

High In-Plane Thermal Conductivity of Aluminum Nitride Thin Films

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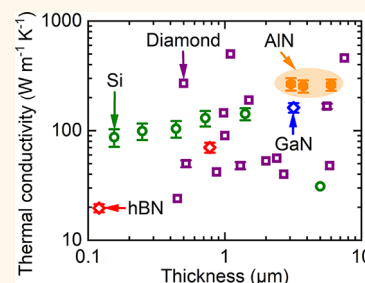
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Supporting Information

ABSTRACT: High thermal conductivity materials show promise for thermal mitigation and heat removal in devices. However, shrinking the length scales of these materials often leads to significant reductions in thermal conductivities, thus invalidating their applicability to functional devices. In this work, we report on high in-plane thermal conductivities of 3.05, 3.75, and 6 μm thick aluminum nitride (AlN) films measured *via* steady-state thermoreflectance. At room temperature, the AlN films possess an in-plane thermal conductivity of $\sim 260 \pm 40 \text{ W m}^{-1} \text{ K}^{-1}$, one of the highest reported to date for any thin film material of equivalent thickness. At low temperatures, the in-plane thermal conductivities of the AlN films surpass even those of diamond thin films. Phonon–phonon scattering drives the in-plane thermal transport of these AlN thin films, leading to an increase in thermal conductivity as temperature decreases. This is opposite of what is observed in traditional high thermal conductivity thin films, where boundaries and defects that arise from film growth cause a thermal conductivity reduction with decreasing temperature. This study provides insight into the interplay among boundary, defect, and phonon–phonon scattering that drives the high in-plane thermal conductivity of the AlN thin films and demonstrates that these AlN films are promising materials for heat spreaders in electronic devices.

KEYWORDS: AlN thin films, in-plane thermal conductivity, steady-state thermoreflectance, phonon–phonon scattering, anisotropy ratio



Thermal dissipation from hot spots presents a bottleneck to the efficient and reliable operation of electronic devices, ranging from low-power logic devices to high-power RF high electron mobility transistors.^{1–7} Different techniques, such as power management,⁸ improved packaging technology,^{6,9} thermoelectric cooling,¹⁰ heat sink design,^{11,12} and lateral heat spreaders,^{4,5,9} have been implemented to circumvent this problem. However, these solutions often require departure from the most efficient electronic device geometry to allow for gains in thermal dissipation. An ideal solution to this problem would be the development of high in-plane thermal conductivity nonmetallic materials that are able to easily remove heat from hot spots. These materials would also need to remain in thin film form to continue to allow current device architectures and form factors. To this end, high thermal conductivity crystals (*e.g.*, diamond, cubic boron nitride, boron arsenide, aluminum nitride, and gallium nitride) and two-dimensional layered materials (*e.g.*, graphene and hexagonal boron nitride) have received significant attention in recent years.^{4,13} Thin films of these nonmetallic materials can be implemented as heat spreaders when their thicknesses are larger than the hot-spot length

scales^{3,4,14,15} in devices. This implementation also requires that the thin films have adequate length scales and crystal qualities to ensure bulk or near-bulk thermal conductivities. However, this is paradoxical, since defects and boundaries arising from thin film growth commonly result in much reduced thermal conductivities as compared to the respective bulk values. Among bulk solids, diamond has the highest thermal conductivity, above $2000 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature.^{4,16} However, implementation of diamond thin films as heat spreaders has several limitations. For example, the thermal conductivities of diamond thin films are much lower than the bulk value due to microstructural features and defects during growth.^{17,18} Additionally, heterogeneous integration of materials onto diamond can lead to poor crystal quality due to lattice constant mismatch. Cubic boron arsenide, isotopically

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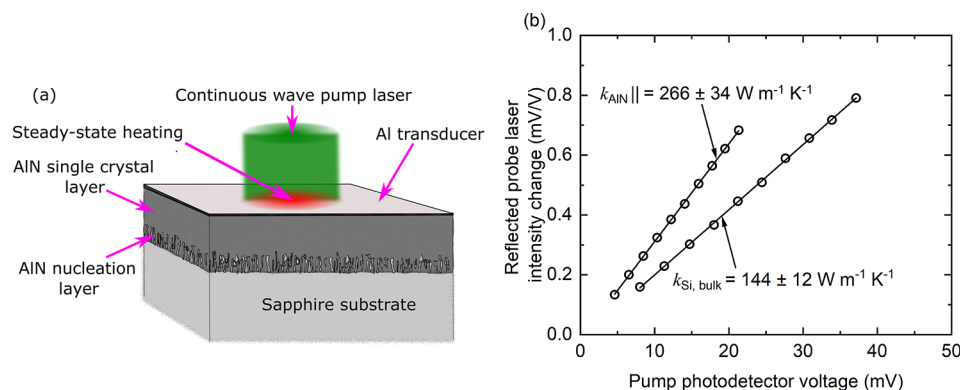


Figure 1. (a) Schematic of the AlN thin film samples measured in this study: Al transducer/AlN film/sapphire substrate. The AlN films are 3.05, 3.75, and 6 μm thick. The Al transducer thicknesses of the samples are tabulated in Table S1. (b) Reflected probe laser intensity change as a function of pump photodetector voltage for SSTR fitting of bulk Si, and 3.05 μm AlN film thermal conductivities. For bulk Si, SSTR measures the geometric mean of in-plane and cross-plane thermal conductivities. However, for the AlN thin films on sapphire substrates, SSTR directly measures the in-plane thermal conductivities of the AlN films.

enriched cubic boron nitride, and boron phosphide also have high thermal conductivity in bulk form.^{16,19,20} Shrinking the length scales of these materials may lead to thermal conductivity reduction issues similar to those of diamond. Two-dimensional (2D) materials, on the other hand, have a small cross-sectional area in the in-plane direction by design. Therefore, in order to increase the thermal conductance and use them as efficient heat spreaders, the thickness of the 2D materials may need to be increased.^{4,21} Moreover, the thermal boundary conductance between 2D layers and substrates can be an additional crucial parameter that controls the heat spreading efficiency as it can reduce the effective thermal conductivity due to mode scattering and suppression.⁴

Compared to the other III–V compound semiconductors, bulk, high-purity aluminum nitride (AlN) crystals have advantageous electronic properties, requisite transparency and higher thermal conductivity, making them suitable for use in optoelectronics, light-emitting diodes and high-power RF devices.^{4,22–30} However, the use of AlN as heat spreaders in high-power electronic devices comes with the challenge of achieving high thermal conductivities in thin film forms. Recently, Koh *et al.*³¹ reported bulk-like cross-plane thermal conductivities in high-quality AlN films with thicknesses ranging from 3 to 22 μm . These promising results suggest that high-quality micrometer-thick films of AlN could act as heat spreaders in high-power devices depending on their in-plane transport properties.

While extensive literature exists on the cross-plane thermal conductivity of AlN,^{23,32–40} reports on the in-plane thermal conductivity are almost non-existent. It is well-known that, in thin films, in-plane thermal transport is much less impacted by boundary scattering compared to cross-plane transport.^{41–43} The intrinsic phonon thermal conductivity^{22,23,28,40,44} of AlN suggests it may exhibit exceptional heat spreading characteristics and high in-plane thermal conductivity in its thin film form. Thus, measurement of the in-plane thermal conductivity of high-quality AlN thin films is paramount to realizing its potential as a radial heat sink.

The optical pump–probe technique steady-state thermoreflectance (SSTR)⁴⁵ provides an ideal platform to measure the in-plane thermal conductivity of high-quality thin films. This recently developed noncontact technique has several advantages over traditional pump–probe spectroscopies such as

time-domain thermoreflectance (TDTR)^{46–49} and frequency-domain thermoreflectance (FDTR).⁵⁰ For example, SSTR is a direct measure of thermal conductivity, and thus, unlike TDTR and FDTR, it does not require prior knowledge of heat capacity due to the steady-state nature of the measurements.^{45,51,52} Also, the measurement length scales (*i.e.*, thermal penetration depths) allow SSTR to probe deeper beneath a sample surface compared to TDTR and FDTR.⁴⁵ As a result, SSTR can measure thermal conductivity of a buried layer when the thermal resistance offered by this layer is much higher than those of the top layer and substrate.^{53,54} Depending on the sample geometries, SSTR can measure the in-plane thermal conductivity of thin films, whereas TDTR and FDTR in typical operating conditions are mostly limited to cross-plane measurements.

In this study, we use SSTR to measure and understand the phonon heat transport mechanisms that drive the high in-plane thermal conductivities of 3.05, 3.75, and 6 μm thick AlN films grown on sapphire substrates. At room temperature, the in-plane thermal conductivities of these high-quality AlN films are much less impacted by boundary and defect scattering as compared to graphite and diamond thin films. As temperature decreases, phonon–phonon scattering continues to dominate the in-plane thermal conductivities of the AlN thin films. This is in contradiction to the phonon scattering mechanisms commonly observed in other thin film materials, such as diamond, where phonon–boundary and phonon–defect scattering processes dominate the thermal conductivity with a reduction in temperature. As a result, at low temperatures, the in-plane thermal conductivities of the AlN films are surpassed only by graphite among all thin film materials of equivalent length scale. Moreover, we find that the point- and line-defect scattering due to the presence of a nucleation layer near the AlN/sapphire interface can cause a large temperature-dependent anisotropy ratio (the ratio of in-plane to cross-plane thermal conductivity) in the AlN thin films.

RESULTS AND DISCUSSION

The AlN thin films used in this work are grown on sapphire substrates using metal–organic chemical vapor deposition (MOCVD).^{55,56} We study three AlN films with thicknesses of 3.05, 3.75, and 6 μm . The AlN films of this study and those of Koh *et al.*³¹ were grown in the same batch. Scanning

transmission electron microscopy (STEM) reveals the existence of a nucleation layer near the AlN/sapphire interface in all samples, as shown in Supporting Information Figure S1. The thickness of this nucleation layer is less than 22% of the total film thickness.³¹ The region above the nucleation layer is a single crystal AlN layer. This single crystal layer has low concentrations of silicon (Si), carbon (C), and oxygen (O) impurities, whereas the nucleation layer has relatively higher concentrations of these point defects.^{31,40} The Al vacancy concentrations in the films used in this study are negligible.⁴⁰ The dislocation density is on the order of 10^8 cm^{-2} in the single crystal layer and 1–2 orders of magnitude higher in the nucleation layer. Details of sample growth and characterizations are provided in the Supporting Information.

A schematic of the AlN thin film samples measured in this study is presented in Figure 1a. Each sample consists of an aluminum (Al) transducer, an AlN thin film, and a sapphire substrate. In SSTR, the thermal conductivity is determined by fitting the ratio of reflected probe laser intensity change and pump photodetector voltage (proportional to pump power) to a steady-state thermal model.⁴⁵ SSTR best fit curves for the thermal conductivity of our bulk Si calibration sample and 3.05 μm AlN thin film sample are shown in Figure 1b. For bulk Si, SSTR measures the geometric mean of in-plane ($k_{\parallel}$) and cross-plane ($k_{\perp}$) thermal conductivities.⁴⁵ However, due to the radial heat spreading in the AlN thin films, SSTR measurements are much more strongly influenced by the in-plane thermal conductivity of the AlN films compared to the cross-plane. We show this in the sensitivity calculations and steady-state temperature rise profiles of the AlN films in Figures S2 and S3, respectively. Details of our SSTR measurements, fitting procedure, and uncertainty analysis can be found in the Supporting Information.

Bulk Si is used as a calibration sample, and its thermal conductivity is measured by both SSTR and TDTR from 120 to 400 K, as shown in Figure 2. At low temperatures, our TDTR-measured Si thermal conductivities are lower than the values reported in literature for bulk Si.⁵⁷ A lower thermal conductivity of Si measured *via* TDTR has also been reported

by Wilson and Cahill.⁵⁸ As discussed extensively in recent literature,^{58–60} TDTR and FDTR have failed to measure the thermal conductivities of Si at low temperatures due to obfuscations from thermal boundary resistances, non-equilibrium processes, and limiting heater length scales. Similar phenomena have also been reported for several other high thermal conductivity crystals and thick alloys.^{58–65} We note that though TDTR fails for Si and several other crystals, the thermal conductivity of sapphire and AlN can be accurately measured by TDTR at low temperatures.^{31,40,66} The nature of such material specific failure of TDTR is an active area of research^{58,63} and beyond the scope of this work. However, due to the measurement time and length scales, SSTR measurements are less sensitive to the above-mentioned limitations. As a result, SSTR can accurately measure the intrinsic, bulk thermal conductivity of Si as evident in Figure 2. Within uncertainty, the Si thermal conductivities measured by SSTR are in good agreement with previous literature.⁵⁷ The small deviations observed in SSTR measurements from the values reported in literature can be attributed to the uncertainty associated with temperature and other experimental variables, details of which are discussed in the Supporting Information.

The room-temperature in-plane thermal conductivity as a function of film thickness for different high thermal conductivity materials are presented in Figure 3a. As shown here, the in-plane thermal conductivities of the three AlN thin films measured in this study are nearly the same, $\sim 260 \pm 40 \text{ W m}^{-1} \text{ K}^{-1}$. For reference, the intrinsic thermal conductivity of bulk, defect-free, single crystal AlN predicted by Slack *et al.*²³ and Lindsay *et al.*²⁸ are ~ 319 and $322 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. Since the defect concentrations are very low in the top single crystal layer of the AlN thin films, in our previous publication,³¹ we showed that the thermal conductivity of this layer is in close agreement with the theoretical predictions.^{23,28} The nucleation layer, on the other hand, possesses a low thermal conductivity due to the presence of relatively higher point- and line-defect concentrations.³¹ With the spot sizes used in this study ($1/e^2$ radii $\sim 10 \mu\text{m}$), SSTR probes through both layers of the AlN thin films. Thus, SSTR measurements represent a thermal conductivity that is influenced by both single crystal and nucleation layers. As a result, the SSTR-measured in-plane thermal conductivities of the AlN thin films are slightly lower than the predictions of Slack *et al.*²³ and Lindsay *et al.*²⁸ From Figure 3a, it is evident that compared to their thicknesses (6 μm or less), these AlN films have one of the highest in-plane thermal conductivities of any thin film material, surpassed only by graphite and diamond. The deposition technique, microstructure, grain size, and defect concentrations highly influence the thermal conductivity values of thin film materials.^{18,73,75,79,81–83} Due to this, the bulk of the prior reports on the in-plane thermal conductivity of diamond, GaN, and hexagonal boron nitride (hBN) thin films with thicknesses on the order of 6 μm or less are lower than $200 \text{ W m}^{-1} \text{ K}^{-1}$ as exhibited in Figure 3a.

In Figure 3b, we have plotted the normalized in-plane thermal conductivity ($k_{\text{film}}/k_{\text{bulk}}$) of various thin film materials with respect to their bulk in-plane values. Figure 3b reveals that the AlN films used in this study have one of the highest normalized in-plane thermal conductivities, higher than nearly all graphite and diamond thin films. This indicates that the thermal conductivity reduction due to defect and boundary scattering is much less severe in our AlN thin films compared

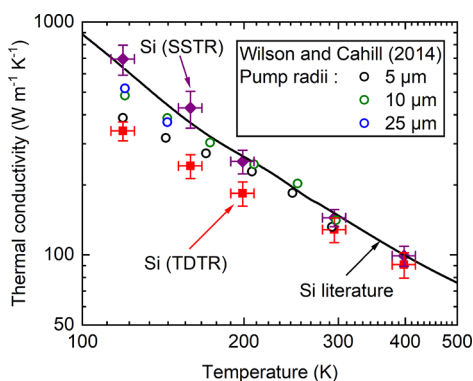


Figure 2. Calibration of SSTR technique *via* bulk Si wafer thermal conductivity measurements. Within uncertainty, the SSTR measurements of Si (filled diamonds) are in agreement with literature Si values⁵⁷ (solid line) and higher than our TDTR measurements of Si (filled squares). TDTR-measured Si thermal conductivities being lower than literature have also been reported by Wilson and Cahill⁵⁸ (open circles) when using $1/e^2$ pump radii of 5, 10, and 25 μm . For comparison, the $1/e^2$ pump radii of our TDTR and SSTR measurements are ~ 8.5 and $10 \mu\text{m}$, respectively.

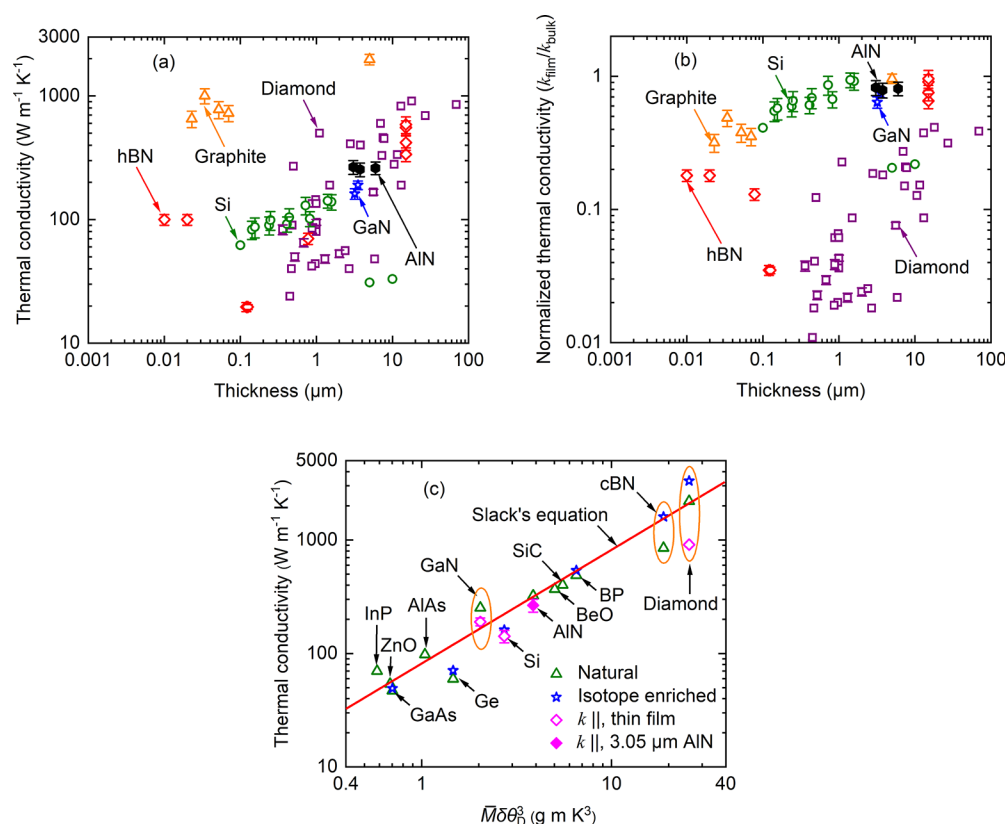


Figure 3. (a) In-plane thermal conductivity as a function of film thickness for different high thermal conductivity materials. The AlN films are measured in this study, while the in-plane thermal conductivities of other thin film materials are taken from literature: diamond,^{17,67–74} Si,^{75–78} graphite,^{79,80} GaN,⁸¹ and hexagonal boron nitride (hBN).^{82–84} (b) Normalized in-plane thermal conductivity ($k_{\text{film}}/k_{\text{bulk}}$) of the films presented in panel a as a function of thickness. The bulk in-plane thermal conductivities of the materials are tabulated in Table S2. (c) Thermal conductivity of natural and isotope enriched adamantane crystals as a function of the Leibfried–Schomann scaling parameter. Adamantine crystals have near isotropic thermal conductivity. The solid line indicates Slack's equation for adamantane crystals.^{13,22,23,85} The values of the Leibfried–Schomann scaling parameter for the crystals are taken from Giri and Hopkins,¹³ and Slack *et al.*²³ The thermal conductivities of the adamantane crystals are taken from literature: InP,⁸⁶ ZnO,⁸⁷ GaAs,⁸⁸ AlAs,⁸⁹ Ge,⁹⁰ GaN,⁹¹ Si,⁹² AlN,³¹ BeO,²² SiC,⁹³ BP,¹⁶ cBN,²⁰ and diamond.^{16,94} For comparison, the highest reported in-plane thermal conductivities of thin films of the adamantane crystals are also included. The 3.05 μm AlN film is measured in this study, while the in-plane thermal conductivities of Si, GaN, and diamond thin films are taken from literature.^{17,76,81}

to the vast majority of the graphite and diamond films reported in literature.

In Figure 3c, we present predictions of Slack's equation for the thermal conductivity of adamantane crystals as a function of the Leibfried–Schomann scaling parameter, $\bar{M}\delta\theta_D^3$ (where $\bar{M}$ is the average atomic mass, δ^3 is the average atomic volume, and θ_D is the Debye temperature).^{13,22,23,85} For comparison, the highest reported room-temperature in-plane thermal conductivities of thin films of the adamantane crystals are also included. Slack's equation has been very successful in predicting the highest achievable thermal conductivity of nearly all the adamantane crystals at room temperature.¹³ The in-plane thermal conductivity of the 3.05 μm AlN thin film is very close to the prediction of Slack's equation as evident in Figure 3c. This indicates that the thermal conductivities of the AlN thin films used in this study are very close to the maximum achievable value for AlN. Figure 3c provides a testament to the high quality of the AlN thin films.

Figure 4a shows the SSTR-measured in-plane thermal conductivity of the 3.05 μm AlN thin film from 120 to 400 K. For comparison, the cross-plane thermal conductivities of a commercial ~500 μm AlN wafer⁴⁰ and bulk, high-purity, single crystal AlN²³ are also shown. We also include the first-

principles calculations of the in-plane phonon thermal conductivity of isotopically pure AlN from Lindsay *et al.*²⁸ Due to the presence of the nucleation layer, the thermal conductivity of the 3.05 μm thin film is lower than bulk AlN and predictions of Lindsay *et al.*²⁸ at nearly all temperatures. As temperature decreases, the in-plane thermal conductivity of the 3.05 μm film increases. This indicates that the thermal conductivity of the 3.05 μm AlN film is mostly driven by intrinsic phonon–phonon scattering, with a lesser influence from phonon–defect scattering.

At low temperatures, the in-plane thermal conductivity of the 3.05 μm AlN thin film is higher than the cross-plane thermal conductivity of the commercial ~500 μm AlN wafer. This can be attributed to the presence of large concentrations of Al vacancy in the commercial wafer.⁴⁰ Among different types of phonon–defect scattering, Al vacancy–phonon scattering plays the dominant role in AlN thermal conductivity reduction.³⁹ The Al vacancy concentrations in the films used in this study are negligible.⁴⁰ On the other hand, the Al vacancy concentration in the commercial AlN wafer is $\sim 3 \times 10^{19}$ cm⁻³.⁴⁰ Near room temperature, as phonon–phonon scattering is the dominant scattering mechanism, the thermal conductivities of the 3.05 μm film and 500 μm commercial

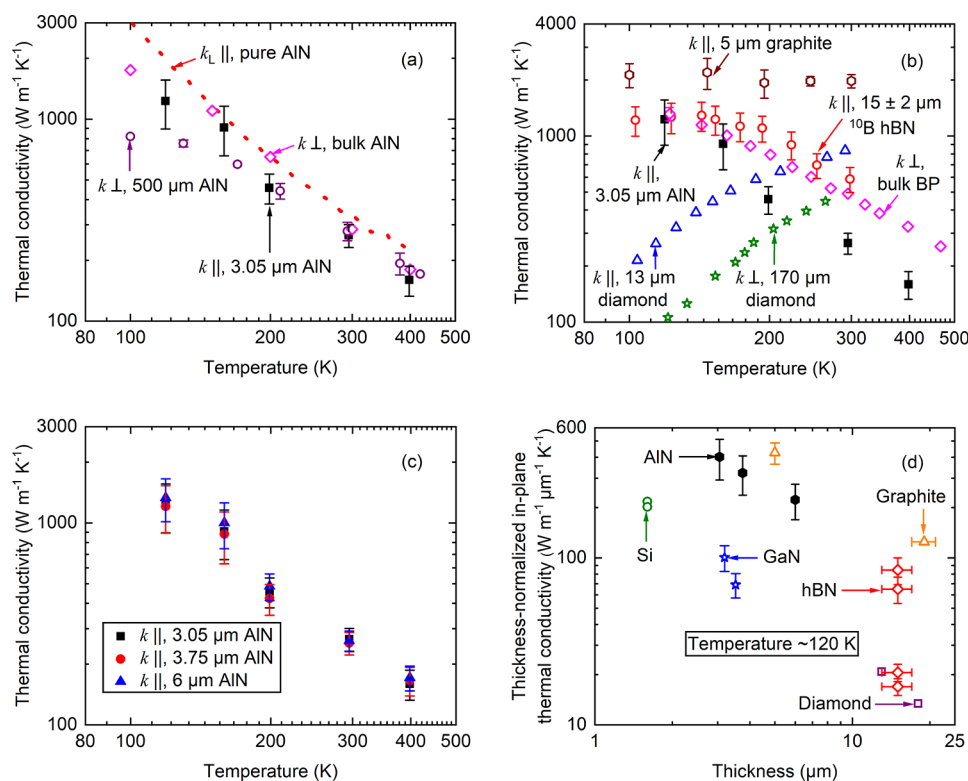


Figure 4. (a) Temperature-dependent in-plane thermal conductivity of the 3.05 μm AlN film. For comparison, cross-plane thermal conductivities of a commercial ~ 500 μm AlN wafer,⁴⁰ and bulk, high-purity, single crystal AlN²³ are also included. The dotted line represents the first-principles calculations of in-plane lattice thermal conductivity of isotopically pure bulk AlN.²⁸ (b) Temperature-dependent in-plane and cross-plane thermal conductivities of several high thermal conductivity materials: 3.05 μm AlN film,¹⁷ 170 μm isotopically enriched diamond film,¹⁸ 5 μm highly oriented pyrolytic graphite film,⁸⁰ 15 $\pm$ 2 μm thick isotopically enriched ¹⁰B hBN film,⁸⁴ and bulk boron phosphide (BP).¹⁶ (c) Temperature-dependent in-plane thermal conductivities of the 3.05, 3.75, and 6 μm AlN thin films. (d) Thickness-normalized in-plane thermal conductivity of micrometer-thick films of high thermal conductivity materials at ~ 120 K. The materials include AlN, diamond,¹⁷ Si,⁷⁶ graphite,^{80,95} GaN,⁸¹ and hBN.⁸⁴ The literature values are taken at temperatures ranging from 116 to 125 K with the exception of the 5 μm graphite film which is taken at 100 K. In panels a–d, filled symbols represent measurements taken in this study and open symbols represent literature values.

wafer are in agreement. However, at low temperatures, the thermal conductivity of the wafer is lower compared to that of the 3.05 μm film due to the dominance of phonon–vacancy scattering over phonon–phonon scattering.

In Figure 4b, the temperature-dependent in-plane thermal conductivities of the 3.05 μm AlN thin film, a 13 μm diamond film,¹⁷ a 5 μm graphite film,⁸⁰ and a 15 $\pm$ 2 μm 99% isotopically enriched ¹⁰B hBN film⁸⁴ are presented. The cross-plane thermal conductivities of a 170 μm isotopically enriched diamond film¹⁸ and bulk boron phosphide (BP)¹⁶ are also shown here. The graphite, diamond, and ¹⁰B hBN films as well as bulk BP have much higher thermal conductivities than the 3.05 μm AlN thin film at room temperature. However, the thermal conductivity of the graphite film remains nearly constant with decreasing temperature because of phonon scattering at the grain boundaries.⁸⁰ Similarly, due to phonon–boundary and phonon–defect scattering, the thermal conductivities of the polycrystalline diamond films decrease with a reduction in temperature.^{17,18} Contrary to these films, the thermal transport mechanisms in our AlN thin films are primarily driven by phonon–phonon scattering. As a result, at low temperatures, the in-plane thermal conductivity of the AlN film surpasses those of the diamond films and becomes much closer to that of the graphite film. As the temperature decreases, the thermal conductivities of the 3.05 μm AlN thin film, ¹⁰B hBN, and BP start to converge. This convergence can

be attributed to the influence of extrinsic scattering on the thermal conductivities of ¹⁰B hBN film, and bulk BP. At low temperatures, phonon scattering by the subgrain boundaries, dislocations, and point defects influence the thermal conductivity of the ¹⁰B hBN film.⁸⁴ Similarly, the thermal conductivity of bulk BP is also impacted by point-defect and isotope scattering as well as other experimental variables.¹⁶ Thus, at 120 K, the in-plane thermal conductivity of the 3.05 μm AlN film becomes comparable to ¹⁰B hBN and BP thermal conductivities.

In Figure 4c, we have plotted the temperature-dependent in-plane thermal conductivities of the 3.05, 3.75, and 6 μm AlN thin films. The thermal conductivities of the three films are in excellent agreement with each other. This indicates that boundary scattering is not significantly impacting the in-plane thermal conductivities of these AlN thin films at any temperature. This further supports that the in-plane thermal conductivities of our AlN films are driven by intrinsic phonon–phonon scattering events, leading to an increase in thermal conductivity as temperature decreases. This is contrary to the behavior commonly observed in traditional thin film materials. In Figure S8, we show that a large number of previously studied thin film materials exhibited a thermal conductivity reduction with decreasing temperature due to boundary and defect scattering.

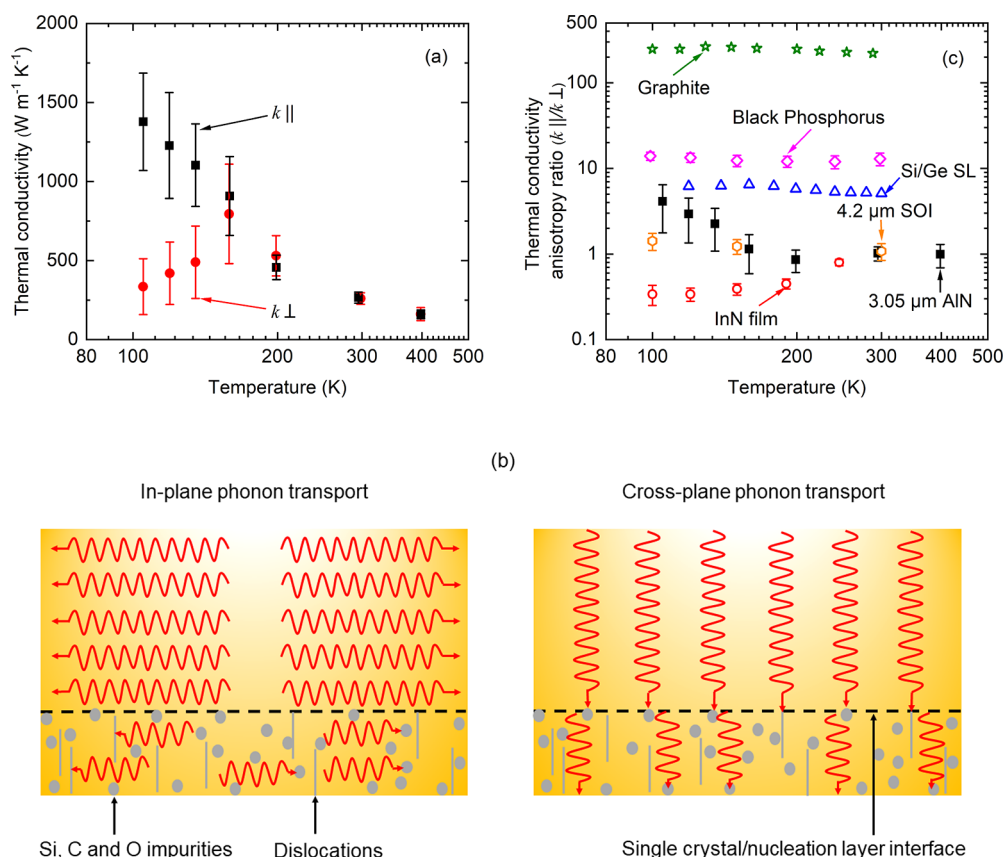


Figure 5. (a) Temperature-dependent in-plane and cross-plane thermal conductivities of the $3.05 \mu\text{m}$ AlN thin film. (b) Phonon heat transport mechanisms along the in-plane and cross-plane directions of the $3.05 \mu\text{m}$ film. The top layer is single crystal AlN, and the bottom layer is the nucleation region with high Si, C, and O impurities, and dislocation density. (c) Thermal conductivity anisotropy ratios ($k_{\parallel}/k_{\perp}$) as a function of temperature for the $3.05 \mu\text{m}$ AlN film, graphite,⁹⁶ black phosphorus (in-plane thermal conductivity is taken along the zigzag direction),⁹⁷ $4.2 \mu\text{m}$ Si on insulator (SOI),^{98,99} Si/Ge superlattice,¹⁰⁰ and InN film (dislocation density $1.1 \times 10^{10} \text{ cm}^{-2}$).¹⁰¹ In panels a and c, filled symbols represent measurements taken in this study and open symbols represent literature values.

In Figure 4d, the thickness-normalized in-plane thermal conductivity of micrometer-thick diamond,¹⁷ Si,⁷⁶ graphite,^{80,95} GaN,⁸¹ hBN,⁸⁴ and AlN films at $\sim 120 \text{ K}$ are presented. These results show that, along with graphite, the AlN films examined in this study possess the highest thickness-normalized in-plane thermal conductivity reported to date. Figure 4d provides evidence that, at 120 K , only graphite possesses higher thermal conductivity than the AlN films among all thin film materials of micrometer length scale. These exceptionally high in-plane thermal conductivities of the AlN films at low temperatures are consequences of in-plane heat transport mechanism being driven by phonon–phonon scattering and not being significantly restricted by boundary and defect scattering.

In Figure 5a, we have plotted the in-plane and cross-plane thermal conductivities of the $3.05 \mu\text{m}$ thin film as a function of temperature. The in-plane and cross-plane thermal conductivities are measured by SSTR and TDTR, respectively. Above 160 K , the in-plane and cross-plane thermal conductivities are nearly the same. Below this temperature, however, the cross-plane thermal conductivity decreases compared to that of in-plane, leading to a pronounced anisotropy. To conclusively show this anisotropy, we extend the temperature-dependent measurements to 105 K . The observed anisotropy cannot be explained from the AlN crystal structure as that would lead to the in-plane thermal conductivity being ~ 10 – 14% higher than the cross-plane thermal conductivity at low temperatures.²⁸

This anisotropy is also not due to the failure of TDTR technique as TDTR has been shown to measure AlN thermal conductivity accurately down to 80 K .³¹ To explain this anisotropy, we review the thermal transport mechanisms along the in-plane and cross-plane directions of the $3.05 \mu\text{m}$ AlN film. For simplicity, we have considered an interface to exist between the single crystal and nucleation layer. The resistance at this interface represents the equivalent resistance from point- and line-defect scattering at the nucleation layer starting region.

As conceptually illustrated in Figure 5b, in the single crystal layer, the phonons carrying heat in the in-plane direction travel relatively uninterrupted, whereas the phonons carrying heat in the cross-plane direction scatter at the single crystal/nucleation layer interface. This is supported by the fact that interface scattering is more dominant in cross-plane transport compared to in-plane.^{41,97,100–103} At low temperatures, phonon–phonon scattering rates decrease and the thermal transport shifts to lower frequency phonons relative to that of room temperature. While carrying heat in the cross-plane direction, the majority of these low-frequency, long-wavelength phonons scatter at the single crystal/nucleation layer interface. This leads to a significant decrease in the cross-plane thermal conductivity of the single crystal layer. For the phonons carrying heat in the in-plane direction, the scattering at the single crystal/nucleation layer interface and subsequent thermal conductivity reduction are much smaller. As a result, in the single crystal AlN layer,

there is a large anisotropy in thermal conductivity at low temperatures. With increasing temperature, thermal transport shifts to high-frequency phonons and phonon–phonon scattering becomes stronger. As a result, the anisotropy in the single crystal layer reduces.

The nucleation layer has a lower thermal conductivity than the single crystal layer as it contains higher concentrations of point defects and dislocations. The point defects scatter cross-plane and in-plane traveling phonons homogeneously.^{104–106} The small thickness of the nucleation layer ($\sim 0.6\ \mu\text{m}$) has a more pronounced impact on the cross-plane traveling phonons compared to the in-plane.^{39,41,42} On the contrary, the vertically oriented dislocation line defects have a stronger influence on the in-plane phonon transport^{40,105} although this effect is likely not very large.⁸¹ Due to a combination of these scattering events, the thermal conductivity of the nucleation layer can be expected to remain near isotropic across all temperatures of interest in this study. TDTR and SSTR probe through both layers of the $3.05\ \mu\text{m}$ AlN thin film.^{45,51,52,60,61} Because of the previously discussed pronounced anisotropy in the single crystal layer, the cross-plane thermal conductivity of the $3.05\ \mu\text{m}$ thin film is much lower compared to the in-plane below 160 K.

The cross-plane thermal conductivity reduction of the $3.05\ \mu\text{m}$ thin film is also not due to phonon scattering at the AlN/sapphire interface. To illustrate this, the AlN cross-plane thermal conductivity accumulations as a function of phonon mean-free-path at 105 and 120 K are presented in Figure S9. According to the AlN mean-free-path spectra, if phonons were allowed to travel uninterrupted throughout the entire thickness of the $3.05\ \mu\text{m}$ AlN film, then the cross-plane thermal conductivities would be ~ 687 and $770\ \text{W m}^{-1}\text{ K}^{-1}$ at 105 and 120 K, respectively. However, the cross-plane thermal conductivities of the $3.05\ \mu\text{m}$ film are much lower than that at these temperatures. This indicates that phonons traveling in the cross-plane direction are being scattered before reaching the AlN/sapphire interface, *i.e.*, at the single crystal/nucleation layer interface.

In Figure 5c, we have plotted the thermal conductivity anisotropy ratios (the ratio of in-plane to cross-plane thermal conductivity) of graphite,⁹⁶ black phosphorus,⁹⁷ $4.2\ \mu\text{m}$ silicon on insulator (SOI),^{98,99} a Si/Ge superlattice,¹⁰⁰ an InN film,¹⁰¹ and our $3.05\ \mu\text{m}$ AlN film as a function of temperature. For materials with anisotropic crystal structures such as graphite and black phosphorus, the in-plane and cross-plane thermal conductivities are dictated by the same phonon scattering mechanisms across the temperature range; thus, the anisotropy ratios are nearly temperature independent.^{97,101} For the Si/Ge superlattice and $4.2\ \mu\text{m}$ SOI, the anisotropy ratios decrease with increasing temperature as phonon–phonon scattering becomes stronger and phonon–interface scattering becomes less dominant.^{100,101,107} A similar trend is observed in the $3.05\ \mu\text{m}$ AlN film. It is to be noted that, in the Si/Ge superlattice and $4.2\ \mu\text{m}$ SOI, phonon–interface scattering originates at a physical interface. However, in the $3.05\ \mu\text{m}$ AlN film, the single crystal/nucleation layer interface is a representation of phonon scattering by point and line defects at the nucleation layer starting region. Similar to the $3.05\ \mu\text{m}$ AlN film, highly temperature-dependent anisotropy ratios induced by crystalline defects have been observed in InN films.¹⁰¹ In our study, anisotropy is observed only at low temperatures. However, we posit that this anisotropy will become more pronounced and be observed even at room temperature if the AlN film

thickness is reduced to sub-micrometer levels.^{39,81} In sub-micrometer thick AlN films, the nucleation layer can be expected to occupy a greater percentage ($>22\%$) of the total film thickness,³¹ thereby significantly limiting the ability of phonons to carry heat in the cross-plane direction. Such crystalline defect-induced anisotropy without any modification in crystal structure can provide guidelines for directed heat dissipation¹⁰¹ and, therefore, has important implications in usage of AlN films for thermal management of high-power devices.

All of the findings of this study are fundamentally different from our earlier works.^{31,40} Although our previous publications^{31,40} have reported on the thermal conductivity of AlN films, the measurements were mostly limited to the single crystal layer and taken along the cross-plane direction. Contrary to those studies, in this work, we probe through both single crystal and nucleation layers along the in-plane direction. Therefore, the thermal conductivity values presented here cannot be accurately estimated from the measurements of Koh *et al.*³¹ and Cheng *et al.*⁴⁰ Our in-plane thermal conductivity measurements establish these AlN films as highly conductive thin film materials both at room and low temperatures. Furthermore, we observe a temperature-dependent anisotropic thermal transport in the $3.05\ \mu\text{m}$ AlN film due to growth-induced crystalline defects. At low temperatures, the in-plane thermal conductivity is dominated by intrinsic phonon–phonon scattering, whereas the cross-plane thermal conductivity is highly influenced by extrinsic scattering. To the best of our knowledge, such high in-plane thermal conductivities along with anisotropic thermal transport detailing the interplay of boundary, defect, and phonon–phonon scattering have not been previously reported in literature for AlN thin films. This study provides insight into the fundamental phonon transport mechanisms in high-quality thin film materials and establishes guidelines for tuning anisotropic thermal conductivity in AlN films *via* defect engineering.

CONCLUSION

We report on the high in-plane thermal conductivities of AlN thin films on sapphire substrates. Using steady-state thermoreflectance, we measure the in-plane thermal conductivities of the AlN films to range from $\sim 260 \pm 40\ \text{W m}^{-1}\text{ K}^{-1}$ to $\sim 1200 \pm 300\ \text{W m}^{-1}\text{ K}^{-1}$ as temperature decreases from 295 to 120 K, respectively. At room temperature, the in-plane thermal conductivities of the AlN films are significantly less impacted by defect and boundary scattering as compared to the majority of the graphite and diamond thin films reported in literature. At low temperatures, the in-plane thermal conductivities of the AlN films are equivalent to boron phosphide and isotopically enriched hexagonal boron nitride, and much higher than diamond thin films. These exceptionally high in-plane thermal conductivities of our AlN films are consequences of in-plane thermal transport being driven by phonon–phonon scattering. This leads to an increase in thermal conductivity with a reduction in temperature. This trend is opposite of what is observed in other traditionally studied high thermal conductivity thin films, where boundaries and defects arising from film growth lead to a thermal conductivity reduction with decreasing temperature. As a result, at 120 K, the in-plane thermal conductivities of our AlN films are second highest only to graphite among all thin film materials of equivalent thicknesses measured to date, quantified *via* the thickness-

normalized in-plane thermal conductivity. Moreover, defect scattering causes a large temperature-dependent anisotropy ratio in the 3.05 μm AlN film. These AlN films with high in-plane thermal conductivities offer a viable solution to the thermal management issue of electronic devices.

METHODS

Time-Domain Thermoreflectance. In our TDTR setup, a Ti:sapphire laser with a central wavelength of ~ 800 nm and a repetition rate of 80 MHz emanates sub-picosecond laser pulses which are split into a pump and a probe path. Using an electro-optical modulator (EOM), the 800 nm pump beam is first modulated at a frequency of 8.8 MHz, then frequency doubled to 400 nm, before it is incident on the sample surface. Using a lock-in amplifier and a balanced photodetector, a time delayed 800 nm probe laser detects the reflectivity change due to surface temperature oscillations and measures the temperature decay up to 5.5 ns. The thermal properties are determined by fitting a radially symmetric, multilayer heat diffusion model^{46,47,108,109} to the ratio of the in-phase and out-of-phase signal ($-V_{\text{in}}/V_{\text{out}}$) monitored by the lock-in amplifier. The pump and probe beams are coaxially focused onto the sample surface and have $1/e^2$ diameters of ~ 17 and 10 μm , respectively, for our measurements. TDTR measurements require a thin Al transducer to be deposited on top of the sample surface to convert the optical energy of the laser into thermal energy.

Steady-State Thermoreflectance. The recently developed optical pump–probe technique SSTR is based on the principle that the reflectivity (R) of a transducer (Al in this study) is linearly proportional to temperature (T). In our SSTR setup, a 532 nm continuous wave (CW) pump laser is modulated at 100 Hz frequency to create a steady-state temperature rise (ΔT) at the sample surface. By changing the pump power, the incident heat flux on the sample surface ($\Delta|Q|$) and corresponding ΔT is changed. The resulting reflectivity change (ΔR) is detected by a 786 nm CW diode probe laser using a balanced photodetector. A linear proportionality relationship exists between the normalized reflectivity change ($\Delta R/R$) and the reflected probe laser intensity change determined by the balanced photodetector ($\Delta V/V$). Moreover, the change in pump power is proportionally captured by a pump photodetector voltage, ΔP . Using Fourier's law, the following equations can be obtained

$$\Delta P \propto \Delta|Q| \propto \Delta T \propto \frac{\Delta R}{R} \propto \frac{\Delta V}{V} \quad (1)$$

or

$$\frac{\Delta V}{V\Delta P} = \gamma \frac{\Delta T(k)}{\Delta|Q|} \quad (2)$$

Here γ is an experimental proportionality constant which is calculated from the comparison of experimentally measured $\Delta V/(V\Delta P)$ of a reference sample with known thermal conductivity to the ΔT predicted by a steady-state thermal model. A detailed description of this steady-state thermal model can be found in Braun *et al.*⁴⁵ After γ is determined from the reference sample, the thermal conductivity of any other material can be calculated from experimental measurements of corresponding $\Delta V/(V\Delta P)$ and relating it to $\Delta T(k)/\Delta|Q|$ predicted by the steady-state thermal model under the assumption that γ does not change between the reference and samples. To ensure the validity of this assumption, the reference and samples are kept in the same conditions as described in Braun *et al.*⁴⁵ during all SSTR measurements. In this study, bulk sapphire is used as the reference sample.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.0c09915>.

AlN thin film growth, characterizations, and thermal resistance model; temperature rise analytical expressions; SSTR sensitivity calculations, fitting procedure, and control samples and single crystal AlN layer measurements; steady-state temperature rise profiles; AlN film and bulk Si TDTR measurements; uncertainty analysis; temperature-dependent thermal conductivities of thin film materials; AlN mean-free-path spectra calculations (PDF)

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Notes

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