron micrographs (TEMs) of 500 nm thick diamond film on Si substrate, with 50 nm thick Al capping layer. (a) Low magnification TEM image. (b) Low magnification high-angle annular dark-field (HAADF) STEM image showing clearer contrast between Al, C, and Si. (c) TEM montage image of region marked in (a) showing the columnar grain structure within diamond and its evolution with distance from substrate. (d) High magnification image of the ~50 nm thick Al transducer layer. (e) High magnification image of the diamond/silicon interface.

are amplitude modulated at a frequency f_{mod} (2–8 MHz), and frequency doubled to 532 nm. The probe pulses travel along a separate path comprising a mechanical delay stage, which controls the probe delay time from 0 to 3.6 ns. The pump pulses, with an average power of ~ 5 mW, heat up the surface of the sample through optical absorption within a ~ 50 nm thick aluminum transducer layer. The optical absorption coefficient of Al at 532 nm is $\sim 1.2 \times 10^6 \text{ cm}^{-1}$,¹⁷ resulting in an optical skin depth of ~ 8 nm. The temporal variations in the temperature of the transducer surface are detected through changes in the reflected probe intensity, which is measured using a lock-in amplifier tuned to f_{mod} . The rate of temperature decay of the transducer layer is a function of the thermal properties of the underlying layers, such as their thermal conductivity and specific heat, and the thermal conductance of interfaces. The output signal consists of the in-phase and out-of-phase components of the lock-in voltage at the frequency of modulation, V_{in} and V_{out} , respectively. Unknown thermal properties are extracted by fitting either the amplitude $\rho = \sqrt{V_{in}^2 + V_{out}^2}$ or the ratio $\varphi = -V_{in}/V_{out}$ to a thermal diffusion model that accounts for Gaussian heating profiles, radial heat spreading, and finite thermal interface conductance between layers. The amplitude signal is typically normalized to its value at short time delay, which is +100 ps in all our measurements.

To mitigate the effects of probe beam divergence and steering during traverse of the delay stage, our setup incorporates a single mode fiber similar to that of Capinski and Maris.¹⁸ The time varying intensity of the probe beam is measured independently of the sample, so as to normalize these effects when fitting the amplitude signal. As will be explained later, our ability to use both the amplitude and ratio data from a TDTR experiment is an important aspect of our data analysis methodology, as it helps improve our extraction of intrinsic diamond properties from the aluminum/diamond TBR.

In our experiments, we use laser spot sizes ($1/e^2$ diameters) of $10.2 \pm 0.1 \text{ } \mu\text{m}$ and $6.2 \pm 0.2 \text{ } \mu\text{m}$ for the pump and probe beams, respectively. The pump spot size is measured using the DataRay Beam' R2-XY scanning-slit beam profiler. To measure the probe spot size, we perform knife-edge measurements in reflection mode using the sharp, lithographically defined step-edge of a 60/5 nm Pt/Ti film on a fused silica substrate (see supplementary material for details¹³). The total optical power incident on the sample is limited to ~ 7 mW in order to minimize steady state heating, while still maintaining a reasonably good signal to noise ratio. The steady state temperature rise is estimated to be ~ 19 K, 10 K, and 2 K for the 0.5, 1.0, and $5.6 \text{ } \mu\text{m}$ thick suspended films, respectively. The volumetric specific heat of diamond is taken from literature,¹⁹ while accounting for its temperature dependence due to optical heating. This is especially important to consider in the case of diamond due to its relatively high Debye temperature ($\theta_D \sim 1900$ K for diamond,¹⁹ compared with $\theta_D \sim 430$ K for aluminum²⁰), which causes the specific heat to increase strongly with temperature in the vicinity of 300 K. This local dependence is given approximately by $C_{v,Diam}(T) = [C_{v,Diam}(300 \text{ K}) + 0.012 \Delta T]$

MJ/m³-K, with $C_{v,Diam}(300 \text{ K}) = 1.8 \text{ MJ/m}^3\text{-K}$. The thermal conductivity of the Al transducer κ_{Al} is taken to be 140 W/m-K based on four-probe measurements of electrical conductivity and the Wiedemann Franz law, while its volumetric specific heat is taken from literature to be $C_{v,Al} = 2.45 \text{ MJ/m}^3\text{-K}$.²¹

B. Validation and sensitivity analysis

We validate the accuracy of our system by measuring reference samples with well-known thermal properties of magnitude comparable with those that we are reporting for diamond in the current study. Single crystalline silicon and single crystalline copper (MTI Corporation) are chosen as reference materials. Measured values of $140 \pm 10 \text{ W/m-K}$ and $390 \pm 30 \text{ W/m-K}$ for silicon and copper, respectively, are obtained, both of which are within 4% of literature values for these materials.²²

We quantify the sensitivity of the normalized amplitude (ρ) and ratio (φ) signals by defining the sensitivity coefficients S_γ as the fractional change in signal per unit fractional perturbation in the parameter γ as in Eq. (1)

$$S_\gamma = \frac{\partial \log(\text{Signal})}{\partial \log(\gamma)}. \quad (1)$$

The unknown parameters of interest are the in-plane and through-plane conductivity of the diamond film (κ_r and κ_z) and the TBR between the transducer and diamond ($TBR_{Al-Diam}$). Sensitivity coefficients for 1.0 and $5.6 \text{ } \mu\text{m}$ thick films are plotted in Figure 3.

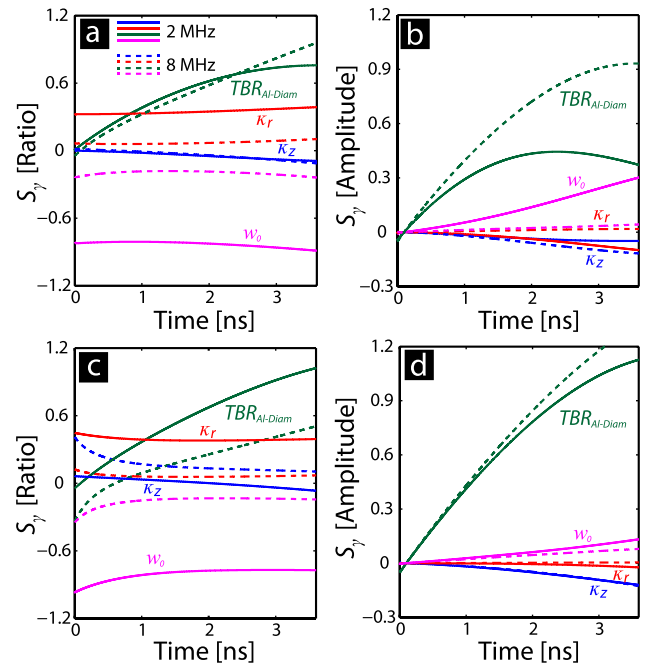


FIG. 3. Sensitivity coefficients for the ratio and normalized amplitude signals for (a) and (b) a $1.0 \text{ } \mu\text{m}$ thick suspended film with $\kappa_r = 70 \text{ W/m-K}$, $\kappa_z = 200 \text{ W/m-K}$, and $TBR_{Al-Diam} = 15 \text{ m}^2\text{K/GW}$ and (c) and (d) a $5.6 \text{ } \mu\text{m}$ thick suspended film with $\kappa_r = 120 \text{ W/m-K}$, $\kappa_z = 700 \text{ W/m-K}$, and $TBR_{Al-Diam} = 15 \text{ m}^2\text{K/GW}$. w_0 is the root mean square diameter of the laser spot. Solid and dashed lines correspond to modulation frequencies of 2 and 8 MHz, respectively. The amplitude is normalized to its value at +100 ps.

Separating the TBR at the Al-diamond interface, $TBR_{Al-Diam}$ from the diamond conductivity κ_r and κ_z is a crucial aspect of data analysis, especially for a high conductivity material like diamond. As mentioned earlier, we use a combination of the amplitude (ρ) and ratio (ϕ) signals in order to uniquely separate these quantities. Specifically, for highly conducting samples, $V_{in} \gg V_{out}$ and $\rho \approx V_{in}$ is largely sensitive to $TBR_{Al-Diam}$ while $\phi = -V_{in}/V_{out}$ is sensitive to both κ_r and κ_z in addition to $TBR_{Al-Diam}$. Sensitivity plots in Figure 3 show that at a high modulation frequency of 8 MHz, ρ is sensitive almost entirely to $TBR_{Al-Diam}$. At lower modulation frequencies, greater thermal spreading in the lateral direction causes ϕ to be more sensitive to the in-plane conductivity κ_r , while sensitivity to the through-plane conductivity κ_z is larger at higher modulation frequencies. The sensitivity to κ_r is further enhanced in our case due to the suspended nature of the diamond membrane. This can be visualized by plotting the three dimensional distribution of the normalized amplitude of temperature oscillations at the frequency of modulation, as shown in Figure 4. These simulations are performed by solving the multilayer heat diffusion equation for a modulated heat source, using methods presented elsewhere.^{14,23} As shown in these plots, greater lateral thermal penetration occurs when the film is suspended, as compared to when it is in contact with the high conductivity silicon substrate. Further, this lateral spreading is more pronounced at the lower modulation frequency, explaining why our sensitivity to κ_r is higher under these conditions.

IV. RESULTS AND DISCUSSION

Based on sensitivity analyses presented above, we use the ρ data at a high modulation frequency, $f_{mod} = 8$ MHz to fit uniquely for $TBR_{Al-Diam}$. We measure values between 10 and 15 m² K/GW for the three films, which are within the range reported in literature for metal-diamond interfaces.^{24,25}

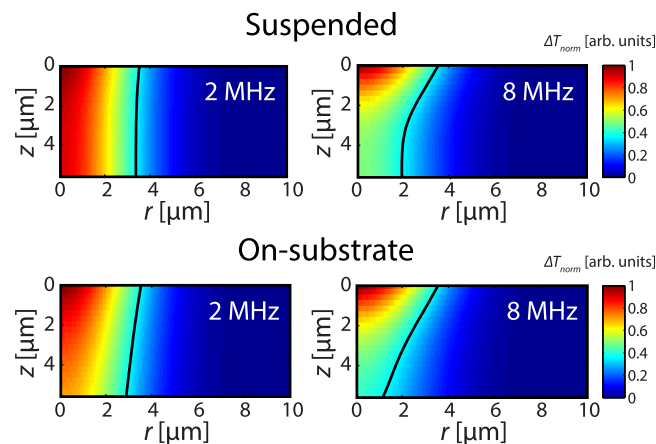


FIG. 4. Normalized amplitude of temperature oscillations, ΔT_{norm} , for sinusoidal heating using a Gaussian optical profile, centered at $r = z = 0$. Two cases are compared: suspended film versus film on substrate (silicon). In each case, $\Delta T_{norm}(r, z)$ is plotted for a low (2 MHz) and high (8 MHz) modulation frequency. Gaussian $1/e^2$ diameter = 10 μm , film thickness = 5.6 μm , $\kappa_r = 120$ W/m-K, and $\kappa_z = 700$ W/m-K. Lateral spreading is greater in the suspended case, and is further pronounced at the lower modulation frequency. Black lines are contours corresponding to $\Delta T_{norm} = 1/e$.

Fixing this value, we then fit ϕ data at a low modulation frequency (2 MHz) to extract κ_r . The low sensitivity to κ_z at these frequencies enables a unique extraction of κ_r . Finally, fixing values of κ_r and $TBR_{Al-Diam}$ based on this procedure, ϕ data taken at a high modulation frequency (8 MHz) are fit to a thermal model with only one unknown parameter, κ_z . This approach is applied to extract the anisotropic conductivities of all three films, measured from both sides. The results are presented in Table I and are plotted on a log-log scale as a function of film thickness in Figure 5(b). Due to low measurement sensitivity, no reliable data for κ_z could be obtained for the 0.5 μm thick film.

Error bars on the reported data are calculated by propagating uncertainties in the aluminum thickness ($\pm 5\%$, estimated based on TEM images), aluminum conductivity ($\pm 10\%$), and root mean square laser spot size ($\pm 2\%$). Spot-to-spot variability in the measurements is also taken into account. A detailed error propagation analysis is provided in the supplementary material.¹³

Because the measurements from the top and bottom sides of the film are more sensitive to large-grained and small-grained regions, respectively, we observe significantly different conductivities from these measurements. For instance, the through-plane conductivities as measured from the top and bottom sides are, respectively, 210 ± 50 W/m-K and 89 ± 20 W/m-K for the 1 μm thick film, and 710 ± 120 W/m-K and 250 ± 30 W/m-K for the 5.6 μm thick film. Sensitivity to the conductivity of a region situated at a distance z from the heating spot is a decreasing function of z , such that the effective homogeneous conductivity is a weighted function of local $\kappa_{r,z}(z)$. While the exact nature of this weighting function depends on details of film geometry, spot size, and measurement frequency, a reasonable first approximation is that this follows an exponential form $\sim \exp(-z/L_p)$, where L_p is the thermal penetration depth based on the modulation frequency f_{mod} . L_p is given approximately by $\sqrt{D/\pi f_{mod}}$, where D is the thermal diffusivity of diamond. For a typical conductivity of 100 W/m-K, $L_p \sim 2.8$ μm and 1.4 μm for $f_{mod} = 2$ MHz and 8 MHz, respectively. Measurements performed on the top-side are significantly more sensitive to properties of the large-grained high-quality region, and therefore, the effective homogeneous conductivities are larger for top-side data. In comparison, measurements on the bottom-side are more sensitive to properties of the small-grained near-interfacial diamond, and the low conductivity of the coalescence region dominates the thermal response.

TABLE I. Measured values of in-plane (κ_r) and through-plane (κ_z) thermal conductivity.

Thickness [μm]	Thermal conductivity [W/m-K]			
	Top side		Bottom side	
	κ_r	κ_z	κ_r	κ_z
0.5	52 ± 8	...	39 ± 6	...
1.0	77 ± 10	210 ± 50	46 ± 8	89 ± 20
5.6	130 ± 20	710 ± 120	120 ± 10	250 ± 30

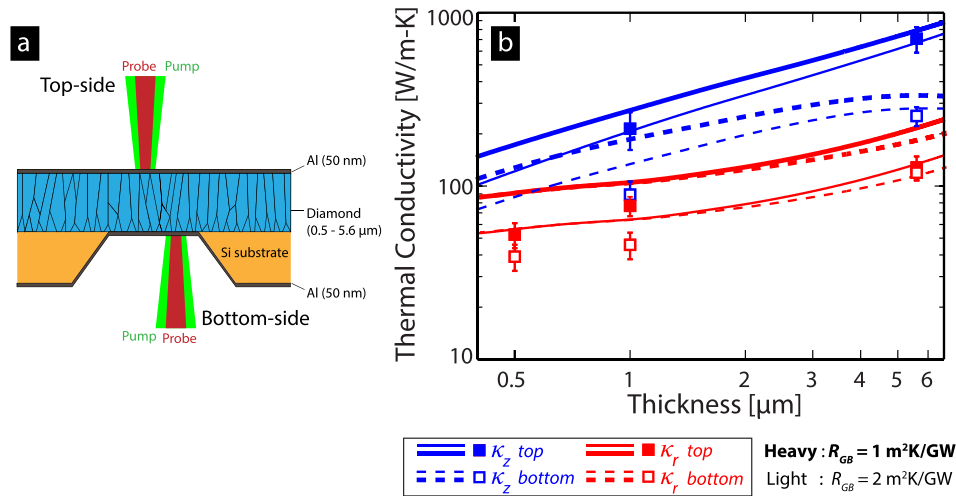


FIG. 5. (a) Sample and measurement schematic (not to scale). (b) Measured thermal conductivity data (square symbols) and model predictions (lines) plotted versus film thickness on a log-log scale. All data markers and model lines colored blue correspond to through-plane, while those colored red correspond to in-plane conductivity. Solid and open markers denote measurements taken on top and bottom sides, respectively. Continuous and dashed lines are model predictions for top and bottom sides, respectively. Two different sets of model curves are included: heavy (light) lines correspond to a grain-boundary thermal resistance of $R_{GB} = 1 \text{ m}^2\text{K/GW}$ ($2 \text{ m}^2\text{K/GW}$). Model parameters: $\lambda_{\text{bulk}} = 1 \text{ μm}$, $\kappa_{\text{bulk}} = 3000 \text{ W/m-K}$, $g = 10$, $\alpha = 0.066$, and $d_0 = 130 \text{ nm}$.

Further, we observe that both κ_r and κ_z increase with film thickness, for measurements made on either side of each film. This increase in the effective conductivity is a result of adding material with increasing quality as the films grow thicker. When measured from the top-side, κ_r increases from $52 \pm 8 \text{ W/m-K}$ to $130 \pm 20 \text{ W/m-K}$ as film thickness increases from 0.5 to 5.6 μm , while κ_z increases from $210 \pm 50 \text{ W/m-K}$ to $710 \pm 120 \text{ W/m-K}$ as thickness increases from 1.0 to 5.6 μm . This inhomogeneity is consistent with the trend seen in recent measurements of the thickness-dependent lateral conductivity of sub- μm diamond films.⁶

The strong columnar grain structure gives rise to a significant anisotropy, with $\kappa_r < \kappa_z$. We find that the anisotropy ratio ($\eta = \kappa_z / \kappa_r$) can be as large as ~ 3 – 5 for the high-quality regions of the 1.0 and 5.6 μm thick films. This contrast is higher than has been measured in previous studies of thicker polycrystalline diamond films. For example, Graebner *et al.*^{3,5} measured $\eta \sim 2$ for $\sim 70 \text{ μm}$ thick films. Figure 6 shows how

our measurements of anisotropy compare with studies from literature. For the sake of clarity, we plot the inverse anisotropy ratio, $1/\eta = \kappa_r / \kappa_z$, versus film thickness. Previous data for films thinner than 30 μm are from Verhoeven *et al.*²⁶ where η as large as 10 was measured for a 1.6 μm thick columnar diamond film, Rossi *et al.*²⁷ where $\eta \sim 2.5$ was measured for films between 0.5 μm and 1.1 μm , and Anaya *et al.*²⁸ where $\eta \sim 3.8$ was measured for a 0.68 μm thick film. Although exact values of anisotropy depend on growth conditions and spatial distribution of defects, a general trend of increasing anisotropy with decreasing film thickness appears from this comparison. As the films become thicker, they are expected to become more isotropic, as grain growth leads to large grain sizes in the lateral and vertical directions, and grain boundary scattering is no longer the dominant factor limiting thermal conductivity.

V. THEORETICAL MODEL

To understand the impact of the complex grain structure on thermal conduction within the polycrystalline film, we develop a theoretical model based on phonon-grain boundary scattering. The key parameter that determines the thermal conductivity tensor at a certain distance from the substrate is the average grain size at that location.

Previous work on modeling grain growth used atomistic methods such as molecular dynamics (MD),^{29,30} combined atomistic and mesoscale methods,^{31,32} and stochastic Monte Carlo techniques³³ to model competition between adjacent grains and development of columnar texture. While these *ab-initio* methods offer significant physical detail into the factors affecting the average grain size and its distribution, they also require accurate knowledge of the various parameters that can affect growth, such as temperature and other deposition conditions, in order to make quantitative predictions of grain size. In this work, instead of modeling grain growth from first principles, we use microstructural characterization techniques to determine how the average grain

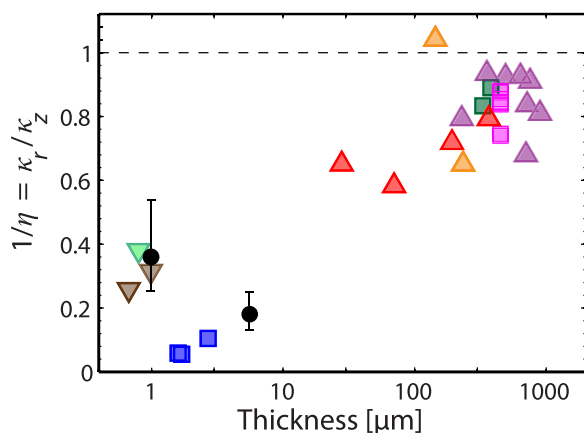


FIG. 6. Inverse anisotropy ratio $1/\eta = \kappa_r / \kappa_z$ as a function of film thickness on a log scale, showing how our data (black filled circles) compare with literature. Legend: red upward triangles,^{3,5} orange upward triangles,⁷ purple upward triangles,⁸ dark green squares,⁹ magenta squares,¹⁰ blue squares,²⁶ light green downward triangle,²⁷ and brown downward triangles.²⁸

size evolves with distance from the substrate, z . Since the grains are columnar, we distinguish the average in-plane grain size $\langle d_r \rangle(z)$ from the average through-plane grain size $\langle d_z \rangle(z)$.

Information about how the average in-plane grain size $\langle d_r \rangle$ varies with z can be obtained accurately from plan-view SEM images, as shown in Figures 1(b)–1(e). The average through-plane grain size $\langle d_z \rangle$, however, is far more difficult to measure directly, as cross-sectional images such as in Figures 1(a) and 2(a)–2(c) do not show the grain boundaries with sufficient clarity. In the first part of this section, we derive, using geometrical arguments, a mathematical expression for the evolution of $\langle d_z \rangle(z)$ in terms of parameters that describe the evolution of $\langle d_r \rangle(z)$. We then relate local variations in grain size to local thermal conductivity using a simplified phonon-scattering model. From the derived evolution of the anisotropic local conductivity, we generate simulated TDTR data, and re-fit this data assuming homogeneity, so as to extract thickness averaged conductivities that can be compared with experimental data. In this way, we seek to correlate the complex grain structure of polycrystalline diamond with the inhomogeneity and anisotropy in its thermal conductivity.

The grains are modeled as trapezoidal regions growing from a flat substrate, with the grain size in the direction parallel to the interface growing linearly with distance z from the growth interface, as in $d_r = \alpha z + d_0$ (see Figure 7). As in the real polycrystalline diamond material, competition occurs between adjacent grains, leading to a columnar texture. This is modeled by enforcing that when two or more grains impinge laterally, a finite fraction $1/g$ of them survives, where g is the inverse survival rate. For simplicity, the derivation that follows is for $g = 2$, but the result can be extended in general for any g .

If the lateral grain size of each grain grows according to the equation above, the average lateral grain size also has the same dependence on z ; therefore, $\langle d_r \rangle = \alpha z + d_0$. The goal is to calculate the average grain size in the perpendicular direction $\langle d_z \rangle$ as a function of z . We first define the values of z at which grains impinge on one another as z_i , $i = 1, 2, \dots, t$ such that z_t equals the film thickness L .

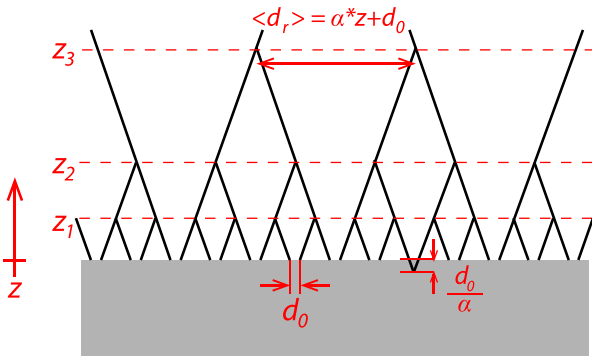


FIG. 7. Schematic showing growth of columnar grains, for the case of $g = 2$. Lateral grain size increases linearly with distance z from the growth interface. z_i ($i = 1, 2, 3, \dots$) denote points where adjacent grains impinge. At each level, a fraction $1/g$ of the grains survive.

At these specific values of $z = z_i$, $\langle d_z \rangle$ is calculated by counting the number of grains that are intersected by a line drawn parallel to the growth interface at z_i , and averaging over their respective lengths in the z direction. For example, the average through-plane grain size at $z = z_2$ for a film whose thickness is $L = z_6$ can be written as

$$\langle d_z \rangle(at z = z_2) = \frac{8z_3 + 4z_4 + 2z_5 + 1z_6 + 1L}{16} = \frac{1}{2}z_3 + \frac{1}{2^2}z_4 + \frac{1}{2^3}z_5 + \frac{1}{2^4}z_6 + \frac{1}{2^4}L. \quad (2)$$

In general,

$$\langle d_z \rangle(at z = z_i) = \frac{1}{2}z_{i+1} + \frac{1}{2^2}z_{i+2} + \dots + \frac{1}{2^{t-i}}z_{i+(t-i)} + \frac{1}{2^{t-i}}L = \sum_{n=1}^{t-i} \frac{1}{2^n}z_{i+n} + \frac{1}{2^{t-i}}L. \quad (3)$$

Next, we relate z_j to z_i for all $j > i$ using the simple geometrical relationship

$$\frac{\left(z_j + \frac{d_0}{\alpha}\right)}{\left(z_i + \frac{d_0}{\alpha}\right)} = 2^{j-i}. \quad (4)$$

Combinin Eqs. (3) and (4) gives

$$\langle d_z \rangle(at z = z_i) = \left(z_i + \frac{d_0}{\alpha}\right)(t-i) - \frac{d_0}{\alpha} \left(1 - \frac{1}{2^{t-i}}\right) + \frac{L}{2^{t-i}}, \quad (5)$$

where $(t-i)$ can be obtained as a special case of Eq. (4) by setting $j = t$ and $z_j = L$. Substituting this in Eq. (5), dropping the subscript i and setting dimensionless quantities: $\zeta = z/L$ and $\beta = d_0/L$, we get

$$\frac{\langle d_z \rangle}{L} = \left(\zeta + \frac{\beta}{\alpha}\right) \left[\frac{1}{\log(2)} \log \left(\frac{1 + \frac{\beta}{\alpha}}{\zeta + \frac{\beta}{\alpha}} \right) + 1 \right] - \frac{\beta}{\alpha}. \quad (6)$$

Generalizing this result for any arbitrary $g > 1$, a generalized expression is obtained for the average through-plane grain size normalized to film thickness

$$\frac{\langle d_z \rangle}{L} = \left(\zeta + \frac{\beta}{\alpha}\right) \left[\frac{1}{\log(g)} \log \left(\frac{1 + \frac{\beta}{\alpha}}{\zeta + \frac{\beta}{\alpha}} \right) + 1 \right] - \frac{\beta}{\alpha}. \quad (7)$$

The parameters α and β can be extracted from measurements of in-plane grain size, which can be written in a similar normalized form

$$\frac{\langle d_r \rangle}{L} = \alpha \left(\zeta + \frac{\beta}{\alpha} \right). \quad (8)$$

Examining Eq. (7) more closely, we look at the extreme cases: (1) for regions close to the growth interface, i.e., as

$\zeta \rightarrow 0$ $\frac{\langle d_z \rangle}{L} = \left(\zeta + \frac{\beta}{\alpha} \right) \left[\frac{1}{\log(g)} \log \left(1 + \frac{\alpha}{\beta} \right) + 1 \right] - \frac{\beta}{\alpha}$, and (2) for regions close to the free surface of the film, i.e., $\zeta \rightarrow 1$, $\frac{\langle d_z \rangle}{L} \rightarrow 1$. Therefore, the average vertical grain size increases linearly with z close to the interface, and as grains grow and compete with each other, most grains extend throughout the film thickness, and $\langle d_z \rangle$ tends towards L . Figure 8(a) shows how $\langle d_r \rangle$ and $\langle d_z \rangle$ vary with z for a 1 μm thick film, whose in-plane grain size is based on SEM measurements made on the current samples [from Figure 1(b)], for different values of $g = 3, 5$, and 10.

Having derived the average grain dimensions in both directions as a function of z , we now turn our attention to calculating the local thermal conductivities $\kappa_r(z)$ and $\kappa_z(z)$. For this, we use the model proposed by Wang *et al.*³⁴ for phonon scattering in polycrystalline nanostructures. This model has been validated recently through Monte Carlo simulations by Hori *et al.*³⁵ The local phonon mean free path in the vertical and lateral directions λ_z and λ_r can be written in terms of local grain sizes $\langle d_z \rangle$ and $\langle d_r \rangle$, respectively, and the bulk phonon mean free path λ_{bulk} using a Matthiessen's rule type approach

$$\lambda_{z,r}(z) = \left(\frac{1}{\lambda_{\text{bulk}}} + \frac{1}{0.75 \langle d_{z,r} \rangle} + \frac{1}{1.12 \langle d_{r,z} \rangle} \right)^{-1}. \quad (9)$$

The coefficients for scattering on grain boundaries parallel and perpendicular to the direction of heat flow are determined based on some assumptions regarding the quality of boundaries, as well as probability of phonon transmission across them. Generally, phonon scattering on grain boundaries oriented parallel to the heat flow is controlled by the specular parameter p_{GB} (third term in Eq. (9)), while scattering on boundaries oriented normal to heat flow depends on the transmissivity t_{GB} ³⁴ (second term in Eq. (9)). In this work, we assume that $p_{GB} = 0$, implying completely diffuse scattering. This is valid due to the significant disorder typically associated with diamond grain boundaries, including that arising from the accumulation of planar defects near them.³⁶ The factor of 1.12 arises from previous calculations of the thermal conductivity for nanowires with square cross-section.³⁵ The phonon transmissivity is fixed at $t_{GB} = 0.5$ due

to identical materials being present on either side of the grain boundary. Finally, we assume negligible phonon scattering on defects present within each grain, such as vacancies and sp² atom clusters. Making these assumptions in the framework described in Wang *et al.*³⁴ results in the Eq. (9).

To determine λ_{bulk} , we refer to previously published *ab-initio* calculations of the phonon mean free path spectrum of diamond. Li *et al.*³⁷ showed that in contrast to materials like silicon, the mean free path accumulation function in diamond is significantly narrower. For instance, in silicon at room temperature, 80% of heat is carried by phonons that have a mean free path between 45 nm and 13 μm , spanning nearly two and a half orders of magnitude. In contrast, in diamond, 80% of the heat is carried by phonons with mean free paths between 550 nm and 3400 nm, which is a much smaller range. Based on these calculations, we make the simplifying assumption of a grey, i.e., frequency independent phonon mean free path in diamond, $\lambda_{\text{bulk}} = 1 \mu\text{m}$, which is the value at which the mean free path accumulation function shows the steepest rate of increase. Using this number for the grey mean free path, the local conductivity within each grain in the two directions is computed by scaling $\lambda_{z,r}(z)$ relative to λ_{bulk}

$$\kappa_{\text{Int}|z,r}(z) = \kappa_{\text{bulk}} \frac{\lambda_{z,r}(z)}{\lambda_{\text{bulk}}}, \quad (10)$$

where κ_{bulk} is the thermal conductivity of bulk single crystal. We assume $\kappa_{\text{bulk}} = 3000 \text{ W/m-K}$ based on calculations by Li *et al.*,³⁷ for diamond nanowires in the large diameter limit (see supplementary material for a sensitivity analysis of the model predictions to the assumed κ_{bulk} ¹³).

To account for the resistance offered to heat flow across grain boundaries R_{GB} , this term is added in series with the thermal resistance within the grain, and the net local conductivity is calculated,

$$\kappa_{z,r}(z) = \left(\frac{1}{\kappa_{\text{Int}|z,r}(z)} + \frac{R_{GB}}{\langle d_{z,r} \rangle} \right)^{-1}. \quad (11)$$

Figure 8(b) shows a plot of the local conductivity $\kappa_z(z)$ and $\kappa_r(z)$ for a 1 μm thick film, for various values of $g = 3, 5$,

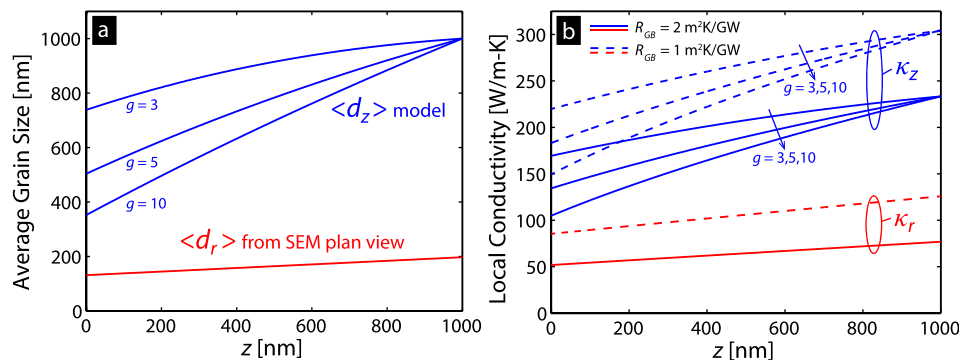


FIG. 8. (a) Average grain size in the in-plane and through-plane directions as a function of distance z from the growth interface for a 1 μm thick film. $\langle d_r \rangle = 0.066z + 130$ [nm], from plan-view SEM measurements, and $\langle d_z \rangle$ is based on the geometrical model given by Eq. (7). (b) Local conductivity values $\kappa_z(z)$ and $\kappa_r(z)$, for a 1 μm thick film. Two different sets of curves are provided for $R_{GB} = 1 \text{ m}^2 \text{ K/GW}$ (dashed) and $2 \text{ m}^2 \text{ K/GW}$ (solid). A bulk conductivity of $\kappa_{\text{bulk}} = 3000 \text{ W/m-K}$, and grey phonon mean free path of $\lambda_{\text{bulk}} = 1 \mu\text{m}$ is assumed for the single crystal. Curves corresponding to three different values of the inverse survival rate g are shown: $g = 3, 5$, and 10.

10, and for two different values of the grain boundary resistance, $R_{GB} = 1 \text{ m}^2\text{K/GW}$ and $2 \text{ m}^2\text{K/GW}$.

Having obtained model predictions for the local thermal conductivity in both directions, our next step is to convert these into a form that can be compared with the TDTR data. To do this, simulated data curves are generated using the same multi-layer heat diffusion model that was used to fit TDTR data, dividing the diamond layer into several discrete sub-layers. The local conductivities of each sub-layer are determined by the procedure described earlier. These simulated curves are then re-fit to a model that assumes the diamond layer is homogeneous across its thickness, so as to mimic our TDTR extraction methodology. Similar to the experiments, κ_r and κ_z are determined by fitting the simulated data at 2 MHz and 8 MHz modulation frequencies, respectively. Results of this model are shown in Figure 5(b) where they are compared with experimental data on a log-log scale. Model calculations are plotted for the following set of parameters: $\lambda_{bulk} = 1 \text{ }\mu\text{m}$, $\kappa_{bulk} = 3000 \text{ W/m-K}$, $g = 10$, $\alpha = 0.066$, and $d_0 = 130 \text{ nm}$, with two sets of curves corresponding to $R_{GB} = 1 \text{ m}^2\text{K/GW}$ and $2 \text{ m}^2\text{K/GW}$. While the goal of this approach is not to provide exact quantitative predictions, we find reasonable agreement between the model and data for the chosen parameter set. In particular, the model successfully captures the following essential features: a strong anisotropy in thermal conductivity, with $\kappa_z > \kappa_r$, a difference in the conductivities measured from the top and bottom-sides owing to inhomogeneity, and overall increasing trends in κ_r and κ_z with film thickness due to the evolving grain size. We note further that the grain boundary resistance R_{GB} has a significant adverse impact on the thermal conductivity. It is possible that the model over-predicts the conductivity measured from the bottom-side of the thinner films, because of an R_{GB} that is higher for grains closer to the nucleation region,⁶ or a grain size that decreases more rapidly with decreasing z in the near-interfacial region than has been modeled here.

VI. CONCLUSIONS

We have used a single experimental technique to probe both the in-plane and through-plane thermal conductivities in CVD diamond films thinner than $6 \text{ }\mu\text{m}$. The use of suspended membranes greatly enhances our sensitivity to the in-plane conductivity, while allowing us to uniquely extract the intrinsic diamond properties unaffected by the TBR at the diamond-substrate interface. A large anisotropy is measured, which is more than in previous reports on thicker films, suggesting that this is linked to the strong columnar morphology of the near-interfacial grain structure, and the fact that the average grain size is smaller than the dominant phonon mean free path. Our measurement of different conductivities from the top and bottom sides of the films, and their dependence on thickness, both illustrate the impact that grain inhomogeneity has on thermal transport. The dependence of thermal conductivity on grain size also provides guidelines for improving the thermal quality of the near-interfacial diamond, in that a larger grain size, lower disorder at the grain boundaries, and a grain distribution that evolves more rapidly with film thickness, can all have a significant favorable

impact on the conductivity of this region. Finally, this work provides a framework for measuring and understanding microstructure-thermal property relationships in polycrystalline thin films, and suggests a theoretical basis for modeling this correlation in columnar-grained materials.

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Supplementary Information for:

Anisotropic and Inhomogeneous Thermal Conduction in Suspended Thin-Film Polycrystalline Diamond

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1. Grain size measurement

To calculate the average in-plane grain size $\langle d_r \rangle$, we use the planimetric method (ASTM E-112 standard¹). The number density of grains N_A is computed by counting the number of grains that lie inside the boundaries of a square drawn on top of a plan-view micrograph, and dividing by its area. The average area per grain is given by $\bar{A} = 1/N_A$, and average grain size is $\langle d_r \rangle = \sqrt{\bar{A}}$. Based on recommendations of the ASTM E-112 standard, to ensure good precision, the size of the square is chosen to be big enough to enclose at least 50 grains. For the three films with thicknesses 0.5, 1.0 and 5.6 μm , we count 150, 103 and 256 grains enclosed within square regions of side 2 μm , 2 μm and 8 μm , respectively. Table S1 below summarizes these calculations.

Film thickness (μm)	Area of square ($\mu\text{m} \times \mu\text{m}$)	# Grains	N_A (μm^{-2})	$\langle d_r \rangle$ (nm)
0.5	2 x 2	150	37.1	164
1.0	2 x 2	103	25.8	198
5.6	8 x 8	256	4.0	500

Table S1: Grain-size calculations based on the planimetric method.

2. Laser spot size measurement

To measure the focused spot diameters of the pump and probe laser beams, w_{pump} and w_{probe} , we use scanning-slit and knife-edge methods, respectively. Scanning-slit profiles for the pump beam are acquired using the DataRay Beam'R2-XY system. Figure S1 (a)-(b) shows beam profiles along the horizontal and vertical axes, along with their respective Gaussian fits. We measure a $1/e^2$ diameter of $w_{pump} = 10.2 \pm 0.1 \mu\text{m}$, with an ellipticity $> 97 \%$.

Measurements of the probe beam cannot be made using this instrument due to the wavelength limit of the Si detector. To measure the spot size of the probe beam, we use a home-built knife-edge technique in reflection mode. Square pads of a $\sim 60/5 \text{ nm}$ Pt/Ti film are patterned on a transparent fused silica substrate, with sharp edges that are defined photo-lithographically. The surface of the Pt film is first brought into focus by maximizing the amplitude of the TDTR signal on the photo-detector. Then, with the pump blocked, the reflected intensity of the probe beam is monitored as the film is scanned in a plane perpendicular to the optical axis in increments of 250 nm using a precision mechanical stage. As the laser spot moves across the step-edge from the high reflectivity Pt to the low reflectivity fused silica, the reflected probe intensity drops sharply. To obtain high signal-to-noise ratio, the probe is chopped at $\sim 225 \text{ Hz}$ using a mechanical chopper, and the output of the detector is demodulated using an audio lock-in synced to the chopper frequency. The resulting normalized reflectivity profiles are fit to an error function form according to the equation,

$$R_{KE}(r_{KE}) = \frac{1}{2} \left[1 - \text{erf} \left(\frac{2\sqrt{2} (r_{KE} - r_{0,KE})}{w_{probe}} \right) \right] \quad \text{Eq. (S1)}$$

where r_{KE} is the coordinate of the knife-edge, $R_{KE}(r_{KE})$ is the reflected probe power normalized to the peak reflected power over the Pt surface, w_{probe} is the $1/e^2$ diameter of the spot, and $r_{0,KE}$ is the center. The two fitting parameters are w_{probe} and $r_{0,KE}$.

Normalized data with error-function fits along the horizontal and vertical axes are shown in Figure S1 (c)-(d). We measure $w_{probe} = 6.2 \pm 0.2 \mu\text{m}$, with an ellipticity $> 93 \%$.

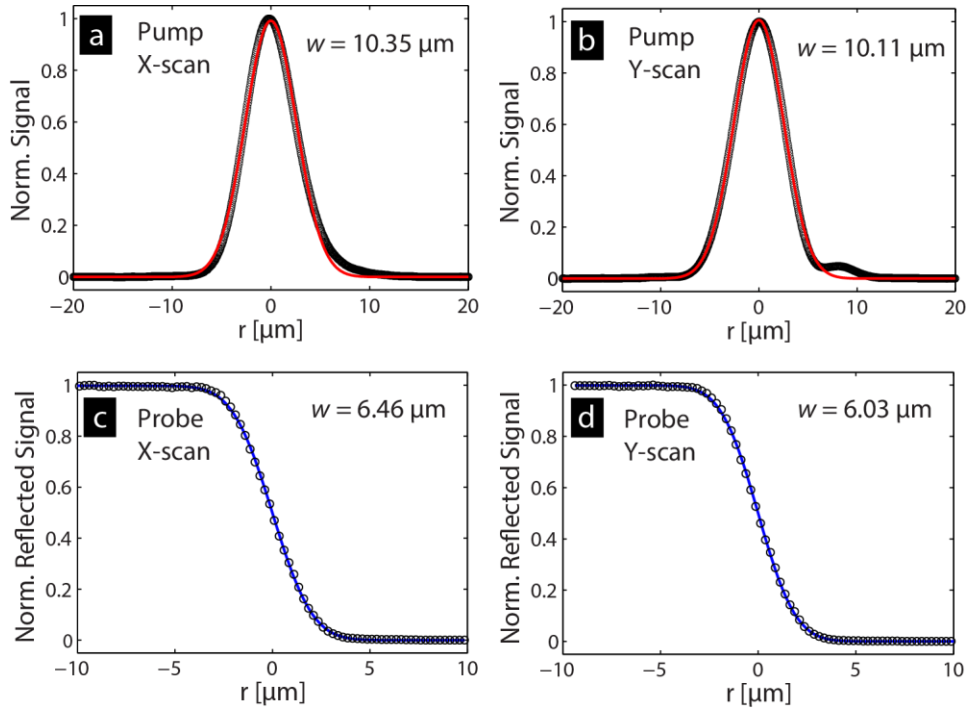


Figure S1: (a), (b): Scanning-slit beam profiles of the pump beam along the horizontal and vertical axes, respectively, with Gaussian fits. (c)-(d): Knife-edge normalized reflectivity profiles of the probe beam along the horizontal and vertical axes, respectively, with fits to the error function.

3. Error propagation analysis

Table S2 below shows the percentage errors contributed towards the extraction of in-plane and cross-plane thermal conductivity values, κ_r and κ_z , respectively, from the various sources of uncertainty. These include the Al thickness t_{Al} ($\pm 5\%$), Al conductivity κ_{Al} ($\pm 10\%$), and the root mean square $1/e^2$ laser spot diameter w_0 ($\pm 2\%$). Note that w_0 is defined as $\sqrt{0.5 (w_{pump}^2 + w_{probe}^2)}$. Also included are errors associated with spot-to-spot variability. Final error bars are calculated by adding up the individual error components in quadrature.

	t_{Al} ($\pm 5\%$)		κ_{Al} ($\pm 10\%$)		w_0 ($\pm 2\%$)		Spot-to-spot variation		Total error	
	% $\Delta\kappa_r$	% $\Delta\kappa_z$	% $\Delta\kappa_r$	% $\Delta\kappa_z$	% $\Delta\kappa_r$	% $\Delta\kappa_z$	% $\Delta\kappa_r$	% $\Delta\kappa_z$	% $\Delta\kappa_r$	% $\Delta\kappa_z$
0.5 μm Top	7.8	...	2.4	...	6.1	...	12.9	...	16.4	...
0.5 μm Bottom	10.5	...	3.4	...	6.6	...	11.5	...	17.2	...
1.0 μm Top	11.2	20.1	1.3	1.2	4.8	0.3	3.8	14.2	12.8	24.6
1.0 μm Bottom	16.3	12.2	2.7	1.1	5.2	0.3	2.3	14.7	17.5	19.1
5.6 μm Top	8.8	13.4	0.4	0.7	4.1	2.0	12.4	9.9	15.7	16.8
5.6 μm Bottom	7.7	6.4	0.5	1.1	4.3	0.3	4.1	10.7	9.7	12.5

Table S2: Error propagation from various sources of uncertainty.

4. Model sensitivity to assumed bulk properties of diamond

Here we test the sensitivity of our model to the assumed bulk conductivity, κ_{bulk} . Calculations are made for two different values of $\kappa_{bulk} = 3000$ W/m-K, and 2000 W/m-K. The grey bulk mean free path λ_{bulk} is scaled in proportion to κ_{bulk} , its corresponding values are $\lambda_{bulk} = 1$ μm and 0.67 μm , respectively. As shown in Figure S2, the assumed value of κ_{bulk} has little impact on the predicted local thermal conductivity in the polycrystalline film. In comparison, the thermal boundary resistance at grain boundaries, R_{GB} , has a far greater impact on κ_r and κ_z . This is consistent with the fact that heat transport in this material is dominated by phonon scattering at grain-boundaries and not phonon-phonon scattering within individual grains.

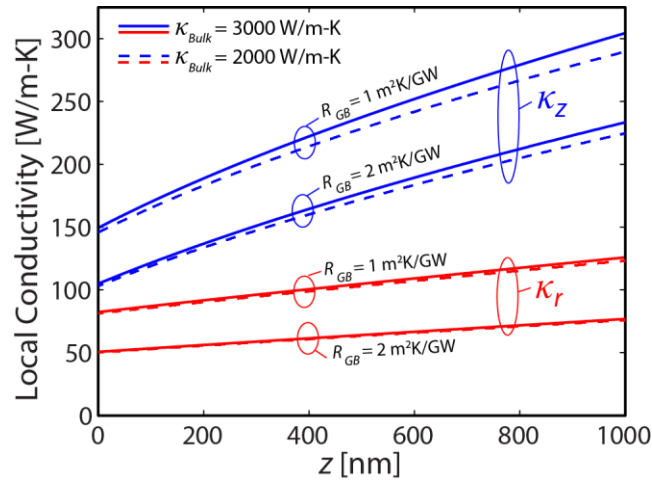


Figure S2: Sensitivity of the local conductivity $\kappa_z(z)$ and $\kappa_r(z)$ to the assumed bulk conductivity κ_{bulk} , for a 1 μm thick film. Solid lines correspond to $\kappa_{bulk} = 3000$ W/m-K, $\lambda_{bulk} = 1$ μm , while dashed lines correspond to $\kappa_{bulk} = 2000$ W/m-K, $\lambda_{bulk} = 0.67$ μm . Two different sets of curves are provided for $R_{GB} = 1$ $\text{m}^2\text{K/GW}$ and 2 $\text{m}^2\text{K/GW}$. Other model parameters: $g = 10$, $\alpha = 0.066$, $d_0 = 130$ nm.

REFERENCES

1. “ASTM E-112: Standard test methods for determining average grain size”, ASTM International