ESRF	**Experiment title: Understanding the thermally induced formation of organic nanostructures from ultra-thin sexythienyl films: a real time GIXD study.**	**Experiment number**: SC- 2702
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Report:

We have investigated in real time and *in situ* the dewetting and the desorption, induced by thermal treatment, of thin sexythienyl (6T) films by Grazing Incidence X-ray Diffraction (GIXD) and X-Ray Reflectivity (XRR). The dewetting phenomenon, used by several nanopatterning techniques to produce arrays of nanostructures of controlled size and lateral distances, is a complex process that can be activated by an external stimulus, e.g. thermal, mechanical or chemical perturbation. At the early stages it can be due to the nucleation and growth of holes or to a collective instability described as a spinodal mechanism, followed by the film rupture and droplets formation. For organic semiconductors relevant to hybrid electronic and optoelectronic devices, such as oligoacenes, perylenes and oligothiophenes, dewetting is considered a problem affecting the growth of flat films and a strong limitation in the perspective of devices applications. It is therefore essential to follow the evolution of thin organic films in real time and *in situ* to examine the evolution of these systems under thermal excitation.

We used a portable UHV chamber equipped for *in situ* Organic Molecular Beam Deposition (OMBD), designed to be compatible with X-ray Diffraction measurements. The UHV chamber has been installed on the ID10B 6-circle diffractometer, as in previous experiment SC-2340. The wavelength was fixed at 0.154 nm. The substrate considered for this experiment is silicon (100) with the surface covered by native oxide (~1 nm). 6T films were deposited under strictly controlled low deposition rate (<0.1 nm/min) and optimal substrate temperature for film growth (120 °C). Before a new 6T film deposition, the substrate has been cleaned through annealing at 600 °C, i.e. well above sublimation temp. for 6T, for at least 10 min. to desorb all the organic material. The recovery of XRR for the bare substrate ensured for surface cleanliness and provided a reference for the bare substrate.

XRR scans and, in particular, the XRR intensity oscillations at the anti-Bragg angular geometry have been recorded during the 6T deposition to monitor the growth mode of the 6T films and the subsequent transformations (Figure 1). The thickness of the 6T thin films was ranging within 1 – 1.5 ML. At the end of the deposition, GID scans (not shown here) yet exhibited diffraction peaks typical of 6T thin film crystalline phase.

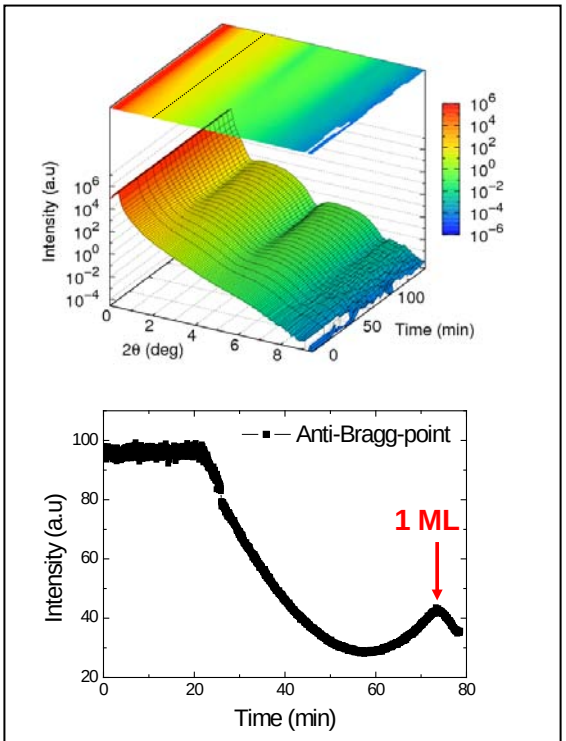

Figure 1. Top: XRR evolution during 6T deposition by OMBD. Bottom: Intensity of the specular reflection at the anti-Bragg condition.

To measure the kinetics of the dewetting and/or desorption processes, and the crystal structure evolution, we raised up the temperature to different values (140°C, 150°C, 160°C) and followed the morphological and structural evolution in real time of 6T. The temperature was maintained within +/- 2°C with respect to the set-point. During the thermal excitation we measured systematically GIXD patterns, in order to follow the changes of the crystal phases. In some cases, after a while the temperature has been further raised up to compare the response of the system with the stationary thermal condition. Figure 2 shows the time evolution of the XRR and GID signals for different annealing temperatures applied to 6T thin films close to 1 ML. A detailed analysis of these trends is in progress and relies on the comparison of the time evolution vs. the temperature and on fit of the XRR curves to estimate quantitatively the RMS roughness and the occupancy of the molecular layers. These trends will be compared to the kinetics of the GID signals to provide a picture of the film crystal phases and morphology. Here we notice that the GID signal is related only to the crystalline nucleation (occurred since the 6T deposition), hence the decrease of the GID signal vs. the annealing temperature is mostly indicative of the activation of desorption processes that reduces the ordered molecular domains. Conversely, a signal intensity enhancement would indicate mass transport on the surface contributing to the enlargement of the crystalline domains. The XRR scans provide information about the whole film mass distribution and agree qualitatively with the trend of the GID signals. It seems therefore that the 6T dewetting observed by AFM measurements is overwhelmed by desorption, at least for temperatures around 150°C-160°C. The slope of the intensities of the GID peaks and of the XRR profile vs. time at the anti-Bragg angular condition will be compared to distinguish if the 6T desorption is the dominant mechanism at all these temperatures or if there is a definite contribution even by thermal dewetting mechanisms.

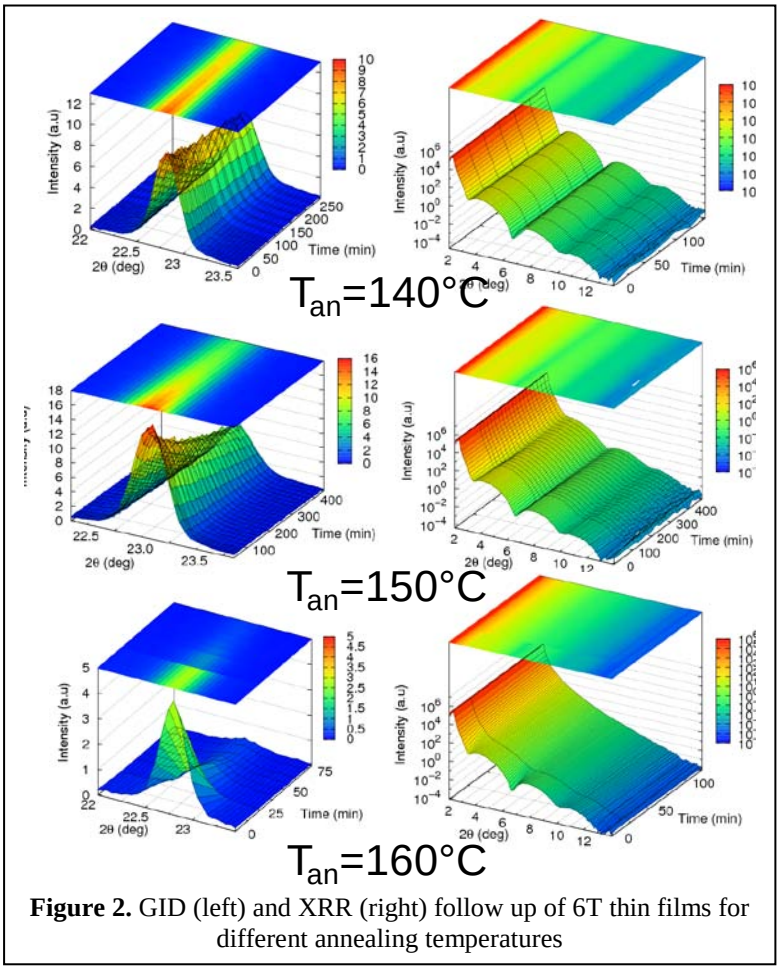

Figure 2. GID (left) and XRR (right) follow up of 6T thin films for different annealing temperatures