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Reduction in thermal conductivity and tunable heat capacity of inorganic/organic hybrid superlattices

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We study the influence of molecular monolayers on the thermal conductivities and heat capacities of hybrid inorganic/organic superlattice thin films fabricated via atomic/molecular layer deposition. We measure the cross plane thermal conductivities and volumetric heat capacities of TiO2- and ZnO-based superlattices with periodic inclusion of hydroquinone layers via time domain thermoreflectance. In comparison to their homogeneous counterparts, the thermal conductivities in these superlattice films are considerably reduced. We attribute this reduction in the thermal conductivity mainly due to incoherent phonon boundary scattering at the inorganic/organic interface. Increasing the inorganic/organic interface density reduces the thermal conductivity and heat capacity of these films. High-temperature annealing treatment of the superlattices results in a change in the orientation of the hydroquinone molecules to a 2D graphene layer along with a change in the overall density of the hybrid superlattice. The thermal conductivity of the hybrid superlattice increases after annealing, which we attribute to an increase in crystallinity.

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I. INTRODUCTION

A new class of hybrid inorganic/organic materials grown via a combination of atomic layer deposition (ALD) and molecular layer deposition (MLD) have recently garnered much attention due to their ultralow thermal conductivities [1–3]. Integrated with their enhanced electrical, optical, magnetic, and mechanical properties in comparison to their conventional organic or inorganic counterparts, these novel nanomaterials make for attractive candidates for a wide array of applications in nanotechnology [4–7]. For example, stemming from the technologies [2,3,8], the low thermal conductivities in these SLs have been shown to be ideal candidates for energy conversion applications [9–18].

Although plenty of interest has been shown towards understanding thermal transport in organic-based nanocomposites [9–18], there has been limited studies focusing on heat capacity measurements of ALD/MLD grown nanomaterials. Understanding the energy storage potential (quantified by the heat capacity, C) along with thermal transport efficiency (quantified by the thermal conductivity, κ) is necessary for a complete understanding of energetic processes in hybrid materials.

We report on the thermal conductivities and heat capacities of TiO2- and ZnO-based SLs with periodic introduction of organic layers in-between thicker inorganic constituents, which drastically reduce phonon transport in the cross plane direction.

II. EXPERIMENTAL DETAILS

A. Sample fabrication and characterization

Hybrid SLs of [(TiO2)m(Ti–O–C6H4–O–)n=1]9 with m = 40 and 4 were fabricated on MgO substrates at 210°C via the ALD/MLD technique [19] from TiCl4, H2O and hydroquinone (HQ) precursors (Picosun R-100 ALD reactor) as described in detail in our previous reports [2,20]. An illustration of a hybrid SL is shown in Fig. 1(a). Additionally, [(ZnO)m(Zn–O–C6H4–O–)n=1]9 with m = 9 and 4 were also fabricated on Al2O3 substrates to complement our previous experiments, reported in Ref. [3]. Along with the SL films, control samples of purely ALD grown inorganic TiO2 and ZnO films were fabricated.

Figure 1(b) shows the characteristic grazing incidence x-ray diffraction (GIXRD) patterns for the films tested in this study. The fact that the intensity of the peaks for the as-deposited TiO2-based SLs are reduced compared to the purely ALD grown TiO2 with anatase phase, suggests that the crystallinity in those samples is hindered due to the inclusion of the HQ layers. In contrast, for the ZnO-based SLs, inclusion of HQ layers for the m = 9 sample does not drastically hinder the peaks in the XRD patterns (that fit the typical ZnO hexagonal wurzite structure). Also, there is negligible change in the
position of the peaks, implying that the crystallinity for this sample is fairly conserved. The $m = 4$ samples for both ZnO and TiO$_2$-based SLs are amorphous in nature.

In order to enhance the crystallinity of the TiO$_2$-based SLs, the samples were heat-treated at 600 °C for 6 hours (Nabertherm GMBH RS 80/500/11). For the $k:m = 1:40$ TiO$_2$-based SL (with inorganic period thickness of ~2 nm), the high annealing treatment leads to enhanced crystallinity, whereas, for the $k:m = 1:4$ TiO$_2$-based SL, GIXRD pattern does not show any change compared to the 1:4 as-deposited SL. Furthermore, the annealing process converts the molecular HQ components to a 2D graphitic layer as depicted in the schematic shown in Fig. 1(a). This conversion was confirmed via Raman Spectroscopy and further details on the characterization of the carbon content in the fine internal interfaces for these hybrid SLs can be found in our previous report [2]. Note, this annealing treatment does not affect the periodic layering of the SLs as demonstrated by the x-ray reflectivity (XRR; PANanalytical X’Pert Pro MPD diffractometer) patterns with interference maxima due to the large period size. The XRR patterns have been discussed in Refs. [22–24]. For this study, we modulate the pump beam at different frequencies and monitor the in-phase ($V_{in}$) and out-of-phase ($V_{out}$) signals of the reflected probe beam with a lock-in amplifier. Prior to TDTR measurements, we metallize the samples with ~80 nm

![FIG. 1. (a) Schematic representation of the TiO$_2$-based hybrid structures for the as-deposited and annealed cases. The HQ layers transition into 2D graphitic layers due to the high annealing treatment. (b) Grazing incidence x-ray diffraction (GIXRD) patterns for the control samples and the hybrid films. (c) XRR patterns for the TiO$_2$ based SLs with $k:m$ ratio of 1:40 and 1:4, as well as for the purely inorganic TiO$_2$ film.](https://www.pnas.org/content/115/15/3854)

## B. Time-domain thermoreflectance

We measure the thermal properties of the samples with the time domain thermoreflectance (TDTR) technique. The details of the experimental procedure as well as the analysis process have been discussed in Refs. [22–24]. For this study, we modulate the pump beam at different frequencies and monitor the in-phase ($V_{in}$) and out-of-phase ($V_{out}$) signals of the reflected probe beam with a lock-in amplifier. Prior to TDTR measurements, we metallize the samples with ~80 nm

### TABLE I. Thicknesses and densities of the thin films measured via XRR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>Density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD-grown TiO$_2$</td>
<td>98.3</td>
<td>3.65</td>
</tr>
<tr>
<td>[(TiO$<em>2$)$</em>{n}$]Ti–O–C$_6$H$<em>4$–O–]$</em>{10}$ (as-deposited)</td>
<td>110.8</td>
<td>2.87</td>
</tr>
<tr>
<td>[(TiO$<em>2$)$</em>{n}$]C$_{12}$–C$_6$H$<em>4$–O–]$</em>{5}$ (annealed)</td>
<td>95.1</td>
<td>3.37</td>
</tr>
<tr>
<td>[(TiO$<em>2$)$</em>{n}$]Ti–O–C$_6$H$<em>4$–O–]$</em>{10}$ (as-deposited)</td>
<td>123.7</td>
<td>1.98</td>
</tr>
<tr>
<td>[(TiO$<em>2$)$</em>{n}$]C$_{12}$–C$_6$H$<em>4$–O–]$</em>{5}$ (annealed)</td>
<td>85.3</td>
<td>2.83</td>
</tr>
<tr>
<td>ALD-grown ZnO</td>
<td>154.0</td>
<td>5.4</td>
</tr>
<tr>
<td>[(ZnO)$_{n}$]Zn–O–C$_6$H$<em>4$–O–]$</em>{5}$</td>
<td>93.8</td>
<td>3.3</td>
</tr>
<tr>
<td>[(ZnO)$_{n}$]Zn–O–C$_6$H$<em>4$–O–]$</em>{5}$</td>
<td>82.7</td>
<td>2.4</td>
</tr>
</tbody>
</table>
We analyze the TDTR data with a three-layer thermal model (layer 1: Al, layer 2: ALD/MLD SL, layer 3: semi-infinite substrate) and simultaneously measure the heat capacities and thermal conductivities of the hybrid SLs. The thermal boundary conductances at the Al/SL film and SL film/substrate interfaces have to be separated from the measurements to correctly predict the intrinsic thermophysical properties of the SL films. To this end, we analyze the sensitivity of the measurements to the various parameters in the thermal model. The sensitivity of the ratio (−V_in/V_out) to a thermophysical quantity is defined by [27]

$$S_x = \frac{\partial \ln(-V_{in}/V_{out})}{\partial \ln(x)}, \quad (1)$$

where x is the thermophysical parameter of interest. Figures 2(a) and 2(b) show the calculations of Eq. (1) for the sensitivity of the ratio to the various parameters in our three-layer thermal model for the TiO_2-based SL with m = 40 at two different pump modulation frequencies [(a) 8.8 MHz and (b) 3.72 MHz]. The most sensitive parameters are the heat capacity (C_{TiO_2:HQ}) and thermal conductivity (κ_{TiO_2:HQ}) of the hybrid SLs. The fact that the sensitivities are different and dynamic in nature allows us to simultaneously measure C_{TiO_2:HQ} and κ_{TiO_2:HQ} as discussed in detail below. The front side interface conductance, h_{K,Al/TiO_2}, and the back side interface conductance h_{K,TiO_2/MgO} are measured from separate measurements on the control sample (Al/TiO_2/MgO). As shown in Figs. 2(a) and 2(b), the measurements are insensitive to h_{K,Al/TiO_2}; however, a 10% uncertainty in h_{K,TiO_2/MgO} leads to a ∼1.2% and ∼2.4% uncertainty in C_{TiO_2:HQ} and C_{TiO_2:HQ} at room temperature for 8.8 MHz frequency, respectively, which quantifies this insensitivity.

We confirm the measurements for h_{K,Al/TiO_2} and h_{K,TiO_2/MgO} by analyzing the thermoreflectance data for the control sample using two different approaches. The first approach analyzes the V_out as well as −V_{in}/V_{out} separately, as we outline in detail elsewhere [28]. The second method utilizes two frequencies to effectively separate the interfacial conductances. At 3.72-MHz modulation frequency, we estimate an effective thermal conductivity that considers the front side conductance and the thermal conductivity of the hybrid structure as a lumped conductance. We fit the data to the model with this effective conductivity and the back side conductance as free parameters. For the higher modulation frequency (8.8 MHz), we fit the data with the free parameters as the thermal conductivity of the SL and front side conductance and assume the back side conductance as an input parameter determined from the lower modulation frequency. It should be noted that this approach to measuring the front side and back side conductances gives agreeable values to the first method outlined in Ref. [28]. Uncertainties in the measured thermal conductivities and heat capacities of the hybrid SLs are derived from the uncertainties in the input parameters and the sensitivity of the three-layer thermal model to those parameters. We measure a value of κ = 5.2 ± 0.3 W m⁻¹ K⁻¹ for the purely ALD grown TiO_2 film, which is in good agreement with the literature value of ∼5.7 W m⁻¹ K⁻¹ for an anatase thin film [29].

For a given frequency, the best fit to our TDTR signal (for hybrid SLs with high interfacial densities) can be produced with multiple combinations of the heat capacities and thermal conductivities, as shown in the sensitivity contour plots in Fig. 2(c) for a k:m = 1:4, as-deposited TiO_2-based SL. The contour plots represent the mean square deviation of the model to the TDTR data with the various combinations of C and κ as input parameters in our three-layer model [30]. Note, our best fits to the TDTR data are usually ≤0.02. As is clear from the sensitivity contour plot, a wide range of values for C can produce the best fit in the least squares sense for a given frequency. Therefore, to accurately determine C and κ, we use 3.72- and 8.8-MHz pump modulation frequencies that give different sensitivity contour maps for the thermophysical properties [see Fig. 2(c)]. The common set of values for C and κ at these two frequencies shown by the overlap of the best fit values represent our measurements for the hybrid multilayers.

III. THERMAL CONDUCTIVITY

Figure 3 shows the measured thermal conductivities for the as-deposited and annealed TiO_2-based samples with m = 40 as a function of temperature. Two aspects of the results shown...
The calculated minimum in thermal conductivity for TiO$_2$ is shown. The calculated minimum in thermal conductivity for TiO$_2$ is attributed to incoherent boundary scattering at 17-nm grain size (Ref. [32]) and anatase thin film (Ref. [29]) are also shown for comparison.

TiO$_2$-based single crystal TiO$_2$ (Ref. [31]), a polycrystalline sputtered film with thermal conductivities. In Fig.3, we have also added the anatase thin film (Ref. [29]) are also shown for comparison.

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FIG. 3. Thermal conductivities of as-deposited and annealed TiO$_2$-based $m = 40$ SLs plotted as a function of temperature. For comparison, the measured thermal conductivities of an ALD grown amorphous TiO$_2$ film along with the thermal conductivities of bulk, single crystal TiO$_2$ (Ref. [31]), a polycrystalline sputtered film with 17-nm grain size (Ref. [32]) and anatase thin film (Ref. [29]) are also shown. The calculated minimum in thermal conductivity for TiO$_2$ is also shown for comparison.

in Fig. 3 are worth noting. First, the thermal conductivities measured for the as-deposited and annealed SLs show a large reduction as compared to the sputtered TiO$_2$ thin films [32]; at room temperature, $\kappa$ for the as-deposited SL is almost 30% lower than the measured $\kappa$ for an anatase thin film (Fig. 3; sold triangle) [29]. For comparison, we have also included the thermal conductivity of bulk, single crystal anatase taken from Ref. [31]. The reason for the decrease in the thermal conductivities is attributed to incoherent boundary scattering at the inorganic/organic interfaces [2]. The results for the hybrid SLs agree well with the model for the minimum limit to thermal conductivity of TiO$_2$ (solid black line in Fig. 3) [32,33]. For comparison, Fig. 3 also shows the measured $\kappa$ for an as-deposited amorphous TiO$_2$ film. Even with the enhancement in crystallinity of the annealed sample, boundary scattering at the inorganic/organic/inorganic interfaces results in the low values for thermal conductivities. In Fig. 3, we have also added the predictions from a minimum thermal conductivity model for a homogeneous amorphous TiO$_2$ sample. This model assumes that the “mean free paths” of vibrations in the amorphous state are limited to the spacing between the atoms. Therefore, following Ref. [33], the thermal conductivity as a result from a random walk between localized oscillators is

$$\kappa_{\text{min}} = \left( \frac{\pi}{6} \right)^{1/3} k_B n^{2/3} \sum_i v_i \left( \frac{T}{\Theta_i} \right)^2 \int_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx,$$

(2)

where the sum is taken over the three sound speeds ($v_i$), $n$ is the atomic density, and $\Theta_i = v_i (\hbar/k_B)(6\pi^2 n)^{1/3}$ is the cutoff frequency for each polarization expressed in degrees [33]. For the calculations shown in Fig. 3 (for a homogeneous TiO$_2$), the longitudinal and transverse sound speeds are taken from Ref. [34]. As is clear from Fig. 3, the predicted minimum in thermal conductivity for TiO$_2$ agrees very well with our measured values for a homogeneous amorphous TiO$_2$ thin film and the thermal conductivity can be further lowered below this minimum limit by the inclusion of periodic monolayers of HQ.

The second aspect to note in Fig. 3 is the increase in the thermal conductivities of the hybrid SLs after annealing at 600 °C for 6 hours. This can be understood as a consequence of enhanced crystallinity of the inorganic constituents due to the high annealing temperatures. However, the role of the different organic constituents (2D graphitic carbon layers in the annealed samples as compared to the HQ monolayers in the as-deposited samples) might affect the vibrational scattering mechanisms differently at these molecular interfaces. To understand the relative contributions of these two competing effects on thermal conductivity, we compare the results for the annealed and as-deposited samples with $m = 4$ as reported in our previous work [2]. We measure $\kappa = 0.62 \pm 0.04$ and 0.66 $\pm 0.04$ W m$^{-1}$ K$^{-1}$ for the as-deposited and annealed samples, respectively. For these samples, even with the high annealing treatments, the inorganic constituents are mostly amorphous in nature, as demonstrated by the GIXRD patterns in Fig. 1. Consequently, the values for the measured thermal conductivities are agreeable within uncertainties, suggesting that the role of the organic layers (in these two samples with the same number of organic interfaces) in thermal transport are similar; in other words, the orientation of the HQ layer does not affect scattering at the inorganic/organic boundary and the resulting vibrational thermal conductivity. Contrary to the $m = 4$ sample, the crystallinity of the $m = 40$ sample is enhanced after annealing as demonstrated by the increase in the 101 peak [see Fig. 1(b)] and, therefore, the increase in $\kappa$ is a consequence of enhanced crystallinity and not due to the intrinsic scattering mechanisms in the organic layers.

Figure 4 shows the measured thermal conductivities for the ZnO-based $m = 9$ SL as a function of temperature. Along with these measurements, we also include the measured thermal conductivities of $m = 99$ and 49 SLs from our previous work [28]. Similar to the results for the TiO$_2$-based SLs, the inclusion of HQ monolayers in-between the thicker inorganic constituents is shown to drastically reduce the thermal conductivities compared to the measurements of a homogeneous thin ZnO film from Ref. [35]. We have attributed the reduction in $\kappa$ for the ZnO-based hybrid SLs as a phonon-boundary scattering limited process (by considering the thermal boundary conductance across ZnO/HQ/ZnO interfaces). The scattered phonon energies almost perfectly transmit across the organic monolayers (depending on the phonon wavelength), and the scattering within the organic layers itself do not contribute significantly to the overall reduction in thermal transport [28]. In comparison to the minimum thermal conductivity calculated for ZnO from the elastic constants reported in Ref. [36], $\kappa$ for the $m = 9$ SL are well below the minimum limit, suggesting that the inclusion of periodic HQ layers can severely limit thermal transport in these hybrid structures.

We plot the measured thermal conductivities as a function of SL period thickness for the ZnO- and TiO$_2$-based SLs in Fig. 5. The results show that as the SL period thickness increases, the thermal conductivities increase monotonically for all the hybrid SLs. The drastic increase in $\kappa$ as a function
FIG. 4. Thermal conductivities of ZnO-based $m = 9$ SLs along with the thermal conductivities of $m = 99$ and 49 hybrid SLs (Ref. [28]), and a 180-nm ZnO film (Ref. [35]). The calculated minimum in thermal conductivity for ZnO is also shown for comparison.

FIG. 5. Thermal conductivities of ZnO- and TiO$_2$-based SLs as a function of SL period thickness. The measured thermal conductivities for a $k:m = 1:1$ hybrid film reported in Ref. [1] is also plotted (hollow triangle). The calculated minimum in thermal conductivity for TiO$_2$ and ZnO are also shown for comparison.

FIG. 6. Measured volumetric heat capacities as a function of temperature for (a) $[[\text{TiO}_2]_{m=40}(\text{Ti–O–C}_6\text{H}_4\text{–O–})_{k=1}n$ and (b) $[[\text{ZnO}]_{m=9}(\text{Zn–O–C}_6\text{H}_4\text{–O–})_{k=1}n$ SLs. The corresponding bulk heat capacities for the inorganic constituents are also shown for comparison [37,38].
heat capacities by their respective measured mass densities (hence, we define the specific heat capacity based on mass, where the specific heat capacity, \( c \), is given by \( c = C/\rho \), where \( \rho \) is the mass density). As is expected, the specific heat capacities of the hybrid SLs deviates from the value of the bulk inorganic constituent as the number of organic monolayer increases. At room temperature, the specific heat of the as-deposited TiO\(_2\)- and ZnO-based SLs with \( m = 4 \) is closer to the value of the organic counterpart, i.e., poly-phenylene oxide (1.204 J g\(^{-1}\) K\(^{-1}\)). Whereas, the specific heat capacities of the SLs with \( m = 40 \) and 9 for the TiO\(_2\)- and ZnO-based SLs, respectively, approach the value of their corresponding inorganic constituents. Unlike the change in the volumetric heat capacities after the high annealing treatment, the specific heat of the annealed SLs show good agreement within uncertainties with their as-deposited counterparts (even though the densities increase with annealing). In Fig. 7(b), we have also included the measured specific heat of a \( k:m = 1:1 \) ZnO-based hybrid sample reported in Ref. [1] (with a density of 5 g cm\(^{-3}\)). Their result matches the decreasing trend in the measured specific heat with increasing mass density as with our hybrid multilayers.

V. SUMMARY

In summary, we have measured the thermal conductivities and heat capacities of TiO\(_2\)- and ZnO-based hybrid SLs with periodic organic layers between the inorganic constituents. The inclusion of organic layers is shown to drastically reduce the thermal conductivities of these SLs. Furthermore, the thermal conductivities of these hybrid SLs increases monotonically with increasing period thickness, suggesting that boundary scattering at the inorganic/organic/inorganic interface dominates the heat transfer in these structures. Similarly, the inclusion of organic layers are also shown to decrease the heat capacities. The effect of high-temperature annealing treatment on the TiO\(_2\)-based SLs is shown to increase both the thermal conductivities and heat capacities. The increase in thermal conductivities due to annealing is attributed to the enhanced crystallinity (not due to any intrinsic vibrational properties of the organic layer), whereas, the increase in heat capacities is attributed to the increase in the densities of the samples.

ACKNOWLEDGMENTS


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