EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** "In situ" monitoring of Laser Induced Periodic Surface Structures on conjugated polymers of interest in Organic Photovoltaics.	**Experiment number**: SC-3977
Beamline:	**Date of experiment**: from: 21/11/2014 to: 25/11/2014	**Date of report**: 16/02/2015
Shifts: 12	**Local contact(s)**: Giuseppe Portale (email: portale@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Marta Castillejo, Instituto de Química Física Rocasolano(IQFR-CSIC)[1]
Esther Rebollar*, Instituto de Química Física Rocasolano(IQFR-CSIC)[1]
Mari-Cruz García-Gutiérrez*, Instituto de Estructura de la Materia (IEM-CSIC)[2]
Álvaro Rodríguez-Rodríguez*, Instituto de Estructura de la Materia (IEM-CSIC)[2]
Tiberio A. Ezquerra*, Instituto de Estructura de la Materia (IEM-CSIC)[2]
Daniel R. Rueda*, Instituto de Estructura de la Materia (IEM-CSIC)[2]
[1]Serrano 119, Madrid 28006, Spain
[2]Serrano 121, Madrid 28006, Spain.

Report:

Report Summary:

The aim of this proposal was to exploit the possibility of monitoring "in situ" by Grazing Incidence X-ray Scattering at small (GISAXS) and wide (GIWAXS) angles the nanostructuring of thin conjugated polymer films, relevant in Organic Photovoltaics(OPV), by means of Laser Induced Periodic Surface Structures (LIPSS).

Scientific background:

Organic electronics provide an opportunity for low-cost, large area electronics in diverse applications such as displays, sensors, solid-state lighting, and photovoltaic cells [1]. The critical performance of organic electronic materials is closely related to their morphology and molecular packing. The typical microstructure for a semicrystalline semiconducting polymer would be nanoscale crystalline domains bounded by highly disordered amorphous regions with some molecules bridging neighbouring ordered domains. The details of the microstructure are important because the local packing of neighbouring molecules determines the intermolecular electronic orbital overlap and the electronic structure of the polymer film. In addition, the connectivity of the domains determine the paths taken by charge carriers through the material. All of these physical properties combine to determine the key electronic property that affects the performance of organic electronic devices through the charge carrier mobility of the polymer.

Laser induced patterning of polymer surfaces is a versatile strategy in order to obtain functional polymer materials. Irradiation of solid surfaces by intense laser pulses may induce the appearance of Laser Induced Periodic Surface Structures (LIPSS) with periodicities closely related to the laser wavelength [2]. In order to assess order in LIPSS on thin polymer films we have proven in a previous proposal (report SC-3478) that GISAXS can be very useful to characterize polymer LIPSS formation in real time[3].

Experimental:

We carried out X-ray scattering experiments on thin polymer films in grazing incidence geometry in the beamline BM26B at ESRF. For GISAXS and GIWAXS experiments, incidence angles $0.2° < \alpha_i < 0.4°$ were chosen depending on the nature of the formed nanostructure. Polymer samples were irradiated "in situ" at normal incidence. Laser irradiation was carried out in ambient air conditions at two different wavelengths with the fourth (266 nm) and second harmonic (532 nm) of a nanosecond laser (Nd:YAG, Lotis TII LS-2131M) with a linearly polarized beam at different fluences. In every experiment pulses of 8 ns were sent to the sample at the selected repetion rates of 2, 5 and10 Hz. The laser beam was directed with the necessary optical elements towards the sample surface with a polarization direction parallel to that of the incident X-ray beam. Simultaneously GISAXS detection was accomplished using an X-ray wavelength of $\lambda = 0.103$ nm (12 KeV), with a beam size (HxV) of 1.1x0.5 mm^2. Scattered intensity was recorded by a PILATUS detector at a sample-to-detector distance of 3.948 m for GISAXS. For GIWAXS, a FRELON detector located 0.1055 m far from the sample was used. Acquisition times were optimized in order to get maximum number of counts avoiding saturation of the detector. In the present case, typical acquisition times of 5 to 30 s were used. A scheme of the experimental set-up is shown in Fig.1.

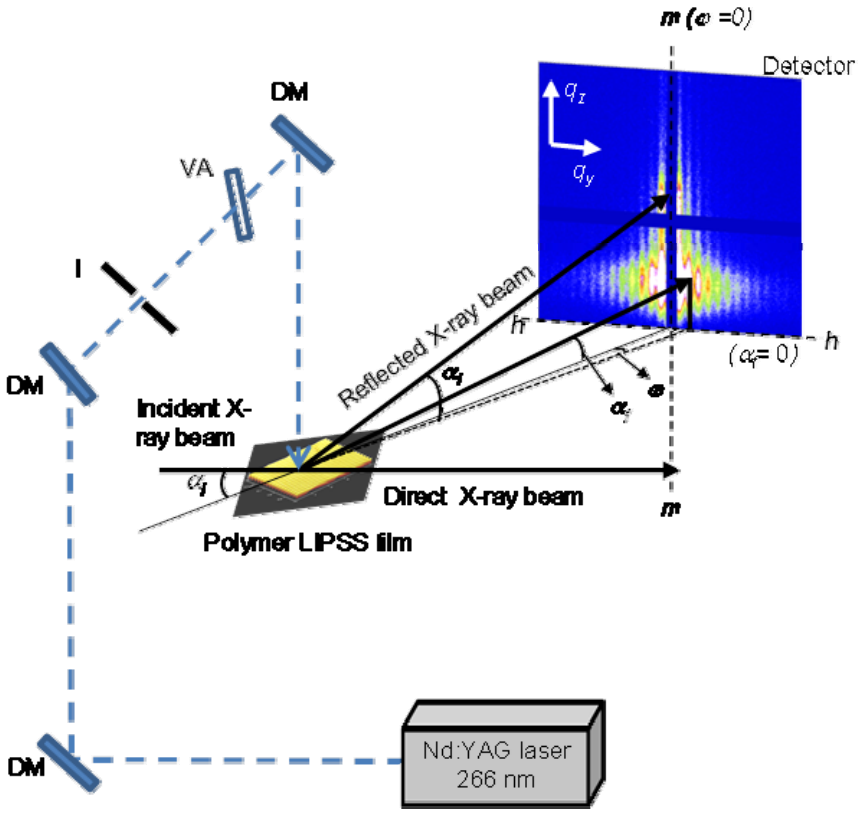

Fig. 1. Scheme of the experimental set-up for in situ LIPSS formation as revealed by Grazing incidence X-ray scattering measurements[3]. The laser beam (blue dashed line) is directed by a set of three dichroic mirrors (DM) to the sample surface so that it impinges on the sample at normal incidence. The laser beam size is controlled by an iris (I) and its intensity by a variable attenuator (VA). The X-ray beam (black line) reaches the sample which is positioned in grazing incidence conditions.

Results and Discussion:

Several conjugated polymers were investigated including: Poly(3-hexylthiophene)(P3HT) (Ossila, Mw=34100 g/mol, PDI= 1.7; regioregularity= 94.7%),Poly[N-9'-heptadecanyl-2,7-arbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3' benzothiadiazole)] (PCDTBT) (Ossila, Mw= 35400 g/mol, PDI= 2.4) and the 50/50 in weight blends of both polymers. Samples were prepared as thin films ≈ 150 nm thickness by spin-coating on silicon wafer substrates from chlorobenzene solutions. As an example, Fig.2 shows a typical series of GIWAXS patterns taken "in situ" during laser irradiation of a P3HT thin film with a fluence of 26 mJ/cm^2 as a function of the number of laser pulses.

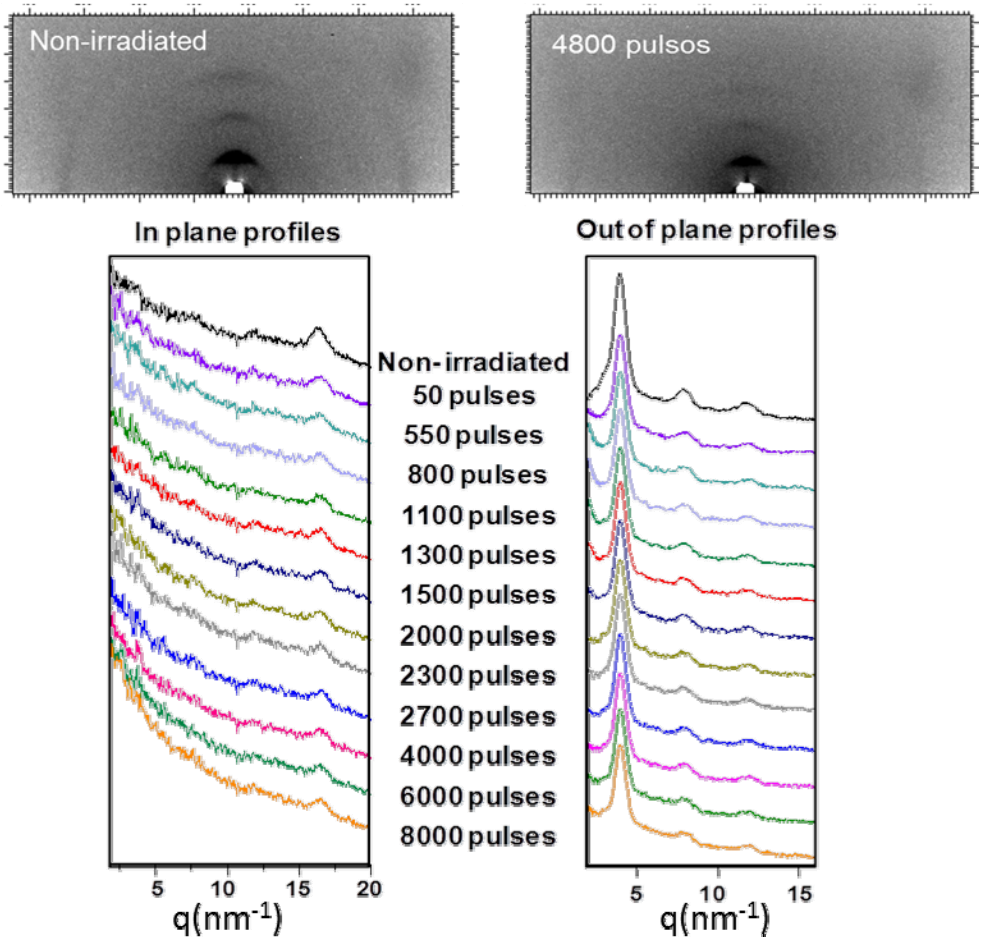

Fig. 2. (Upper panel) 2-D GIWAXS patterns of P3HT before and after irradiation with 4800 laser pulses at 26 mJ/cm^2. (Lower pannel) In situ GIWAXS patterns obtained during laser irradiation at 26 mJ/cm^2 of a P3HT thin film at different number of pulses. In plane (left) out of plane(right).

In Fig. 2 we show the one dimensional diffraction patterns extracted from the 2-D GIWAXS patterns along the parallel (q_y) and perpendicular (q_z) directions, as a function of the number of pulses. The main result is that the crystalline structure is not significantly affected during LIPSS formation. This effect further support the chemical stability of P3HT during LIPSS formation observed by Raman spectroscopy and Near Edge X-ray Absortion Fine Structure (NEXAFS). A close inspection of the diffraction patterns reveals that the intensity of both the 100 and the 020 peaks in comparison with those of the pristine sample decreases for 50 pulses and remain essentially constant for the rest of the irradiation process. LIPSS formation in polymers proceeds by heating of the polymer surface enhancing polymer dynamics in order to

reorganize into the characteristic ripples[2,3]. The GIWAXS results suggest that for P3HT, irradiation with a sufficient number of pulses leads to the melting of the polymer superficial layer. Moreover, comparison of initial and final GIWAXS patterns indicates a decrease in the crystallinity of LIPSS in relation to the initial thin film, as revealed by the reduction of the intensity of the crystalline reflections. This explanation is in agreement with an observed increment of the amorphous phase observed by Raman spectroscopy. Moreover, by comparison with the Current image AFM (C-AFM) results (Fig.3), the GIWAXS results support that in P3HT LIPSS formation produces ridges with lower molecular order than that of the original thin film. The ridges are over a continuous P3HT thin film whose initial crystallinity seems to be unaffected. As a consequence, electrical conduction in the ridges is smaller than in the trenches (Fig. 3).

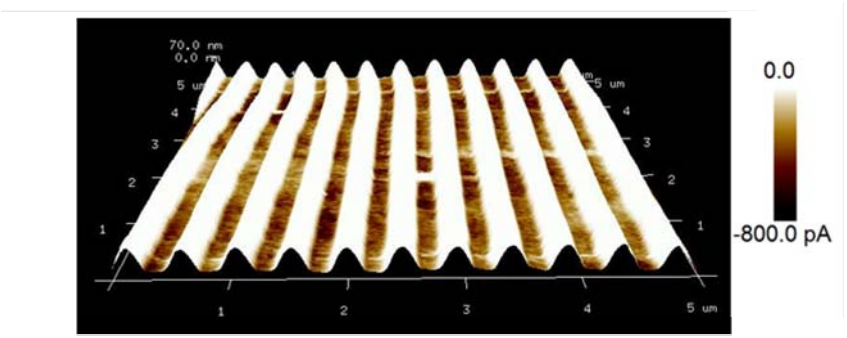

Figure 3. Overlapped AFM height image (contact mode) and C-AFM measured at constant bias of -5 V for a LIPSS of P3HT.

References

[1] Brabec C.J., Gowrisanker S., Halls J.M., et al., Adv. Mater. 2010, 22, 3839.
[2] E. Rebollar, J.R. Vázquez de Aldana, J. Pérez-Hernández, T.A. Ezquerra, P. Moreno, M. Castillejo,Appl. Phys. Lett. 100, 041106, 2012.
[3] E. Rebollar, D. R. Rueda, I. Martín-Fabiani, A. Rodríguez-Rodríguez, M.C. García-Gutiérrez, G. Portale, M. Castillejo, T. A. Ezquerra. Lagmuir (submitted).