Advances in optical nanocalorimetry techniques for the characterization of thin films

Insplorion's Nanoplasmonic Sensing (NPS) technology enables measurements of the transition temperatures of thin polymer films. Here, NPS is applied to assess the effect of film thickness on the thermal stability of semi-crystalline, liquid-crystalline and glass organic semiconductor thin films. down to the *sub*-100 nm film thickness regime.

Introduction

Organic semiconductors are key materials for the next generation of thin film electronic devices like field-effect transistors, light-emitting diodes and solar cells. Accurate thermal analysis is essential for the fundamental understanding of these materials. However, classical experimental techniques are insufficient because the active layer of most organoelectronic devices is typically only on the order of a hundred nanometers or less. Scrutinizing the thermal properties in this size range is, nevertheless, critical because strong deviations of the thermal properties from bulk values due to confinement effects and pronounced influence of the substrate become significant. Here, it is shown how NPS can be used to study the thickness dependence of the thermal stability of semi-crystalline, liquid-crystalline and glassy organic semiconductor thin films down to the *sub*-100 nm film thickness regime.

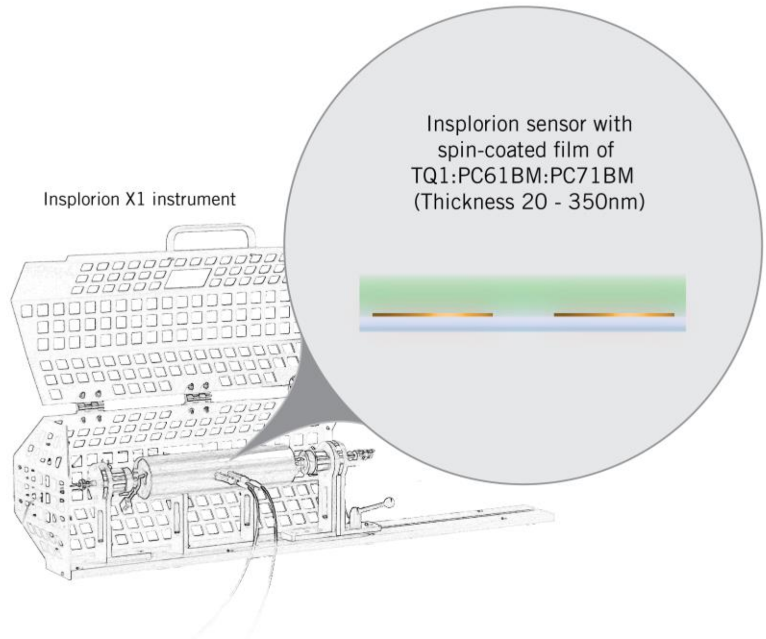

Figure 1: Insplorion system setup. The inset shows a schematic illustration of the sensors used in this application example (not to scale).

Experimental Procedure

TQ1, PC61BM:PC71BM and TQ1:PC61BM:PC71BM were spin-coated onto silicon dioxide coated NPS sensors. Films with different thicknesses were obtained by controlling the spin-coating speed and the polymer solution concentration. The sensors were then mounted in an Insplorion X1 instrument and, for each material and thickness, the glass transition temperature (T_g) was determined. Briefly, the NPS signal is plotted as a function of temperature during a linear temperature ramp from 60°C to 180°C. The T_g is detected as the temperature at which a change in the slope of the "NPS signal" vs. "Temperature" curve is detectable.

Results

NPS data obtained from 150nm supported films of TQ1, $PC_{61}BM:PC_{71}BM$ and $TQ1:PC_{61}BM:PC_{71}BM$ is shown in Figure 2. TQ1 displays a T_g value around 117 °C while the binary polymer mixture PC61BM:PC71BM shows a higher T_g value (around 128 °C). The ternary mixture, containing all components, displays an intermediate T_g at 123 °C. Both the fullerene mixture and the ternary blend show a single T_g, similarly to TQ1, which is predicted for finely

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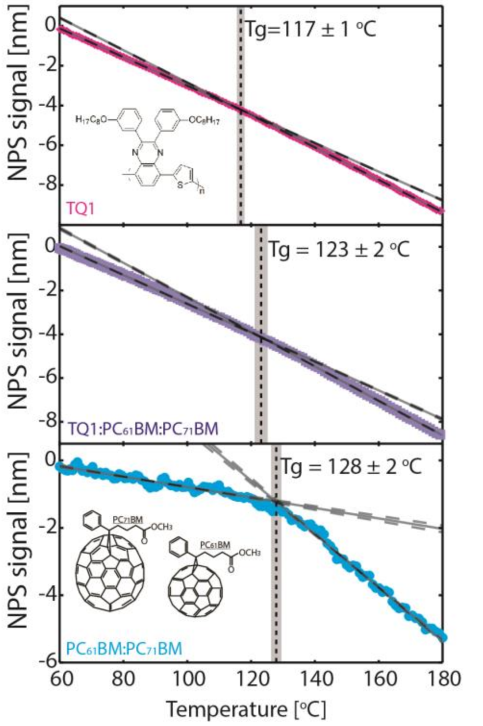

Figure 2: Determination of T_g from NPS measurements. The dashed lines represent the linear fits for each of the linear regions, the intersection indicates the T_g. The gray areas show the uncertainty with a 95% confidence interval of the linear fits.

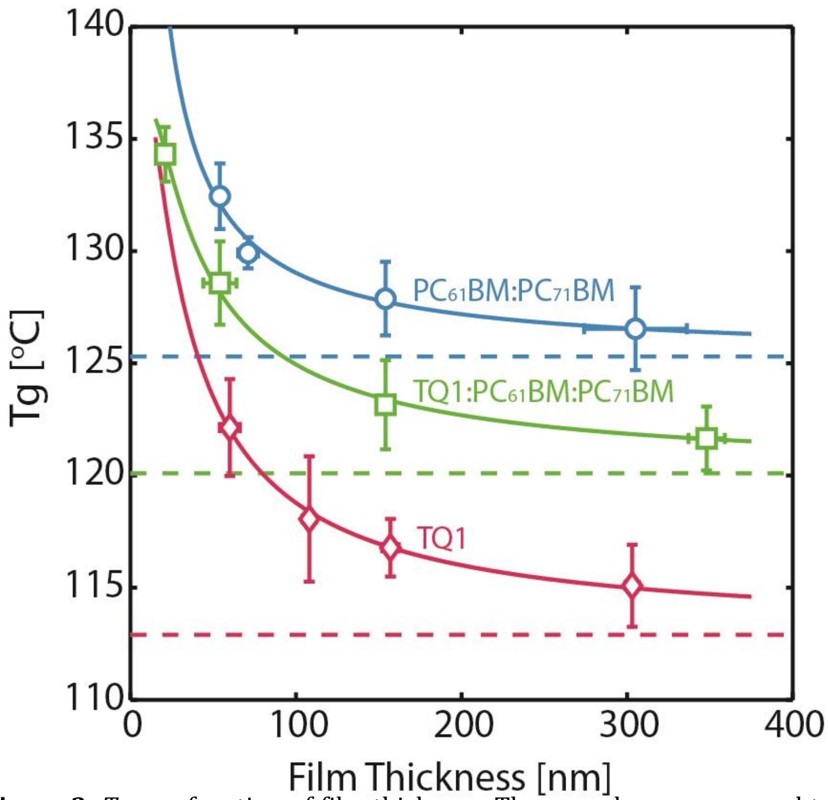

Figure 3: T_g as a function of film thickness. The error bars correspond to the uncertainty in the procedure used to determine T_g. Solid lines represent the best fit to the model described in [2] and the horizontal lines the derived bulk T_g for each of the polymers and mixtures tested.

intermixed blends. Other polymeric materials may display more than one transition temperature, for example, originating from a melting transition, a nematic-isotropic transition or even further local glass transitions caused by the films' interaction with the surface.

NPS can be used to measure the film thickness dependence of any transition temperature.

The thickness dependence of the glass transition temperature of TQ1, PC61BM:PC71BM and TQ1:PC61BM:PC71B films, respectively, is shown in Figure 3. All materials show a clear decrease in T_g as the thickness of the film is increased. The largest effect is seen for film thicknesses below 200 nm. The T_g values are observed to increase up to 20 degrees for the thinnest films.

Conclusions

The very high surface sensitivity of Insplorion's NPS technology in combination with the possibility to measure during temperature sweeps provides a unique method for studying dependence of polymer film thickness on transition temperatures. Here it is shown how NPS can be used to determine the glass transition temperature of semi-crystalline, liquid-crystalline and glassy organic semiconductor thin films down to the *sub*-100 nm film thickness regime.

This study was originally performed by researchers at the Department of Physics and Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Sweden.

References

[1] *Plasmonic Nanospectroscopy for Thermal Analysis of Organic Semiconductor Thin Films, Ferry Nugroho, Amaia Mendaza, Camilla Lindqvist, Tomasz Antosiewicz, Chritian Müller and Christoph Langhammer, Analytical Chemistry 89(4), 2017, 2575–2582.*

[2] *Estimation of the Thickness Dependence of the Glass Transition Temperature in Various Thin Polymer Films, Jae Kim, Jyongsik Jang and Wang-Cheol Zin, Langmuir 16 (9) (2000) 4064-4067*