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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Studying the structural and molecular origin of the piezoresistive behaviour of conjugated polymers	**Experiment number**: SC 4670
Beamline: ID 03	**Date of experiment**: from: 28/09/2017 to: 04/10/2017	**Date of report**: 27/02/2018
Shifts: 18	**Local contact(s)**: Linus Pithan	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists): Giovanni Calogero Li Destri Nicosia*, Nunzio Tuccitto*, Pietro Livio*

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Report:

Overview

As stated in the proposal, we have performed structural characterization of poly-3-hexylthiophene (P3HT) thin films under ultrasounds application. The aim was to correlate the already observed conductivity increase during ultrasound application with changes in the film structure and crystallinity. P3HT films bearing different thicknesses and degrees of crystallinty were prepared before the arrival at ESRF. Ultrasounds were applied with an ultrasonic tip (30 kHz). As the direct contact with the tip would destroy the P3HT films, a soft polydimethylsiloxane (PDMS) 2 mm thick layer was placed in between, allowing the transfer of 67% of the ultrasonic power. The structural characterization was carried out by grazing incidence X-ray diffraction (GIXRD), to monitor the evolution of P3HT crystalline peaks. A 24 keV beam, enabling the transmission of 70% of the incoming x-rays, was used at a grazing angle of 0.05°. The GIXRD patterns were recorded with a Pilatus 300k and a Maxipix detector. An initial assessment of radiation damage on our samples revealed that an Ag 400 μm thick attenuator allowed to avoid any structural alteration. As a detailed quantitative analysis of our samples is ongoing, we present here some preliminary findings.

Quality of measurement and data

ID03 beamline fits perfectly our needs because of its surface diffraction expertise and resolution. The recorded data are of high-quality with high signal-to-noise ratio, despite the low diffraction signal arising from thin organic films (~ 100 nm). The beam was quite stable and reliable during our beamtime, with the exception of two beam losses, and we managed to succesfully characterize most of our samples. Figure 1 shows the characteristic GIXRD patterns, recorded with the Pilatus 300k, of our P3HT films without (A) and

with (B) the PDMS layer on top. It can be seen that the patterns show in both cases high signal-to-noise ratio peaks and are basically unchanged, apart from the PDMS structure factor peak covering the <200> P3HT one. Therefore, in order to maximize our chances to detect any structural changes during ultrasound application, we focused our study on the most intense peak, e.g. the <100>. Additionally, as we also expected peak shifts to occur, we decided to employ Maxipix detector, since its lower pixel size ensure higher q-space resolution during the detailed analysis of the the structural evolution of P3HT crystals under ultrasounds. This analysis showed that, the main effect of ultrasounds on the crystalline structure is a peak shift toward lower qs (Fig. 2A) analogous to the one observable by heating (Fig. 2B). However, if the heat generated by ultrasounds is disspated by fixing the sample to the sample stage with heat-conductive Ag paste, the peak does not shift but its intensity increases when ultrasounds are applied (Fig. 2C).

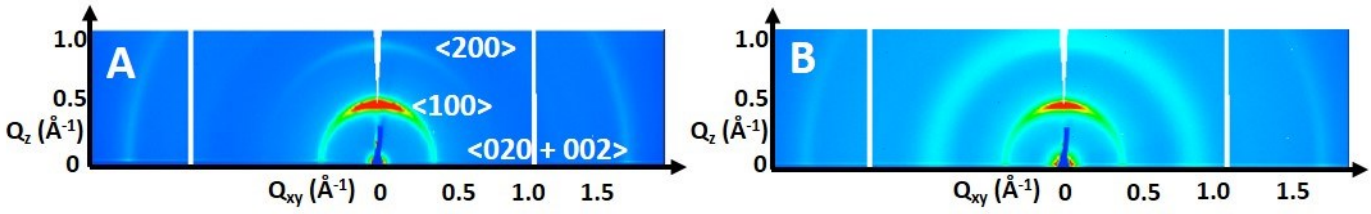

Fig. 1: GIXRD pattern of a 100 nm thick P3HT crystallized by annealing at 250°C (A), and of the same sample with a 2 mm PDMS layer on top. In (A), the Miller indices of the observed P3HT diffraction peaks are reported.

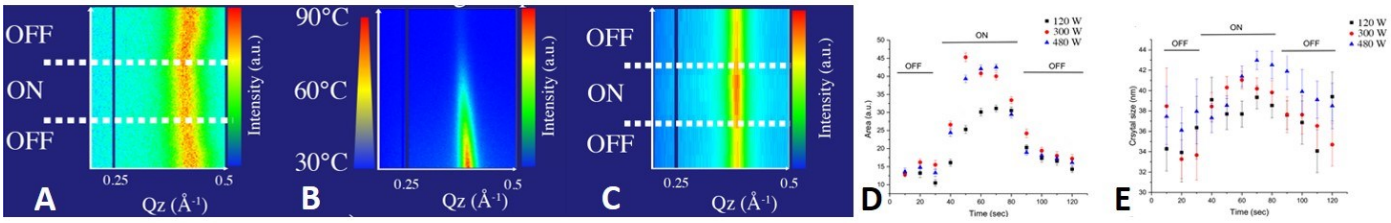

Fig. 2: Evolution of the <100> GIXRD P3HT peak with ultrasounds (A), it is evident a reversible shift toward lower qs analogous to the one observed when heating the sample (B). On the contrary, if the ultrasound-generated heat is efficiently dissipated, the peak doesn't shift but an itensity increases occurs (C). By fitting the peaks we observed that this intensity increase is proportional to the applied ultrasonic power up to 300 W (D) and it is also accompained by a decrease of the peak FWHM, e.g. by a fully reversible increase of the average crystal size.

The quantitative analysis of this intensity increase has revealed that it is proportional to the applied ultrasonic power up to approximately 50% of the ultrasound maximum power (600 W) (Fig. 2D). Overall, a threshold power value, at about 200 W/cm^2 (obtained by considering that PDMS layer allows the transfer of 67% of the applied power), seems to be the limiting value for the allowed intensity increase. Additionally, we observed this intensity increase to be accompained by a reduction of the FWHM peak, e.g. to an increase of the average crystal size (Fig. 2E). As polymer nanocrystals are formed by chain segments, parallel each other, with a characteristic length, we suggest that nanocrystal growth may occur via the ultrasound-promoted ordering of previously randomly oriented chain segments. In order to prove this hypothesis we tested the effect of ultrasounds on the structure of several P3HT films bearing different thicknesses, from 50 to 200 nm,and degrees of crystallinity, which were varied by thermally annealing the samples at different temperatures.

Status and progress of evaluation

GIXRD data are currently under treatment to understand the dependence of the ultrasound-induced crystal growth on the degree of crystallinity and thickness. This would help to understand the origin of the phaenomenon and to better correlate it to the already observed ultrasound-induced conductivity increase.

Finally, we wish to acknowledge the very precious and prompt support of our local contact, Dr Linus Pithan.