ESRF	**Experiment title:** **In-situ x-ray characterization of voltage induced changes in organic semiconductors**	**Experiment number**: MA-820
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Report:

The field of molecular electronic devices covers great amount of applications (optochemical sensors, light emitting devices, organic field effect transistors, etc) with a huge profitable demand due to its low-cost fabrication and device miniaturization. The probed organic semiconducting materials and their crystal structure arrangement affiliated with the electronic poperties comprise a tremendous commercial interest. However, the interrelationship of the crystal structure and the electronic performance of the different organic materials are not fully understood. Therefore several investigation techniques, e.g. scanning transmission X-ray microscopy (STXM) have been used to get a closer look to this context [1].

The purpose of this work has been to investigate the interrelationship of crystal structure and electronic behavior of the used organic materials in a real device structure with X-ray diffraction. Starting with the spin casted polymer poly (3-hexylthiophene) (P3HT) as active layer between two gold contacts, several in - situ X-ray diffraction experiments have been performed, while applying an electrical field. Traditional ex - situ works of Bao [2] and Sirringhaus [3] give useful hints for the performance of P3HT based organic thin film transitors (OFETs) however in - situ experiments should clarify the device performance in detail. Several thin film transistor with different thickness of the active layer and variation of the channel length as well as the molecular weight of P3HT on either SiO_x substrates or glass substrates have been investigated. However, there has not been found any clear tendency apart from a steady decrease of the diffracted intensity, which hints at an influence of the radiation itself. Further measurements with pentacene (5A) and sexithiophene (6T) show stable diffraction peak intensity even after much longer radiation exposure. On the first sight, one can only observe different reflection peak behavior of the different organic materials, which points to an influence of the X-ray radiation on the diffracted intensity.

In - situ X-ray diffraction measurements with applied electrical field have been performed under helium atmosphere at the ID10b at ESRF using a self-developed measurement chamber (fig. 1). The synchrotron radiation of energy was 8079 eV and a position sensitive sensor (PSD) with 1024 channels has been used for the measurements. The sample has been covered with a graphite dome and electrically been connected with a Keithley 2400 source measure unit. Fig. 2 gives a scheme of the beam propagation between the two gold electrodes (source and drain). During the grazing incidence X-ray diffraction (GIXD) the source and drain have been sourced by a voltage between 0 and 150V and the current in the P3HT film has been measured in the 2mm channel

Figure 2: Self-developed measurement chamber with a graphite dome for inert measurements

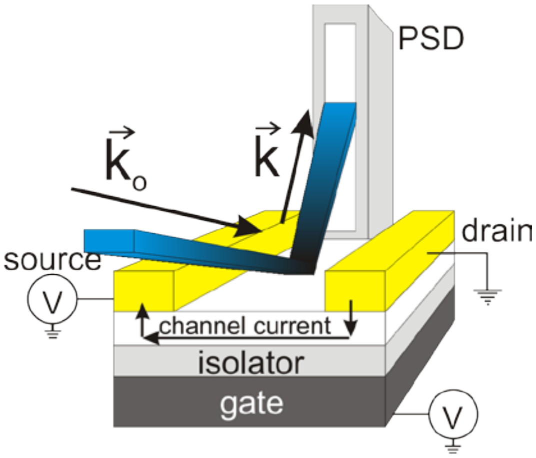
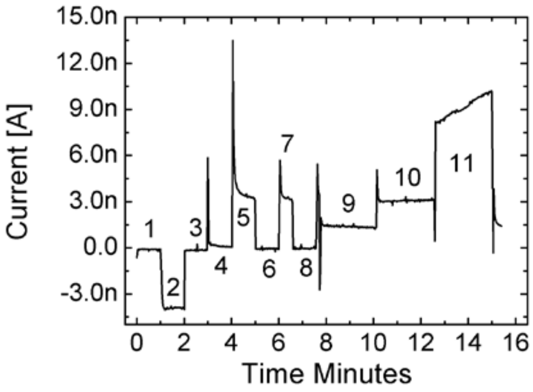


Figure 1: Schematic view of the experimental setup

First measurements were performed without applied voltage and the current in the channel has been measured by opening and closing the shutter as well as by varying the incidence angle of the incoming X-ray beam during open shutter conditions. Fig. 3 shows the current characteristic of this measurement with the different shutter positions (table). One can clearly indentify photo induced current generated by the X-ray radiation. Additionally, the photo current increases as the incidence angle of the X-ray is increased, i.e. for the larger penetration depth of X-ray, while keeping the incidence angle α_i below the critical angle of the layer.



1	Start data
2	Open Shutter
3	Close Shutter
4	Voltage to 1V
5	Open Shutter (1V)
6	Close Shutter (1V)
7	Open Shutter (1V)
8	Close Shutter (1V)
9	mv α_i=0.11° (1V)
10	mv α_i=0.14° (1V)
11	mv α_i=0.17° (1V)

Figure 3: Current characteristic with different shutter positions and varying incidence angle of the beam (left) and the shutter status as well as the incident angle of the primery beam during the measurement (right)

In GIXD data of a thin P3HT film, the 001 diffraction reflex as well as the 020 diffraction reflex are observable. The intensity as well as the peak position of these diffraction features was observed to changed during the insitu measurements at fixed incidence angle (α_i=0.15°) and varying the voltage. These changes were first assigned to the increasing voltage, however during the experiment, measurements without the voltage have been performed, which indicates a destructive influence of the X-ray beam to the spin casted, soft P3HT layer. A series of scans through 001 and 020 diffraction reflexes measured without any voltage sourcing is shown in fig. 4. The ongoing decrease of the intensity and the shift in the peak position of both diffraction peaks result from the structural damage in the polymer, which can either come from melting the material or from chemical changes in the polymer chain [4]. During the exposure the sample has been irradiated with a flux density of 1.08e+013 photons/(s mm^2). The integrated diffraction peak intensity as a function of the delivered photons show a rather linear decrease for both peaks (fig. 5). In average for P3HT samples, the decrease of the 001 diffraction peak was two times faster compared to that of 020 diffraction. (see slopes of lines in fig 5.)

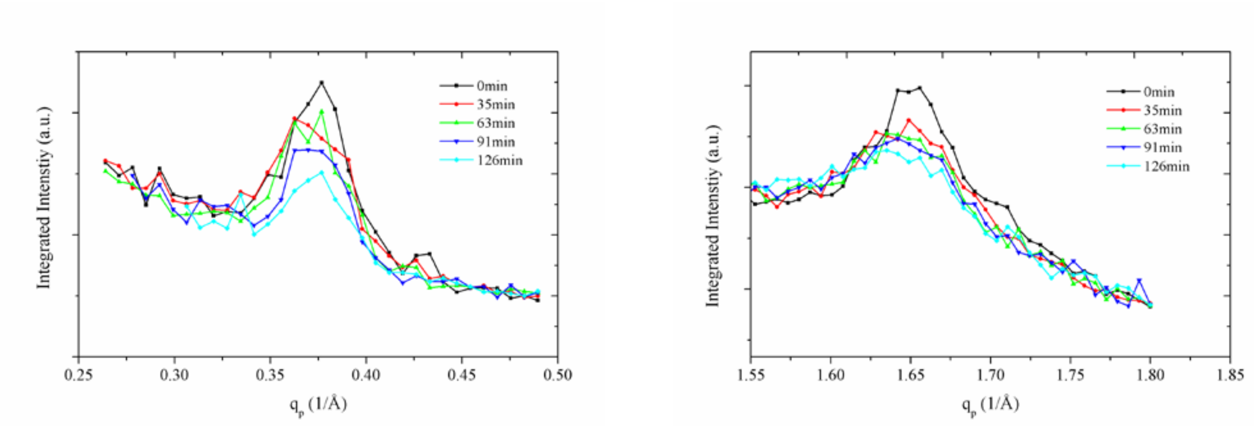
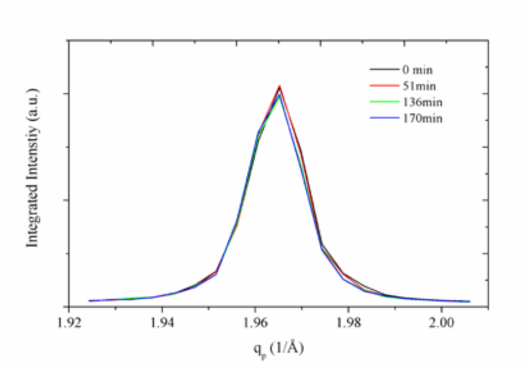


Figure 4: Intensity integrated along the q_z direction (i.e. perpenticular to the sample surface) as a function of q_p (the in-plane component of the scattered vector) for 001 and 020 diffraction peak (left and right, respectively) for a P3HT film on SiO_x substrate measured after different irradiation times.

For comparison, structural stability of pentacene and 6T, i.e. small molecules, were investigated by GIXD and coplanar XRD without applied electric field. The organic layers were produced by vacuum depostion on SiO_x substrates. A series of GIXD scans through the -121 diffraction peak measured after different sample irradiation times is shown in fig. 6. Pentacene demonstrates a stable diffraction peak profil and intensity after even higher irradiation, than for was applied for P3HT. The table on the right hand-side contains the slope of the integrated intensities of all possible pentacene rods with respect to the number of delivered photons. The flux density during the measurement has been 6.791e+013 photons/(s mm²).



rod	Integraded Intensity slope (y=k*x)
{11L}	**- 5.5e-20*x**
{02L}	**- 1.1e-20*x**
{12L}	**- 2.8e-20*x**
{20L}	**- 1.4e-21*x**
{21L}	**- 1.9e-21*x**

Figure 5: Linscan onlong the q_p direction in the reciprocal space of the -121 diffracton peak (left) of pentacene on SiO_x substrate and the slope of the integrated intensities of the measured rods of pentacene (right)

Sexithiophene (6T) behave like the pentacene under irradiation. The coplanar diffraction peak in fig. 7 comprise the evolution of the 400 peak during beam exposure. The density flux during irradiation has been 7.49e+013 photons/(s mm²) and the slope of the integrated intensity with respect to the delivered photons has been 3 orders of magnitude less then the pentacene rods.

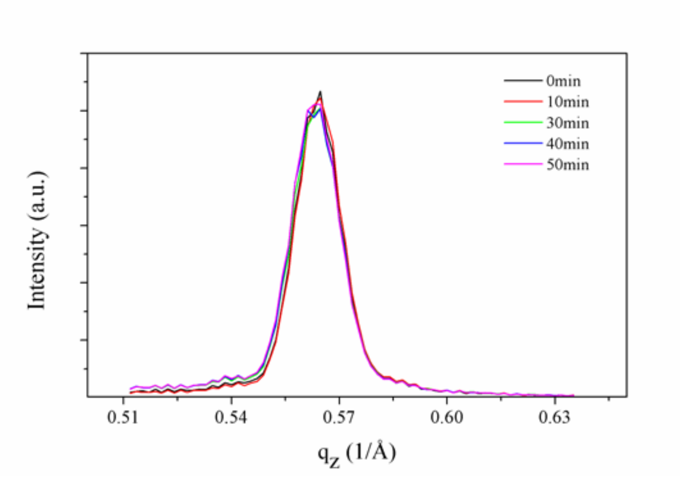


Figure 6: Coplanar diffraction scan of the 400 peak of sexithiophene (6T) on SiO_x *substrate during several minutes of X-ray irradiation*

Conclusions:

In conclusion, in our GIXD measurements, we have not observed any impact of applied electric field on the crystal structure of P3HT based OFETs. However, the ongoing decrease of both P3HT diffraction peaks during X-ray exposure pointed to a radiation damage on this thin polymer film, independent on the applied voltage. The intensity of the 001 peak decreases always faster than the 020 intensity. The stability against X-ray radiation damage can be important e.g. for solar cell applications with P3HT in space industry research. In contrast, thin films of pentacene and sexithiophene have been investigated on radiation damage while applying compareable X-ray dose. These two materials show hardly any intensity decrease in all of their diffraction peaks. In general we observed that thin organic films from small molecules like pentacene and sexithiophene are rather stable against X-ray radiation and on the other hand one has to keep an eye on X-ray radiation damage of thin polymer film like P3HT.

References

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