Confinement Effect on the Glass Transition Temperature in Thin Polymer Films

Insplorion's Nanoplasmonic Sensing (NPS) technology enables measurements of polymer glass transition temperatures in thin supported films. Here NPS is applied to study the confinement effect in thin films of a polymer composite used as the light-harvesting layer in organic solar cells.

Introduction

The glass transition temperature, T_g, of amorphous polymers is considered to be one of the most important parameters for describing fundamental viscoelastic properties, as well as for targeting technological applications. Confining polymer molecules e.g. at interfaces or in thin films alters the mobility of the molecules and therefore the T_g. In this application note it is shown how Insplorion's NPS technology can be used to measure the effect of confinement on the T_g in thin polymer films of a conjugated polymer (TQ1) as well as a composite of this polymer and two fullerene derivatives ($PC_{61}BM$ and $PC_{71}BM$), a composite that is relevant for polymeric solar cells.

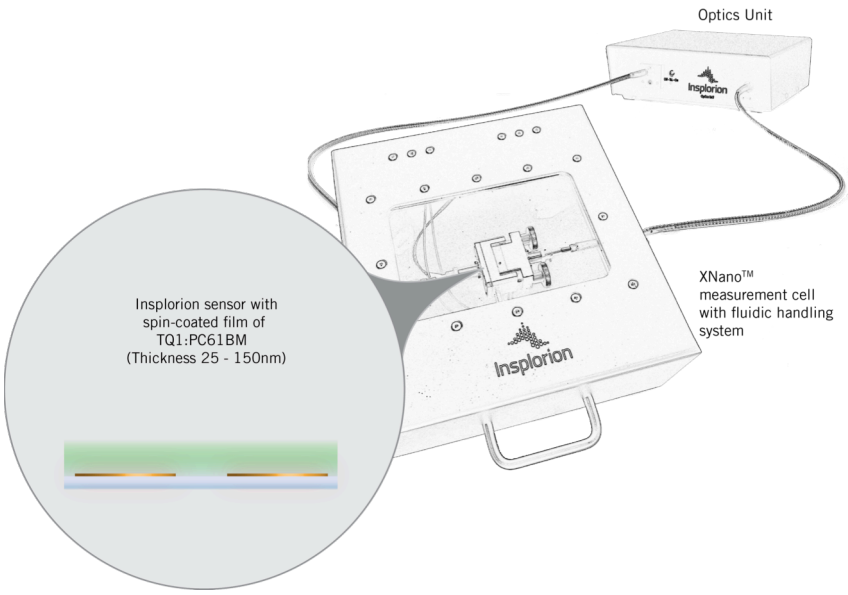

Figure 1: Insplorion system setup. The inset shows a schematic illustration of the sensors used in this application example (not to scale!).

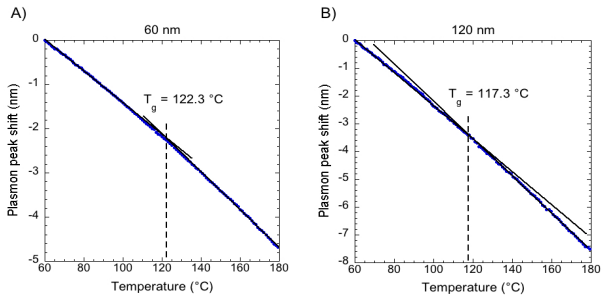

Figure 2: Change in NPS signal while sweeping the temperature from 60°C to 180°C for a spin coated film of TQ1. A) 60 nm thick film. B) 120 nm thick film.

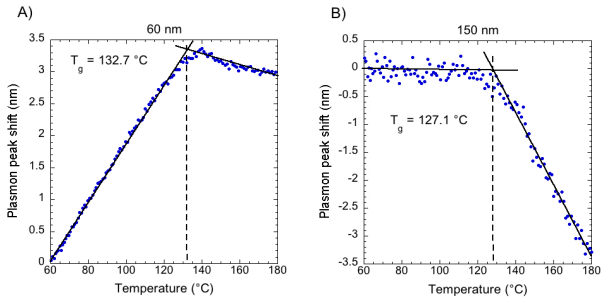

Figure 3: Change in NPS signal while sweeping the temperature from 60°C to 180°C for a spin coated film of the fullerene derivative mixture $PC_{61}BM$:$PC_{71}BM$. A) 60 nm thick film. B) 150 nm thick film.

Experimental Procedure

Thin films of (i) TQ1, (ii) a mixture of the two fullerene derivatives ($PC_{61}BM$:$PC_{71}BM$) and (iii) a 5:4:1 composite of TQ1 and the two fullerene derivatives (TQ1:$PC_{61}BM$:$PC_{71}BM$) respectively, were deposited onto Insplorion sensors with a silicon nitride coating via spin coating. The respective film thicknesses were 60 nm and 120 nm for TQ1, 60 nm

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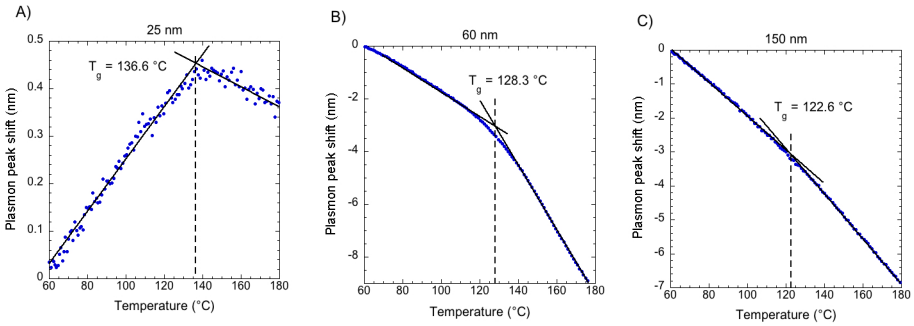

Figure 4: Change in NPS signal while sweeping the temperature from 60°C to 180°C for a spin coated film of the polymer and fullerene derivative mixture TQ1:$PC_{61}BM$:$PC_{71}BM$. A) 25 nm thick film. A) 60 nm thick film. C) 150 nm thick film.

and 150 nm for the fullerene derivative mixture $PC_{61}BM$:$PC_{71}BM$, and 25nm, 60 nm and 150 nm for the composite TQ1:$PC_{61}BM$:$PC_{71}BM$. The sensors were placed, one at a time, in the Insplorion instrument.

Prior to the measurements the samples were heated to

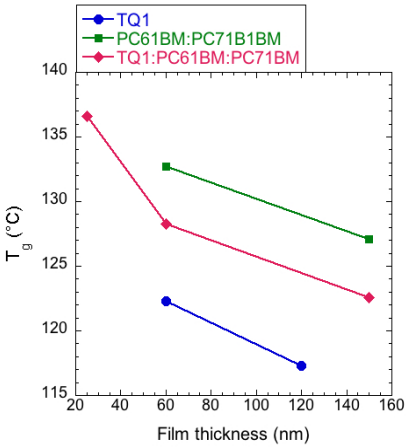

Figure 5: Glass transition temperatures for thin films, of different thicknesses, of TQ1 $PC_{61}BM$:$PC_{71}BM$ and TQ1:$PC_{61}BM$:$PC_{71}BM$.

80°C for 2 hours in inert gas (Ar, 50 ml/min) in order to remove solvent remains and humidity adsorbed during the exposure of the samples to air. The measurements were performed by sweeping the temperature from 40 °C to 180 °C at a rate of 2 °C/min in an inert (Ar) atmosphere.

Results

Figures 2, 3 and 4 show the NPS data obtained from thin supported films of TQ1, $PC_{61}BM$:$PC_{71}BM$ and TQ1:$PC_{61}BM$:$PC_{71}BM$, respectively. The data plotted is the plasmon peak shift as a function of temperature when the temperature is swept from 60°C to 180°C. The T_g is detected as a change in the slope of the "Plasmon peak shift" vs. "Temperature" curve as indicated in Figures 2, 3 and 4.

For the pure polymer film (TQ1) a glass transition at ~120 °C was found (Figure 2), which is in good agreement with an earlier published value measured by variable-temperature ellipsometry[2].

For the composite TQ1:$PC_{61}BM$:$PC_{71}BM$ a transition was found at ~130 °C (Figure 4), which is caused by the onset of domain formation within the amorphous films and can be correlated to the T_g of the composite.

The T_g's for the different film thicknesses are summarized in Figure 5. It is clear that, for both TQ1, $PC_{61}BM$:$PC_{71}BM$ and TQ1:$PC_{61}BM$:$PC_{71}BM$, confining the material into a thin film causes the T_g to increase.

Conclusions

The very high surface sensitivity of Insplorion's nanoplasmonic sensing technology in combination with the possibility to measure during temperature sweeps provides a unique method for studying the glass transition temperature of thin polymer films. Here it is shown how NPS can be used to study the effect of confinement on the T_g.

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

References

[1] *Indirect Nanoplasmonic Sensing: Ultrasensitive Experimental Platform for Nanomaterials Science and Optical Nanocalorimetry, Christoph Langhammer, Elin M. Larsson, Bengt Kasemo, and Igor Zoric, Nano Letters 10 (2010) 3529-3538.*

[2] *Fullerene mixtures enhance the thermal stability of a non-crystalline polymer solar cell blend , Camilla Lindqvist, Jonas Bergqvist, Olof Bäcke, Stefan Gustafsson, Ergang Wang, Eva Olsson, Olle Inganäs, Mats R. Andersson, and Christian Müller, Appl. Phys. Lett. 104 (2014) 153301-153304*

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