Phonon scattering and heat transport mechanisms in atomic/molecular layer-deposited hybrid inorganic/organic superlattices

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Abstract

We study the influence of molecular monolayers on the phonon scattering mechanisms and thermal conductivities of hybrid inorganic/organic superlattice thin films fabricated via atomic/molecular layer deposition. In comparison to their homogeneous counterparts, the thermal conductivities in these superlattice films are considerably reduced. We attribute this reduction in the thermal conductivity as a boundary-scattering dominated process that is limited by the period thickness of the inorganic constituent and not due to reduced transmission of phonons across the organic layer limited by the vibrational modes of the molecule. We show that the thermal boundary conductance across the molecular monolayers approaches the maximum possible conductance dictated by the phonon flux in the inorganic layers.
The introduction of material interfaces in solid nanocomposites has provided the opportunity for user-defined thermal transport in nanosystems. The inclusion of these interfaces gives rise to both phonon-boundary scattering, effectively reducing the thermal conductivity of the solid due to classical size effect [1], and/or partial transmission of thermal energy across the interface driving the thermal boundary conductance [2], or Kapitza conductance [3], across the solid/solid boundary. It is important to note that the reduction in the thermal conductivity of a material due to phonon boundary scattering may not be entirely correlated to the intrinsic thermal boundary conductance between two solids, and is strongly correlated to ballistic transport and phonon mean free paths incident upon the interface, as has been shown both computationally [4] and experimentally [5].

To effectively engineer the phonon thermal conductivity of a nanosystem with a high density of material interfaces, an understanding of the interplay and relationship of phonon-boundary scattering and thermal boundary conductance across the interfaces must be understood. The consideration of both of these phonon energy transport processes has major implications for the development of novel nanomaterials for applications such as thermoelectric energy conversion [6–8], where careful placement of interfaces has proven to be useful in efficiently lowering the phononic conductivity while still maintaining electronic conductivity.

As an example of a novel class of nanocomposites of recent interest, hybrid organic-inorganic nanomaterials grown by a combined alternation of atomic layer deposition (ALD) and molecular layer deposition (MLD) have exhibited enhanced electrical, optical, magnetic and mechanical functionalities compared to conventional organic or inorganic materials [9–12]. For example, using this ALD/MLD technique, inorganic/organic superlattices have shown promise as potential thermoelectric materials [13, 14]. However, paramount in advancing ALD/MLD hybrid structures for use in thermoelectric, or other applications, is an understanding of the phonon transport and scattering processes in these materials; referring to ALD/MLD superlattices, this requires understanding phonon scattering at the ALD/MLD boundary, and its correlation with phonon transmission and resulting boundary conductance across the ALD/MLD/ALD interface. There have been limited previous works focusing on measurements of thermal conductivity of ALD/MLD grown materials [13, 15], and an understanding of the phonon scattering mechanisms in layered ALD/MLD superlattices, and the thermal boundary conductance across their molecular interfaces, is lacking.
Given the recent interest in thermal transport in organic-based nanocomposites [16–20] and heat transport across molecular interfaces [21–27], systematically studying the thermal conductivity of a series of ALD/MLD-grown hybrid superlattices also provides an ideal platform to advance our understanding of phonon scattering at, and heat transfer across, thin molecular interfaces. In this letter, we experimentally study the phonon transport mechanisms in a series of ALD/MLD grown superlattice thin films comprised of multiple layers of either zinc oxide/hydroquinone or titanium dioxide/hydroquinone. Thin films of zinc oxide (ZnO) or titanium dioxide (TiO$_2$) interspersed with single monolayers of hydroquinone (HQ) were grown on either Al$_2$O$_3$ or MgO substrates to create the hybrid organic/inorganic superlattice films, an illustration of which is shown in Fig. 1a. Using time domain thermorelectance (TDTR), we measure the thermal conductivity of the superlattices providing a platform to study the role of organic interface density on phonon scattering at the inorganic/organic interface and thermal boundary conductance across the inorganic/organic/inorganic interface. We describe the thermal conductivity in the superlattices as a boundary-scattering dominated process that is limited by the period length and ballistic phonon flux in the inorganic layer, thereby reducing the thermal conductivity of the crystalline inorganic layer. Our model suggests that the entire spectrum of phonon mean free paths in the inorganic layer is limited by scattering at the inorganic/organic interface. As an alternative analysis, we derive a thermal boundary conductance across the ZnO/HQ/ZnO interfaces, and using semi-classical mismatch theory, we demonstrate that the phonon transmission across the HQ layer is not limited by molecular vibrations and the thermal conductance approaches the maximum limit for the ZnO phonon flux with 100% transmission.

(ZnO)$_x$/HQ (where $x$ is the period thickness of the ZnO layers) SL thin films of two different periodicities were fabricated on single-crystal Al$_2$O$_3$ (0001) substrates. The details of the sample fabrication and characterization processes along with the explanation of the experimental setup have been discussed in the Supporting Information.

Figure 1b shows the measured thermal conductivities for the (ZnO)$_x$/HQ superlattice thin films with $x=13.0$ nm (solid squares) and $x=7.2$ nm (hollow squares) at different sample temperatures. The thermal conductivities of these superlattices demonstrate a ten-fold decrease compared to the homogeneous ZnO thin films [28]. Figure 1a also shows the thermal conductivity measurement of our (TiO$_2$)$_x$/HQ SL with $x=15.5$ nm at room temperature. A
comparison to the thermal conductivity measurement for a homogeneous TiO$_2$ thin film (reported in the Supporting information) shows that the reduction in thermal conductivity for the TiO$_2$ based SL is in line with the results reported for the (ZnO)$_x$ SLs. The reduction in the thermal conductivity due to the periodic monolayers is consistent with the decrease in thermal conductivity with increased interface density in superlattices due to incoherent boundary scattering [29, 30].

Figure 2a plots the results in Fig. 1b as a function of period thickness for two representative sample temperatures. To describe the results in Fig. 1b, we consider the thermal conductivity in these hybrid samples being described by a phonon flux in the inorganic material that is limited only by phonon/boundary scattering at the organic/inorganic interface (as shown by the schematic illustration in Fig. 1a depicting the heat flow pathway in the hybrid SL structure). In other words, we assume that the thermal conductivities of the SL films is minimally affected by scattering mechanisms in the bulk of the inorganic constituent (such as phonon-defect or phonon-phonon scattering in the individual layers). Therefore, the thermal transport is limited by the combination of the phonon flux, $q$, in the inorganic layers and the thickness, $d$, of the layers. The phonon flux in the inorganic layer can be approximated by [31],

$$q = \frac{1}{8\pi^2} \sum_j \int_{k_1} \hbar \omega_k^2 v_j f dk$$

(1)

where, $j$ is the polarization, $\omega$ is the phonon frequency, $\hbar$ is Planck’s constant, $f$ is the Bose-Einstein distribution and $v$ is the group velocity (note, this assumes an isotropic Brillouin Zone). With the flux, $q$, determined from the phonon dispersion, the inorganic-thickness-limited thermal conductance, or the effective ballistic thermal conductivity of the SL film is given by,

$$\kappa_{\text{ballistic}} = \frac{\partial q}{\partial T} d$$

(2)

where $T$ is the temperature. Calculations of Eq. 2 for ZnO at two temperatures as a function of the layer thickness are shown in Fig. 2a. For these calculations, we use all 12 branches of the bulk phonon dispersion relation for ZnO in the $\Gamma \rightarrow M$ direction, as calculated in Ref. 32 via an $ab$ initio technique. The measured thermal conductivities at 78 and 300 K for the SL films show good agreement with our calculations of Eq. 2, supporting our assertion that size effects in the inorganic layers of the hybrid superlattice limit thermal transport in
these SL films. This analysis suggests that the entire spectrum of phonon mean free paths in the ZnO layer is limited by scattering at the inorganic/organic interface.

In our analysis above, we considered the thermal conductivities of these hybrid SLs to be driven by a ballistic phonon flux limited by scattering at the inorganic/organic interface. This implies that the thermal boundary conductance across HQ interfacial region is solely dictated by the phonon flux in ZnO alone, and not due to any properties intrinsic to the HQ. To study this hypothesis, we consider an alternative analysis of our results in Fig. 1b by considering the reduction in thermal conductivity to be driven by a thermal boundary conductance across the inorganic/organic/inorganic interface.

In the typical picture of thermal boundary conductance across solid interfaces (i.e., the acoustic or diffuse mismatch models [2, 33, 34]), a mismatch in acoustic properties or vibrational density of states, limits the interfacial phonon transmission, and therefore restricts the phonon flux that transmits across the organic-based interfaces. This could potentially offer an alternative explanation for the large reduction in the measured thermal conductivity of these hybrid nanomaterials. We model the thermal boundary conductance through the organic interface as [35],

\[ h_K = \frac{1}{8\pi^2} \sum_j \int_{k_1} \hbar\omega(k_j)k^2 \frac{\partial f}{\partial T} v_{1,j}(k) \zeta_{1\to2} dk \]  

(3)

where \( \zeta_{1\to2} \) is the phonon transmission coefficient from side 1 to 2 (from inorganic, through the organic monolayer, and emitted into the next inorganic layer) and \( k \) is the wavevector. According to Eq. 3, the maximum conductance occurs when \( \zeta_{1\to2} = 1 \) and all available phonon modes are transmitted from side 1 to 2. We note that this is the maximum possible thermal boundary conductance for an interface and is solely limited by the phonon flux that impinges upon the interfaces.

To consider the possibility of an inorganic/organic/inorganic limiting thermal boundary conductance, we model \( h_K \) across the ZnO/HQ/ZnO interface using Eq. 3 and assuming maximal phonon transmission across this interface. This assumption implies that the phonon transmission from the ZnO across the HQ is unimpeded by any properties of the HQ; that is, we assume \( \zeta_{1\to2} = 1 \). For these calculations, we make the same assumptions for ZnO density of states and phonon velocities as in Eq. 1.

Calculations of this maximal conductance as a function of temperature for a ZnO phonon flux are shown in Fig. 2b (solid line). In most real nanosystems, due to both a mismatch of
vibrational density of states and imperfections around the interfacial regions, the transmission coefficient is not unity (for a review of TBC dictated by various interfacial conditions, readers are referred to Ref. 36). For this reason, the measured values of $h_K$ in the literature have never approached this maximum thermal boundary conductance for any interface. From the measured thermal conductivities in our ZnO SLs (c.f., Fig. 1b), we assume a series resistor model and calculate the thermal boundary conductance across the individual ZnO/HQ/ZnO interfaces assuming that the transmission of phonons from one ZnO layer to the next ZnO layer (across the HQ) is the sole reason for the reduction in the thermal conductivity of the SLs. We calculate the thermal conductance across the oxide/HQ/oxide structure by comparing the effective thermal conductivity of the SL films to that of the homogeneous film.

Figure 2b shows $h_K$ calculated for ZnO/HQ/ZnO as a function of temperature for the two ZnO SL films studied in this work. The calculated values of the TBC for the two SL films with $x=13.1$ and 7.0 nm are similar within the uncertainties in the experiment, indicating that our derived values for $h_K$ are intrinsic for the ZnO/HQ/ZnO interface, and consistent with our analysis in Fig. 2a treating all phonon mean free paths being limited by scattering at the ZnO/HQ interface. The appreciable agreement between the measured $h_K$ across ZnO/HQ/ZnO to that of the maximum conductance in ZnO suggests that the HQ molecules have minimal resistance to heat transfer and allow the majority of the phonon modes in the ZnO to transmit across the molecule. This is also consistent with the results from Refs. 24 and 25 demonstrating that heat flow is ballistic through hydrocarbon molecules and is only limited by the phonon scattering at the metal/SAM interface.

However, the results from Fig. 2b suggest that the measured conductances approach the theoretical limit to heat conductance across prefect ZnO/ZnO interfaces, where the transmission coefficient is close to unity. The implication that $\zeta_{1\rightarrow2}=1$ in our calculations of Eq. 3 assumes that there is no mismatch of acoustic impedance or vibrational spectra encountered by the impinging ZnO flux on the HQ monolayer. Although this would be true for a pure ZnO/ZnO interface in which phonons are specularly scattered, this clearly would not be the case if considering phonon thermal conductance limited by transmission across the ZnO/HQ/ZnO interface due to properties of the HQ. To exemplify this more quantitatively, we performed molecular dynamics simulations on a plane of HQ molecules to obtain the power spectral density (details of the simulation are given in the Supporting
The power spectral density is compared to the $D(\omega)$ spectrum for bulk ZnO calculated from the phonon dispersion [32], and, as expected, the relatively discrete modes in the phonon frequencies calculated for the HQ layer do not completely overlap the $D(\omega)$ for ZnO (Fig. S8 in Supporting Information). Therefore, under the typical DMM picture of phonon transmission from the ZnO across the HQ and into the next ZnO layer, it is not possible for a HQ-limited transmission to be unity. Due to this reason, this concept of diffusive phonon scattering at the ZnO/HQ interface and resulting thermal boundary conductance limited by phonon transmission and mismatch of vibrational modes across the ZnO/HQ/ZnO interface fails to explain the thermal conductivity of our hybrid SLs.

Although the DMM-like picture cannot explain the derived thermal boundary conductance in Fig. 2b, we note that this perfect transmission could in fact occur at a specular interface between two identical materials, as predicted by the AMM. If the HQ were simply to serve as a scattering site/boundary, and the properties intrinsic to the HQ do not affect $h_K$ (as we assert above), then this interface is simply a ZnO/ZnO interface. Again, the DMM picture cannot explain our results in Fig. 2b since the phonon transmission resulting from diffusive scattering across an interface of identical materials is 50%. However, from the AMM, the specular scattering would result in 100% transmission for two identical materials comprising the interface. This is consistent with our data in Fig. 2b, in that the scattering event, initiated by the HQ boundary, is not influenced by the properties of the HQ. Therefore, our results suggest that the reduction in thermal conductivity in these (ZnO)$_x$/HQ SLs is reduced by a ZnO phonon flux limited by specular phonon scattering at the HQ monolayer. This reduction in thermal conductivity can be characterized by a thermal boundary conductance that is consistent with the AMM for a ZnO/ZnO interface.

We conclude that the heat transfer mechanisms in our hybrid superlattices are driven by phonon-boundary scattering, where the entire spectrum of phonon mean free paths in the inorganic layer is limited by scattering at the inorganic/organic interface. The scattered phonon energies then ballistically traverse across the organic monolayer, and are not limited by the vibrational properties of the HQ. Therefore, the resulting thermal conductivity of this hybrid nanostructure is limited by the phonon flux and period spacing of the inorganic layers. To further verify this conclusion, we derive the conductance across the TiO$_2$/HQ/TiO$_2$ from the thermal conductivity measurement for the TiO$_2$-based SL at room temperature (Fig. 1b). We determine $h_K = 414 \pm 37$ MW m$^{-2}$ K$^{-1}$ for TiO$_2$/HQ/TiO$_2$, a value which is lower than
that of the ZnO-based SLs at room temperature. This is due to the fact that the phonon flux and maximal conductance calculated for TiO$_2$ are relatively lower than those in ZnO, further supporting our conclusion (details of the calculations are given in the Supporting Information).

We also conclude that the mismatch of vibrational states and densities between the organic and inorganic layers do not affect phonon transport in our samples, implying that the typical DMM-description of thermal conductivity limited by density or vibrational mode mismatch between the inorganic film and organic monolayer can not explain the reduced thermal conductivity of these hybrid structures. Our analysis suggests that the phonon flux in the inorganic layer, which scatters at the inorganic/organic interface and limits the thermal conductivity of the SL, is nearly maximally transmitted across the HQ. Our data is consistent with the predicted thermal boundary conductance driven by specular scattering events at an interface of two identical materials, indicating again that scattering at, and not transmission through the HQ monolayer is the cause for the reduction in the thermal conductivity of these hybrid materials.

Future studies should consider the role of organic layer density and organic/inorganic bonding on these scattering processes in hybrid composites. Furthermore, since we only considered a monolayer of HQ-molecule, increasing the thickness of the MLD-grown layer could offer the ability to transition from AMM-like to DMM-like thermal boundary conductance where the vibrational modes in the molecular layer begin to influence the inorganic/organic conductance, similar to that discussed by Ong et al. [16, 17] We do not consider the thermal resistances at the inorganic/organic boundary and that due to the molecules as separate resistances in this work, since the resulting thermal boundary conductance across the inorganic/organic interface would be unphysical. For example, if we were to take the calculated $h_K$ in Fig. 2b and consider this the sum of two interfacial resistances at the ZnO/HQ and subsequent HQ/ZnO interfaces, this would result in a value that is 70% larger than the theoretical maximum $h_K$ (model in Fig. 2b). Therefore, the MLD layers in our SLs in this work can be considered as infinitely thin interfacial planes. However, increasing the thickness of this layer could allow for separation of $h_K$ at the inorganic/organic interfaces from the thermal transport in the molecular layer.

Our results indicate that the thermal conductivity can be designed based on the thermal conductance in the inorganic layer. Furthermore, this demonstrates the ability to create
interfaces with thermal boundary conductances approaching the theoretical maximum limit
with near unity interfacial transmission, offering unique platforms to study the phonon
coupling and scattering processes at solid interfaces.

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Figure 1. (a) 2D Schematic representation of the ZnO$_x$/HQ superlattice (bottom panel) along with an illustration of the heat flow pathway that induces a temperature gradient in the superlattice (top panel). (b) Thermal conductivity for ZnO superlattice films with 6 layers (solid squares) and 12 layers (hollow squares) of HQ as a function of temperature. The measured value for superlattice with TiO$_2$ as the inorganic constituent is also shown (black circle).
Figure 2. (a) The effective thermal conductivity as a function of superlattice period thickness calculated from Eq. 2 at 78 K (solid black line) and 300 K (solid red line). (b) Thermal boundary conductance for ZnO/HQ/ ZnO as a function of temperature for the two ZnO based superlattice films. The calculations of maximum conductance in ZnO with phonon transmission coefficient equal to unity is also shown (solid line). The appreciable agreement between the model and our measurements suggests that phonons ballistically traverse the HQ layers.