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Namsu Kim, Benoit Domercq, Seunghyup Yoo, Adam Christensen, Bernard Kippelen et al.

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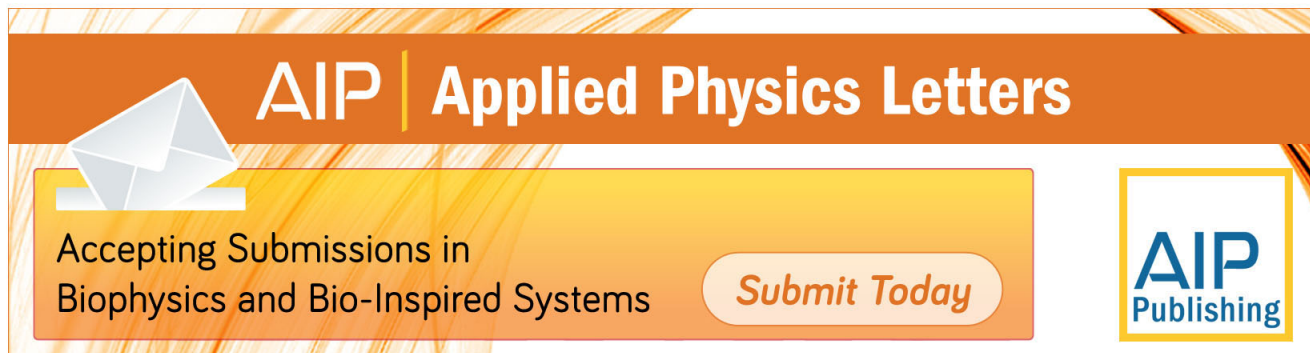
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Thermal transport properties of thin films of small molecule organic semiconductors

Namsu Kim

Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

Benoit Dornier and Seunghyup Yoo

School of Electrical and Computer Engineering and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332

Adam Christensen

Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

Bernard Kippelen

School of Electrical and Computer Engineering and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332

Samuel Graham^{a)}

Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

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A series of harmonic Joule-heating experiments have been employed to determine the thermal conductivities of thin films of pentacene, *N,N'*-diphenyl-*N,N'*-di(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine, and tris(8-hydroquinolato)aluminum, three widely used organic semiconductors. Room-temperature thermal conductivity values of 0.51, 0.24, and 0.48 W/mK were measured for films of these three compounds, respectively. These values are over two orders of magnitude lower than those of inorganic semiconductors. While amorphous films were found to display only small thermal conductivity changes over the temperature range of 228–350 K, pentacene exhibited stronger variations that are typical of phonon-phonon scattering observed in polycrystalline semiconductors. © 2005 American Institute of Physics. [DOI: 10.1063/1.2140478]

The development of organic electronics using semiconducting conjugated molecules and polymers has seen dramatic advancements over the past several years. The attractiveness of such materials lies in their relative ease of processing at room temperature, potentially low-cost, and inherent mechanical flexibility. Conjugated polymers can be processed from solution while small molecules can be deposited by physical vapor deposition techniques making both classes of materials amenable to scalable mass production needed for large area light sources and energy conversion devices. Materials such as pentacene and *N,N'*-diphenyl-*N,N'*-di(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) have been used extensively as hole-transport materials and tris(8-hydroquinolato)aluminum (Alq₃) as an electron transport and emissive material in a variety of organic semiconductor devices, including organic field-effect transistors, organic photovoltaic cells, and organic light-emitting devices.^{1–8} While much effort has been placed on the understanding of the optical and electronic transport properties of materials and devices, little has been done to investigate their thermophysical properties. Accurate thermal modeling of organic devices is becoming increasingly important as discrete organic electronic devices are being integrated into more complex arrays and subsystems in which thermally induced phenomena will play an important role.

Thermophysical properties of material are of primary importance for assessing thermal management, reliability,

and electrothermal characterization of devices. Temperature changes in organic electronic devices may induce shifts in the material band gap, induce thermomechanical failures, increase transport mobilities under variable range hopping (amorphous materials) or decrease mobility under band-type transport (crystalline materials).^{9–11} While the thermal masses of most organic materials used in thin film devices are small, the details of heat generation, dissipation, and its impact on the device require knowledge of the local thermal conductivity and specific heat of the materials that comprise the device. Furthermore, thermoelectric applications such as solid-state energy conversion based on the Peltier effect for cooling and the Seebeck effect for power generation require materials with high electrical conductivity and low thermal conductivity to increase the thermoelectric figure of merit.¹² A detailed characterization of the thermophysical properties of organic semiconductors is therefore needed to assess their potential in these applications.

Here, we report on a series of thermophysical experiments that have been employed to determine the thermal conductivities of thin films of pentacene, TPD, and Alq₃, three widely used organic semiconductors. The experiments were based upon a harmonic Joule heating method (3ω) established by Cahill.¹² Thermal conductivity experiments were conducted in a temperature range from 228 to 348 K on thin films with thicknesses ranging from 0.2 to 1 μm .

Pentacene, TPD, and Alq₃ were purchased from Aldrich Chemicals and subsequently purified once by thermal gradient zone sublimation under vacuum. The purified materials were deposited using physical vapor deposition in vacuum

^{a)} Author to whom correspondence should be addressed; electronic mail: sgraham@me.gatech.edu

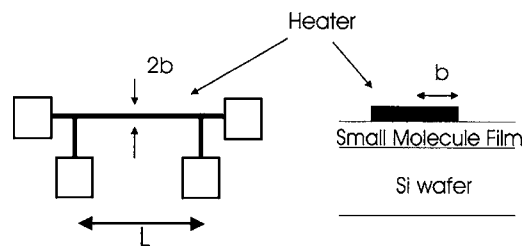


FIG. 1. Top and side view of the geometry used in the 3ω Joule heating experiments used to measure the thermal conductivity.

($<10^{-7}$ Torr) on precleaned Si substrate at 0.2 \AA/s for pentacene and 1.0 \AA/s for TPD and Alq_3 . Substrates were held at room temperature during deposition. Film thickness measurements were carried out using a Dektak 6 M profilometer and yielded values of 200 nm for films of pentacene and Alq_3 , and $1 \mu\text{m}$ for TPD films. Pentacene is known to form polycrystalline phases with polymorphs and grain sizes that are dependent on the substrate and deposition conditions. Since film morphology is likely to impact thermal conductivity,^{13,14} atomic force microscopy experiments were performed on the pentacene films to evaluate grain size. Based on previous research, the pentacene films were anticipated to develop the more dense bulk phase rather than the thin-film polymorph.¹⁴ Transition from the thin-film phase to the bulk phase generally occurs for film thicknesses above 100 nm.

To prepare the samples for the 3ω testing, a metallic wire was deposited onto each sample to act as both a heater and temperature sensor while a modulated current passed through it (Fig. 1). Au was used as a metallic line and Ti was used as an adhesion layer between Au and the organic semiconductors. Both Au and Ti metal lines were deposited using electron-beam evaporation at 1.0 \AA/s through a Si shadow mask. The thickness, width, and length of the metal lines were controlled to produce a resistance on the order of 50Ω to match the impedance output of the power supply used in the test. The heater width was $50 \mu\text{m}$ which induced one-dimensional heat conduction in the films. The use of an additional dielectric layer between the heater and the material under test was not required here since the films of pristine small molecules were semi-insulating.

Experiments were carried out at temperatures between 228 and 348 K with 10 K intervals in a vacuum cryostat at a pressure of 10^{-7} Torr. Data were analyzed by fitting the analytical solution for a multilayer anisotropic 3ω sample to deduce the film conductivity as described by Olson *et al.*¹⁵ In the experiments, both the film and substrate conductivities were determined simultaneously. Since the thermal conductivity of single crystal Si has been well characterized as a function of temperature,¹⁶ this method provided an internal reference to check the validity of the experiments.

Thermal conductivity data measured in thin films of three different materials as a function of temperature are shown in Fig. 2. The lowest room temperature thermal conductivity is observed for films of TPD with a value of 0.24 W/mK and displays very little temperature dependence over the temperature range studied here. The thermal conductivity of Alq_3 films also displays a small temperature dependence, decreasing with increasing temperature from 0.55 W/mK at 228 K to 0.45 W/mK at 345 K. Such behavior in these two films is consistent with the characteristic

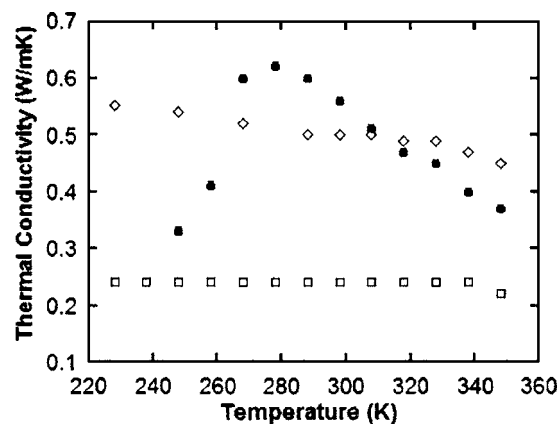


FIG. 2. Temperature dependence of the thermal conductivity measured in thin films of pentacene (circles), TPD (squares), and Alq_3 (diamonds) in the temperature range from 228 to 348 K.

plateau seen in the thermal conductivity of amorphous materials. The lack of the temperature dependence in conductivity over the current temperature regime can be attributed to the strong scattering of atomic vibrations found in amorphous materials. In general, phonon-wave behavior is ill defined in most amorphous materials and Boltzmann transport equations do not readily apply. To first order, the thermal conductivity can be approximated from kinetic theory by¹⁷

$$K = \frac{C\nu l}{3}, \quad (1)$$

where ν is the speed of the heat carriers (approximated by the sound velocity in amorphous materials), l is the mean free path of heat carriers (equal to the average atomic spacing), and C is the specific heat. Since ν and l are considered temperature independent in amorphous materials, the thermal conductivity of an amorphous solid will develop a plateau in regions where the specific heat has weak temperature dependence. Additional research is needed to investigate if these results on specific heat can be applied to TPD and Alq_3 as well as the applicability of theories based on the lower limit to thermal conductivity.¹⁷

The thermal conductivity of pentacene shown in Fig. 2 displays a strong temperature dependence which is indicative of a polycrystalline or crystalline semiconductor material. At room temperature, the thermal conductivity is 0.51 W/mK , and peaks near 273 K with a value of 0.62 W/mK . Increasing the thermal conductivity above room temperature shows strong negative temperature dependence with a thermal conductivity of 0.38 W/mK at 345 K (60% of the sublimation temperature for pentacene). The strong temperature dependence of thermal conductivity will impact the use of pentacene based transistors designed for use at elevated temperature as the thermal conductivity may decrease by a factor of 2 when compared to room-temperature values. Previous research has shown that the carrier mobility in pentacene may increase by a factor of 3 at 403 K compared to room temperature, allowing larger currents and more heat dissipation for a fixed voltage.¹⁸ However, the impact of changes in thermal properties must be accounted for in the design and performance of such high temperature transistors. Thermal properties of pentacene were not observed to degrade upon prolonged exposure to air unlike electronic properties, sug-

gesting that the conduction is dominated by phonon transport.

Atomic force microscopy characterization of these pentacene films revealed grain sizes of the order of 350 nm in diameter. Such a granular structure is indicative of the polycrystalline nature of the film. In contrast to the previous amorphous films of TPD and Alq₃, the temperature dependence of thermal conductivity above 273 K can be attributed to phonon-phonon scattering processes, causing a temperature dependent decrease in the phonon mean free path (l). The peak at which phonon-phonon scattering becomes dominant will depend greatly upon film structure (grain size and film thickness) as increased boundary scattering will tend to push the peak to higher temperatures. Variations in the thermal conductivity of pentacene with processing are expected due to its polymorphic nature and the effect of deposition conditions on grain size.

In summary, a 3ω technique has been utilized to measure the thermal conductivity of three small molecule organic semiconducting materials. Increase in the temperature dependence of the thermal conductivity is shown to correlate with increased structural order in the film. Thermal conductivities are shown to be over two orders of magnitude less than that of Si (150 W/mK) and a factor of 2–5 times less than that of thermally grown SiO₂ (1.4 W/mK) at room temperature. Such low thermal conductivities may be advantageous to the development of thermoelectric devices or polymer temperature sensors.

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