

Thermal Transport in Nanostructured Polymers

In recent years, with the discovery of low-dimensional materials and the advance of fabrications, nano-structuring has opened new possibilities for a variety of novel applications with either increased or reduced thermal conductivity. Nanostructured organic materials or polymer-based materials have received much less attention compared to inorganic materials although there are significant application advantages, such as being easy to process, light-weight, and flexible. Extreme thermal conductivity and fundamental new physics of phonon dynamics and thermal transport might exist in nanostructured polymers, either polymers with aligned chains or hybrid organic-inorganic materials. The objective of this thesis is to investigate the thermal transport in nanostructured polymers by simulation and characterization.

The universally low thermal conductivity of bulk amorphous polymer materials is regarded as one of the bottleneck for the macro- and micro- electronic devices. All-atom model molecular dynamic simulation was conducted in this thesis to investigate the effect of the chain parameters of polymers, such as chain orientation, monomer type, and molecular weight, on the thermal transport in polymers. Thermal conductivity of amorphous polymers is related with the orientational order parameter (a quantitatively indicator of the chain conformations and alignments) through an exponential relation. Moreover, the thermal conductivity of single extended polymer chain of various polymers, which can be 1-2 orders of magnitude higher than their bulk counterparts, is a strong function of their monomer types and molecular weights.

To enable the systematic measurement of thermal properties of nanostructured polymeric materials, the ultrafast pump-and-probe time-domain thermoreflectance (TDTR) method, which is a powerful tool for measuring thermal properties of materials, was extended to frequency-dependent TDTR for simultaneously measuring multiple thermal properties of nanostructured thin film materials, including in-plane and cross-plane thermal conductivity, heat capacity, and interfacial thermal conductance between materials. This developed frequency-dependent TDTR method has been verified through the measurements on the reference samples and ready to be employed to study the thermal properties of nanostructured materials. In this thesis, thermal properties of two types of nanostructured polymeric materials have been studied using this method, including hybrid organic-inorganic materials and ultrathin polymer thin films.

A new class of hybrid organic-inorganic materials with improved functionality was enabled by the atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques with atomic level control. The cross-plane thermal conductivity and volumetric heat capacity of three types of hybrid organic-inorganic zincone (*i.e.* zinc alkoxide) thin films enabled by MLD processes and alternate ALD:MLD processes were measured using the frequency-dependent TDTR method. We revealed the critical role of backbone flexibility in the structural morphology and thermal conductivity of MLD zincone thin films by comparing the thermal conductivity of MLD zincone films with

aliphatic backbone to that with aromatic backbone. Much lower thermal conductivity values were obtained in ALD/MLD-enabled hybrid organic-inorganic zinc oxide thin films compared to that of the ALD-enabled W/Al₂O₃ nanolaminates reported by Costescu *et al.* [*Science* **2004**, *303*, 989-990], which suggests that the dramatic material difference between organic and inorganic materials may provide a route for producing materials with ultralow thermal conductivity.

Ultrathin polymers have recently been shown to exhibit different chain dynamics and physical properties, as compared to their bulk counterparts. The effective cross-plane thermal conductivity of polystyrene (PS) thin films was measured using frequency-dependent TDTR method. The effective thermal conductivity of PS films is found to increase with decreasing film thickness when the thickness of the PS film is comparable to or smaller than the radius of gyration of bulk PS. By correlating the effective thermal conductivity with the ratio of the film thickness to radius of gyration, we find that this increase is mainly due to the increase of interfacial thermal conductance between PS thin film and the substrate, which likely results from the changing chain structure near the PS/substrate interface.

These findings in this thesis on how the thermal properties of polymeric and hybrid organic-inorganic materials change with the atomic/chain structure and interactions with other materials could be useful for further understanding and engineering of nanostructured polymeric materials for thermal management and energy conversion.