ESRF	**Experiment title:** Impact of oxygen doping on organic semiconductor thin films: *In situ* real-time x-ray scattering and optical spectroscopy	**Experiment number:** SI-2248
Beamline: ID 10B	**Date of experiment:** from: 8/06/2011 to: 14/06/2011	**Date of report:** 03/11/2011
Shifts: 18	**Local contact(s):** Dr. A. Vorobiev	*Received at ESRF:*

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Report:

1. Introduction

As descried in the proposal, the purpose of the experiments at ID10B was to investigate the impact of oxygen gas doping on the film structure of picene (Fig. 1). It has been reported that the doping enhances the hole carrier mobility by a factor of ~100 in organic field-effect transistors (OFETs) [1,2]. Understanding the mechanism behind this effect requires detailed information on both the pristine and the O_2-doped film structure.

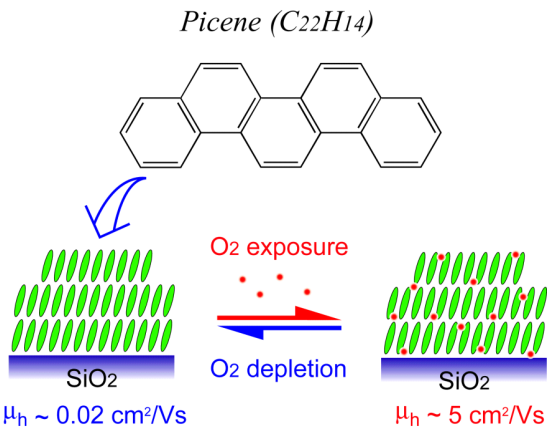

Fig. 1: Chemical structure of picene (top) and reversible OFET device performance with and without O_2 gas.

Using *in situ* x-ray scattering techniques, we studied the film growth in real time and the film structure of O_2-doped picene films grown on SiO_2 at a substrate temperature of 303 K (nominal film thickness ~40 nm). We performed *in situ* x-ray reflectivity (XRR), grazing incident x-ray diffraction (GIXD), and 2-dimensional GIXD (2D-GIXD) both in real time and post growth. Optical spectroscopy was not measured at the ESRF because the experimental accessories were not available at the time.

Below we give a short summary of results from the beam-time (SI-2248) at ID10B.

2. 1 Growth mode and crystal structures of picene thin films

The film structure evolution of picene deposited on SiO_2 was thoroughly studied before the O_2-doping experiment. Figure 2(a) shows real-time XRR data covering a q_z-range which includes the first Bragg point (=0.465 Å^{-1}). While there is a clear increase of the Bragg peak intensity, changes of the Kiessig oscillations with increasing thickness are difficult to see. As shown in Fig. 2(b) the reflectivity at the anti-Bragg-point (marked as $½q_{Bragg}$ in Fig. 2(a)) does not exhibit a periodic oscillation, but a sudden drop at a thickness of 11.1 nm. This thickness corresponds to 8.2 monolayers (ML), as estimated by the thickness divided by the lattice constant of 13.5 Å. According to the established real-time scattering formalism [3] the absence of oscillations at $½q_{Bragg}$ indicates 3D island-growth of the molecules from the very start. This conclusion is supported by atomic force microscopy data (not shown), which reveal a pronounced 3D island growth below ~10 nm and filling of the voids between the islands thereafter.

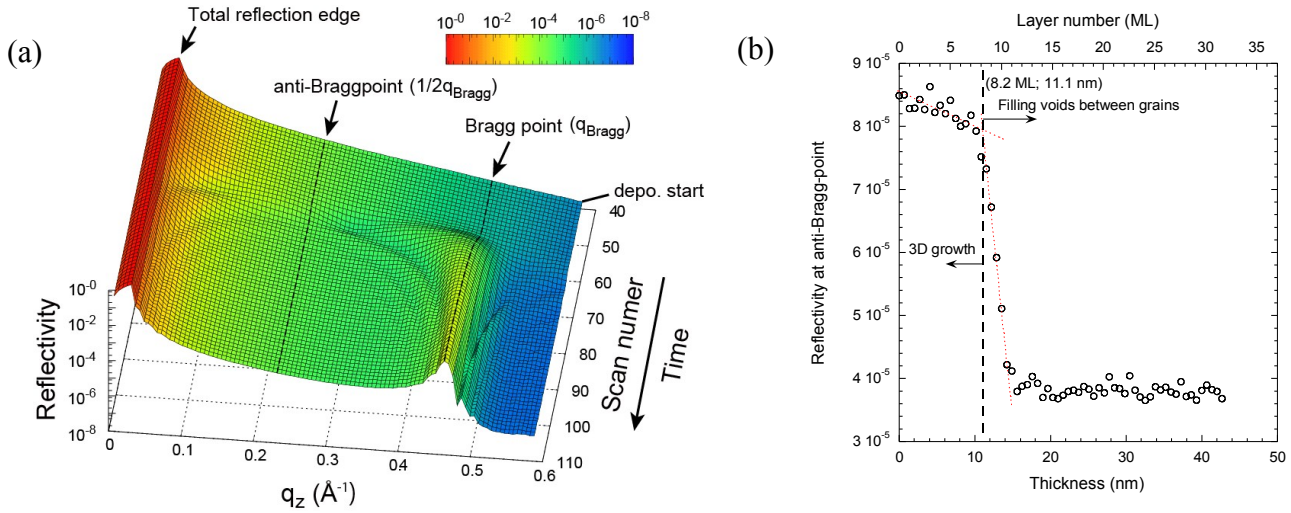

Fig. 2: (a) Real-time XRR of picene film growth. (b) Thickness dependent-oscillation at anti-Bragg-point..

In situ 2D-GIXD was measured both in real-time and post-growth using a MarCDD detector to obtain information on the crystal structure of the picene films. The post-growth measurements (Fig. 3(a)) show a number of crystal truncation rods, i.e. (11*l*)(20*l*)(21*l*)(02*l*), derived from highly oriented standing picene molecules [4]. Interestingly, we found gradually shifting in-plane peaks (*hk*0) and new peaks appearing above ~8 ML , see Fig. 3(b). This film thickness coincides with the reflectivity drop at the anti-Bragg point observed in Fig. 2(b). This implies that the change in in-plane structure occurs when the molecules filled

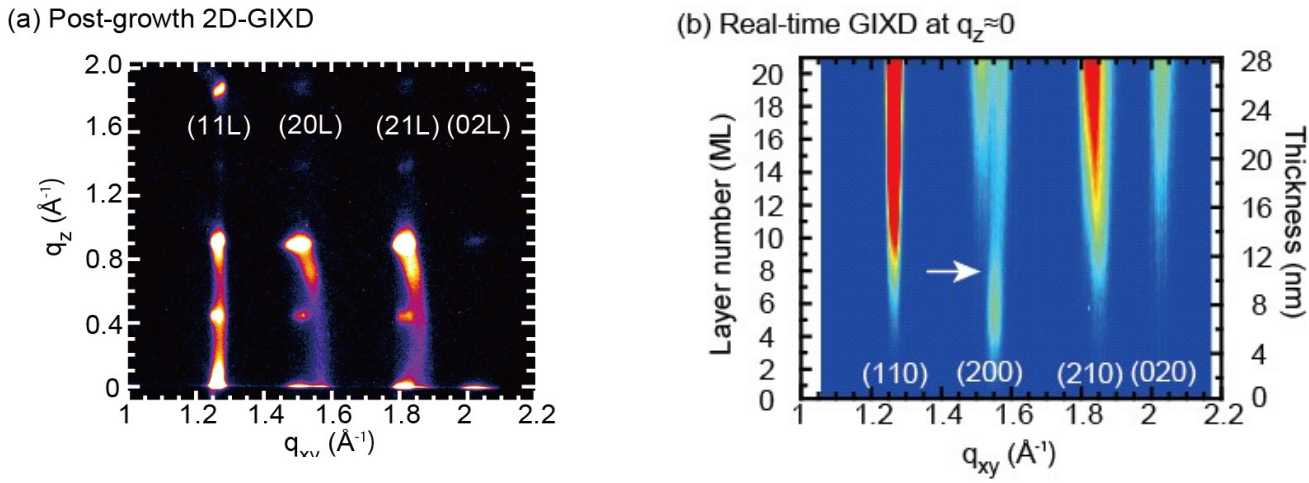

Fig. 3 (a) Post-growth 2D-GIXD of picene (42 nm)/SiO_2 by using a MarCCD area detector. (b) Real-time GIXD measured during picene film growth at q_z≈0 (extracted the from the real-time 2D-GIXD).

voids between 3D picene grains. Such thickness dependent structural changes in the initial stages of growth have been reported for several large molecules, e.g., diindenoperylene [5], perfluorinated copper phthalocynines [6] and quaterrylene [7] deposited on SiO_2. In these cases, however, the film growth always followed the Stranski-Krastanov mode (layer-to-island growth), whereas in the case of picene we found the Volmer-Weber mode (island-growth from the very first layer). Therefore, we demonstrate that the Volmer-Weber type growth can be accompanied by structural changes in organic thin films.

2. 2 Experiments of oxygen gases doping

After characterizing the picene films we introduced O_2 gas (Air Product Inc, purity: 5N) into the vacuum deposition chamber (final pressure of 0.7 bar). Unexpectedly, we found no change in the out-of-plane and in-plane diffraction patterns as shown in Figs. 4(a) and 4(b), respectively. Rocking scans (not shown) around (001) Bragg peak showed were nearly identical (FWHM around 0.01°). Therefore, we conclude that the dosing of O_2 gas does not influence the structure of the picene film.

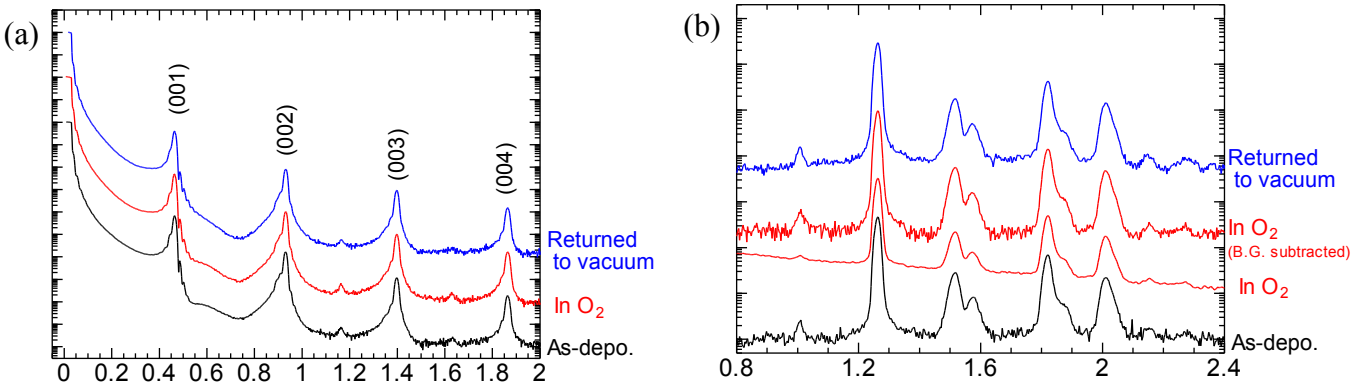

Fig. 4: (a) X-ray reflectivity and (b) GIXD of picene films at various conditions: as-deposition, in O_2 atmosphere (0.7 bar), vacuum condition after O_2 exposure..

3. Summary

We performed detailed *in situ* x-ray scattering experiments on picene thin films. While we observed new phenomena during picene film growth, no clear structural change was found when introducing O_2 gas. One question arises: How does O_2 gas penetrate the picene thin film? To understand this and the reported mechanism leading to an enhancement of device performance of picene-based OFETs by O_2 doping, further experiments are necessary.

We are preparing a paper to be submitted to an international journal. Finally, we wish to thank our local contact for the excellent support on ID10B.

4. References

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