Bulk-like Intrinsic Phonon Thermal Conductivity of Micrometer-Thick AlN Films


ABSTRACT: Aluminum nitride (AlN) has garnered much attention due to its intrinsically high thermal conductivity. However, engineering thin films of AlN with these high thermal conductivities can be challenging due to vacancies and defects that can form during the synthesis. In this work, we report on the cross-plane thermal conductivity of ultra-high-purity single-crystal AlN films with different thicknesses (~3–22 μm) via time-domain thermoreflectance (TDTR) and steady-state thermoreflectance (SSTR) from 80 to 500 K. At room temperature, we report a thermal conductivity of ~320 ± 42 W m⁻¹ K⁻¹, surpassing the values of prior measurements on AlN thin films and one of the highest cross-plane thermal conductivities of any material for films with equivalent thicknesses, surpassed only by diamond. By conducting first-principles calculations, we show that the thermal conductivity measurements on our thin films in the 250–500 K temperature range agree well with the predicted values for the bulk thermal conductivity of pure single-crystal AlN. Thus, our results demonstrate the viability of high-quality AlN films as promising candidates for the high-thermal-conductivity layers in high-power microelectronic devices. Our results also provide insight into the intrinsic thermal conductivity of thin films and the nature of phonon-boundary scattering in single-crystal epitaxially grown AlN thin films. The measured thermal conductivities in high-quality AlN thin films are found to be constant and similar to bulk AlN, regardless of the thermal penetration depth, film thickness, or laser spot size, even when these characteristic length scales are less than the mean free paths of a considerable portion of thermal phonons. Collectively, our data suggest that the intrinsic thermal conductivity of thin films with thicknesses less than the thermal phonon mean free paths is the same as bulk so long as the thermal conductivity of the film is sampled independent of the film/substrate interface.

KEYWORDS: aluminum nitride, thermal conductivity, TDTR, phonon, thin film

INTRODUCTION

The ever-decreasing length scales and faster working speeds in electronic devices have led to critical challenges in their thermal mitigation, thus leading to critical issues in their implementation, performance, and feasibility. As a result, high-thermal-conductivity materials are often sought after for packaging techniques that facilitate efficient power dissipation in electronic devices.¹⁻³ Diamond, with its exceptionally high intrinsic thermal conductivity of over 2000 W m⁻¹ K⁻¹ at room temperature, is often sought as one of the primary materials for thermal dissipation in devices. However, the difficulty with heterogeneous integration of wafer-scale diamond can make this often times impractical.¹⁻⁴ Alternatives to diamond are III⁻⁵ V compound semiconductors such as aluminum nitride (AlN) and gallium nitride (GaN), which in their bulk, single-crystalline forms have high thermal conductivities (in the 150–300 W m⁻¹ K⁻¹ range); however, achieving high thermal conductivities in these materials requires high-quality crystals since impurities and defects can significantly lower their thermal conductivities.² Along with the high cost, the difficulty in producing high-quality crystals of bulk or thin-film nitrides limits their viability as materials for thermal mitigation in high-power electronic devices. Therefore, to overcome these challenges, this work demonstrates that scalable AlN films, with thicknesses ranging from ~3 to 22 μm, grown on sapphire substrates can possess bulk-like cross-plane thermal conductivities of ~320 ± 42 W m⁻¹ K⁻¹, thus demonstrating a substantial improvement over the current state-of-the-art for thermal mitigation. In fact, for any material thin film with equivalent thicknesses, we find that the cross-plane thermal conductivities of our AlN films have some of the highest...
thermal conductivities ever reported, second only to that of the cross-plane thermal conductivities of diamond thin films.

In general, high thermal conductivities for nonmetallic solids are often accompanied by a strongly bonded crystal structure with light atoms arranged in a simple lattice. This is exemplified in Figure 1a, where we plot the room temperature bulk thermal conductivity of various semiconductors as a function of their atomic volume. With the low atomic mass and relatively small unit cell volume, the thermal conductivity of AlN remains one of the highest measured at room temperature in its single-crystal, bulk form (see Figure 1a), and thus it possesses large intrinsic phonon mean free paths. With the advent of thin-film growth techniques, reductions in the thermal conductivity of materials are routinely observed at room temperature when characteristic thin-film thicknesses approach micrometers or less, the approximate length scales of thermal phonon mean free paths in high-thermal-conductivity crystals. As shown in Figure 1b, the cross-plane thermal conductivities of our epitaxially grown AlN films on sapphire substrates (with a range of thicknesses that span the thermal phonon mean free paths in AlN) are some of the highest measured to date, only slightly lower than diamond films.

Figure 1. (a) Room-temperature thermal conductivities of the different high-thermal-conductivity materials versus atomic volume (Å³ atom⁻¹). These include diamond,7 silicon,9 arsenides (e.g., BaAs,10–12 AlAs,13 GaAs,13,14 and InAs15), silicon carbide Sic,16,17 oxides (e.g., BeO18 and MgO19), phosphides (e.g., BP,20 GaP,21 and InP22), and antimonides (e.g., GaSb23,24 and InSb25). (b) Comparison of the selected highest room-temperature thermal conductivity of diamond,29–31 AlN,32–35 GaN,5,36 and Si37 thin films as a function of their characteristic size. All of the open symbols are based on the literature value, while the filled symbols are based on the present effort. (c) Corresponding normalized thermal conductivity κfilm/κbulk of (b).

Results and Discussion

Using metal-organic chemical vapor deposition (MOCVD), we grow a series of AlN films on sapphire substrates ranging in thickness from 3 to 22 μm. Previous literature shows that the thermal conductivity of AlN is strongly affected by impurity
concentration and crystalline structure. Secondary-ion mass spectrometry (SIMS) analysis of our AlN films shows lower silicon (Si), carbon (C), and oxygen (O) impurities compared to AlN single crystals available in the literature; the growth and characterization details are discussed in the Experimental Section. Representative scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) micrographs of the 22-μm-thick film are shown in Figure 2a–d. Figure 2a shows a full cross-sectional SEM micrograph of the 22 μm sample, while Figure 2b shows the bottom ∼10 μm of the sample near the AlN/sapphire substrate interface. Figure 2c,d shows two-beam-condition (1120) STEM micrographs in plan view and cross section, respectively. The STEM micrographs in Figure 2c,d are taken on the bottom ∼2.0 and ∼2.5 μm films near to the AlN/Al₂O₃ interface. Regardless of the overall AlN total film thickness, we observe two distinct regimes in the AlN films: (1) a high-defect nucleation AlN region that is ∼1.50 μm thick near the AlN/sapphire interface, and (2) a low-defect single-crystal AlN growth region above the nucleation layer extending to the surface of the film. The dislocation density in the AlN/sapphire interface regime is high, but decreases with increasing film thickness. A plan-view STEM micrograph in Figure 2e shows that the near-surface regime of the 17.5 μm AlN film is of high quality and has a relatively low dislocation density. The dislocation density of the high-quality regime is low and is 1.6 × 10⁶ cm⁻² when analyzed by STEM. From the observations in Figure 2a–e, we hypothesize that a thicker AlN film is required to ensure that the high-quality monocrystalline AlN on the top regime is thick enough for the measurements.

We measure the thermal conductivity of these films with time-domain thermorelectance (TDTR), a well-established thin-film thermal conductivity measurement technique, and steady-state thermorelectance (SSTR), a recently developed pump–probe technique. TDTR and SSTR are uniquely suited for this study since both are a single-sided measurement of thermal conductivity, and the depth to which the thermal conductivity of the material is probed (i.e., the thermal penetration depth of the experiment) can be controlled via either the pump modulation frequency in TDTR or the pump and probe spot sizes in SSTR. More details of our specific TDTR and SSTR experiments are discussed in the Experimental Section.

The thermal conductivities of 17.5- and 22-μm-thick AlN films measured via SSTR are shown in Figure 3a. The details of the thermal penetration depth calculation for the SSTR measurement, which we vary from ∼2 to 15 μm, are shown in the Supporting Information. The measured SSTR thermal conductivities of the 17.5 and 22 μm films are in line with the previously reported literature value, with a consistent value of 300 ± 30 W m⁻¹ K⁻¹, regardless of laser spot size. The thermal conductivities of the 17.5 and 22.5 μm AlN films measured from 80 to 500 K using TDTR are shown in Figure 3b. The TDTR data on these thick films were corroborated using measurements on four different TDTR systems across three institutions (University of Virginia with both two-tint and two-
color configurations on two different systems, Georgia Tech, and Notre Dame), and the reported data represent the average value from measurements on all systems. The thermal conductivities of these AlN films are among the highest reported experimentally measured values, for both thin film and bulk sample geometries (for example, we measure 22 μm AlN film thermal conductivities of 1656 ± 257 W m⁻¹ K⁻¹ at 79 K, 320 ± 42 W m⁻¹ K⁻¹ at room temperature, and 185 ± 50 W m⁻¹ K⁻¹ at 498 K). We also compare our measurements to the previously reported thermal conductivity of high-quality bulk single-crystal AlN, the extrapolated “defect-free” bulk AlN value, and an ab initio theoretical prediction of defect-free bulk AlN. The agreement between our measured values for the thermal conductivity of our thick AlN films and those previously reported measured and predicted values for the “defect-free” single crystals demonstrates the extremely high-quality, low-defect concentrations of our AlN films, as rigorously discussed in our prior work.

With the validation of the high thermal conductivity of thicker single-crystal AlN films both as a function of penetration depth and over temperature as shown in Figure 3a,b, we further investigate the extrinsic effects of AlN film thickness on the thermal conductivity by measuring films of thickness 3.05, 3.75, 6, and 17.5 μm from 80 to 500 K, as shown in Figure 3c. Above ~250 K, regardless of film thickness, the measured thermal conductivities are all the same when accounting for experimental uncertainty. Based on phonon mean free paths in AlN across these temperatures, we would expect phonon-boundary scattering at the AlN/sapphire interface to play a pronounced role in reducing the thermal conductivity if this scattering process was accounted for in the thermal conductivity of the AlN. This implies that boundary scattering is an extrinsic thermal boundary resistance (TBR) mechanism, supporting the theory by Zeng and Chen (i.e., \( \kappa_{\text{extrinsic}} = (\text{TBR} / d + 1 / \kappa_{\text{intrins}}} \)). While we observe a reduction in the thermal conductivity for the 6 μm film at 80 K, this reduction is most likely arising not from boundary scattering, but from a change in film quality from the disordered AlN near the AlN/sapphire interface, which we discuss in more detail below.

The thermal conductivity of AlN can be strongly reduced due to the presence of point defects (e.g., vacancies) and crystalline disorder (e.g., grain boundaries). Due to the presence of point defects (e.g., vacancies) and discus in more detail below. Scattering, but from a change in \( K \), this reduction is most likely arising not from boundary scattering, but instead due to phonon-defect scattering from a reduction in crystalline quality. This is consistent with our measurements of a thermal conductivity accumulation as a function of the phonon mean free path (see the Supporting Information). Also shown in Figure 4 are predictions from first-principles Boltzmann transport equation (BTE) calculations of the thermal conductivity accumulation as a function of the phonon mean free path (see the Supporting Information for more details). Our BTE results show that phonons with mean free paths (MFPs) up to ~0.2 μm in AlN contribute ~50% of the thermal conductivity of bulk AlN at room temperature, with full accumulation occurring around 3 μm. Our measured data do not capture these accumulation trends, and for all five films, we measure a constant thermal conductivity regardless of the thermal penetration depth up to ~2 μm. In all of these measurement cases, the measurements do not probe deep enough to be sensitive to the highly defective 1.5 μm near the AlN/sapphire interface. Thus, the thermal conductivities of these films are all similar regardless of thickness and do not exhibit size effects in the high-quality region near the surface. In the case of the two thinnest AlN films, when our measurement’s thermal penetration depth is increased to sample the highly defected 1.5 μm near the AlN/sapphire interface, the thermal conductivity is reduced. This phenomenon is not due to boundary scattering, but instead due to phonon-defect scattering from a reduction in crystalline quality. This is consistent with our measurements of a reduction in the thermal conductivity of the 6 μm film at 80 K. These results demonstrate an opposite trend than the thermal conductivity measurements of alloy semiconductor materials conducted using TDTR and frequency domain thermoreflectance (FDTR) with heater length scales less than the thermal phonon mean free paths; the measured thermal conductivities at these heater length scales are reduced relative to bulk in these prior reports.

Our results are in agreement with the theories of Zeng and Chen, Wilson and Cahill, and Regner et al., in that a heater length scale-dependent thermal conductivity in nonalloy single crystals is not expected.

CONCLUSIONS

We report on the exceptionally high cross-plane thermal conductivities in micrometer-thick AlN films, in the range of frequency from ~1 to 9 MHz, correlating to a thermal penetration depth of ~0.2–3.5 μm (as detailed in the Supporting Information).
1656 ± 257 W m⁻¹ K⁻¹ at 79 K, to 185 ± 50 W m⁻¹ K⁻¹ at 498 W m⁻¹ K⁻¹, and a value of 320 ± 42 W m⁻¹ K⁻¹ at room temperature. The thermal conductivity is in good agreement with the BTE prediction of the bulk thermal conductivity. Two pump-probe optical techniques, TDTR and SSTR, are used to characterize these high-quality AlN films. For any material thin film with equivalent thicknesses, we find that the cross-plane thermal conductivities of our AlN films have some of the highest thermal conductivities ever reported, second only to that of the cross-plane thermal conductivities of diamond thin films.

Collectively, our data suggest that the intrinsic thermal conductivities of thin films with thickness less than thermal phonon mean free paths are the same as bulk as long as the thermal conductivity of the film is sampled independent of the TBR at the film/substrate interface. Our results are in strong support of Zeng and Chen’s theory that the observed size effects in the thermal conductivity of thin films can be ascribed to a TBR effect, and phonon-boundary scattering rates should not impact the cumulative scattering rates in thin films, but instead should be treated as a resistor in series with the bulk phonon thermal conductivity of the material, even when the film thickness is less than the thermal phonon mean free paths. Additionally, these findings are in direct support of the work by Wilson and Cahill, showing that in a crystalline semiconductor, there is no thermal conductivity reduction observed due to intrinsic effects even when probing lengths are smaller than the thermal phonon mean free paths.

**EXPERIMENTAL SECTION**

Metal-Organic Chemical Vapor Deposition (MOCVD). All AlN growths for this study were carried out in a custom metal-organic chemical vapor deposition (MOCVD) reactor with a fast switching manifold. The growth pressure was kept at 45 torr, and basal plane sapphire substrates with a 0.2° miscut (toward the m-plane) were used. Trimethylaluminum and NH₃ were used as the Al- and N-precurors. For all the reported growths, a two-stage growth process was employed. For the first stage of the process, the growth temperature and the V/III precursor ratios were kept at 1000 and 3000 °C, respectively. In the second stage, the growth temperature was increased to 1300 °C, and the precursor flows were adjusted to decrease the V/III ratio to around 500. Using this two-stage process, crack-free AlN layers with thickness ranging from 3 to 25 μm were grown. Following growth, the AlN layers for the study were characterized for their surface roughness using atomic force microscope (AFM) scans. Their crystalline quality was determined by measuring the (10−12) off-axis X-ray scans. The RMS surface roughness values ranged from 0.3 to 0.5 nm for a 5 μm X 5 μm scan. The full width at half-maxima (FWHM) of the (1012) X-ray scan peaks were from 330 to 375 arc-sec.

Time-Domain Thermoreflectance (TDTR). TDTR is a transient optical pump–probe technique to characterize the thermal conductivity of thin films. The details of the TDTR are discussed in refs 48–50. In TDTR, a Ti:Sapphire laser creates sub-picosecond pulses with a central wavelength of ~800 nm (bandwidth ~10.5 nm) and a repetition rate of 12.5 ns. The laser pulses are split into a pump beam and a probe beam. In our two-color system, a second harmonic crystal is used to convert the wavelength of the pump pulses into ~400 nm central wavelength. The pump beam has a higher power than the probe to heat the sample surface and is modulated at a frequency of ~9 MHz. The radius of the pump spot is focused to ~8 μm at the surface of the sample. An ~80 nm aluminum transducer is deposited on the sample surface to transduce the optical laser energy into thermal energy within ~10 nm of the sample surface (i.e., the optical penetration depth). The radius of the probe laser is ~5 μm at the sample surface. The reflected probe beam signal from the sample surface was collected by a Si-photodetector and an radio frequency (RF) lock-in amplifier. The increase of the sample surface temperature during the measurements was limited to much less than 10 °C using a suitable laser power. The obtained probe beam signal that is a function of the transient surface temperature was fitted with a three-dimensional (3D) thermal diffusion model based on thermal quadrupoles.

Steady-State Thermoreflectance (SSTR). A newly developed technique, SSTR, is employed to measure the thermal conductivity of the AlN film. SSTR is an optical pump–probe technique to measure the thermal conductivity of materials using a continuous-wave laser pump heat source and a continuous-wave laser probe. This technique induces a steady-state temperature rise in the material via prolonged exposure to the pump laser. The probe beam is used to detect the change of thermoreflectance due to the temperature rise on the surface. Increasing the pump laser power will induce a higher-temperature surface rise. This method relies on square-wave modulation of the continuous-wave pump laser. The continuous pump beam is modulated continuously between “on” and “off” states. Using both a lock-in amplifier and a periodic waveform analyzer with a boxcar average, the change of the reflectance of the sample is measured via the continuous-wave probe beam. The thermoreflectance as a function of pump power is analyzed with a multilayer steady-state thermal model and fit for the thermal conductivity of the AlN.

Boltzmann Transport Equation (BTE) of the AlN Thermal Conductivity. The phonon Boltzmann transport equation (BTE) is solved iteratively using first-principles force constants. We relax the AlN atomic structure to the optimized positions using the Quantum Espresso package. Then, the second-order force constants, which provide phonon frequencies, group velocity, and scattering phase space, are calculated using the density functional perturbation theory (DFPT), using an 8 × 8 × 4 grid. Finite different methods implemented in thirdorder.py are used to calculate the third-order force constants to calculate three-phonon scattering rates based on a 4 × 4 × 4 supercell. Linearized phonon BTE is solved iteratively using the package ShengBTE in a 12 × 12 × 12 Monkhorst–Pack grid.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c03978.

Details of the BTE; thermal penetration depth of the TDTR; characterization of AlN with Raman, TEM, and SIMS; SSTR measurements; calibration of the TDTR system (PDF)

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Notes
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References
(22) Slack, G. Thermal Conductivity of MgO, Al2O3, MgAl2O4, and Fe2O4 Crystals from 3° to 300°K. Phys. Rev. 1962, 126, 427.

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