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.

<table>
<tr><td>ESRF</td><td>Experiment title: Fine crystalline structure of fullerene nanowires prepared by Laser Induced Periodic Surface Structures (LIPSS) as revealed by GIWAXS.</td><td>Experiment number:
SC 4521</td></tr>
<tr><td>Beamline:</td><td>Date of experiment:
from: 3 Jul 2017 to: 7 Jul 2017</td><td rowspan="2">Date of report:
11/01/2018
Received at ESRF:</td></tr>
<tr><td>Shifts:</td><td>Local contact(s):
Daniel Hermida (email: hermidam@esrf.fr)</td></tr>
<tr><td colspan="3">Names and affiliations of applicants (* indicates experimentalists):
Dr. Tiberio Ezquerra*
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</table>

Report:

Summary:

The aim of the experiment is to investigate by Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) the crystallinity of [6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) nanostructures prepared by Laser Induced Periodic Surface Structures (LIPSS) with a post-solvent treatment. It was seen by Atomic Force Microscopy(AFM) that LIPSS spontaneously appear on spin-coated films of $PC_{71}BM$ 100 nm thick after adequate fluence and number of pulses at a laser wavelength of 532 nm. The energy profile of the laser beam produces a spot with different chemical products along the illuminated area. After a washing process performed by spin-coating chlorobenzene on the samples an insoluble LIPSS area remains which exhibits zones with different morphology. In some of them it is revealed the presence of nanocrystals 20-40 nm size. These nanocrystals are of semiconducting nature as revealed by C-AFM measurements. Preliminary GIWAXS measurements performed in the center of an irradiated area suggest the formation of a graphene oxide phase by laser irradiation. The elucidation of the crystalline phases in different zones of the irradiated LIPSS area by GIWAXS is expected to help to understand the physical and chemical processes involved during the laser illumination as well as the solvent treatment process.

Scientific background:

Laser induced patterning of organic surfaces is a versatile strategy in order to produce functional materials. The formation of Laser Induced Periodic Surface Structures (LIPSS) is a spontaneous phenomenon which may occur by illumination of solid surfaces by intense either nanosecond or femtosecond laser pulses[1]. The structures consist of ripples whose

periodicities are closely related to the wavelength of the irradiating laser. Among organic materials both, semiconducting polymers and fullerenes have attracted much attention due to their potential applications in optics, electronics and photovoltaics among others [2]. Nanostructuring by laser of semiconducting polymers has been recently accomplished by us rendering to functional surfaces of selective electrical conductivity[3]. At nanometer scale, ordering of fullerenes typically implies bottom-up strategies involving a template surface[4]. We are currently investigating a one-step top-down laser-induced method based on LIPSS capable of nanostructuring fullerene materials. We have proven the possibility of producing nanostructured functional surfaces on spin-coated $PC_{71}BM$ films.

Experimental:

The scattering experiments were carried out at the BM26 beamline of the European Synchrotron Radiation Facility (ESRF) sited in Grenoble (France). A standard GISAXS configuration was used[3]. A longitudinal beamstop was used. An X-ray wavelength of λ = 0.103 nm, was used in our experiments. The scattered intensity was recorded by a two-dimensional (2D) Frelong detector ((2048x2048 pixels, pixel size=46.8 μm) with a camera of 981x1043 pixels (size of the pixel 172x172 μm^2) and a sample-to-detector distance of 121.93mm . Different incidence angles of the beam of between α_i = 0.1º and 0.4º were chosen. The treatment of the GISAXS images was performed using the software FIT2D.

Results and Discussion:

GIWAXS measurements were carried on thin films, ≈100 nm thick, of $PC_{71}BM$ spin-coated from chlorobenzene solutions (40mg/ml) . The films were laser irradiated in air at normal incidence at λ_{laser}=532 nm (Nd-YAG) with an iris of 1.2 mm in diameter and at seven fluences in this range: 13.6–24.4 mJ/cm^2.

Figure 1a shows an optical micrography of the fingerprint let by the laser after irradiation with 3600 pulses at a fluence of F=17.2mJ/cm^2 . Figure 1b and 1c show AFM topographic images in the indicated positions of the spot showing the characteristic grating like morphology obtained by LIPSS as previously described in other materials[1-3]. After washing this sample with chlorobenzene part of the laser spot seems to disappear (Fig.1d). However close inspection by AFM reveals the presence of characteristic nanowires (Fig.1e and 1f) reminiscence of the previous LIPSS in the unwashed sample.

Figure 2 shows GIWAXS patterns of an spin-coated $PC_{71}BM$ sample. The pattern exhibit the characteristic features of low crystallinity $PC_{71}BM$[5]. After laser irradiation (3600 pulses, F=17.2mJ/cm^2) the most striking effect is the appearance of a new ring (indicated by arrows in Fig.2b), with the characteristic spots produced by a dispersion of single crystals. We propose that heating during laser irradiation can produce a melting and recrystallization of $PC_{71}BM$. After washing with chlorobenzene although weak one detects the single crystal ring. We speculate about the possibility that laser irradiation provokes the formation of $PC_{71}BM$ single crystals, responsible for the dotted ring (Fig. 2b). Some of this single crystal phase seems to remain after washing contributing to the observed dotted ring. By comparison with the AFM data we can, in a first approach, attribute this single crystal phase to the tiny dots observed in the nanowires (Fig. 1f). This explanation is being corroborated by Raman spectroscopy experiment and by Conducting AFM. A paper is being prepared.

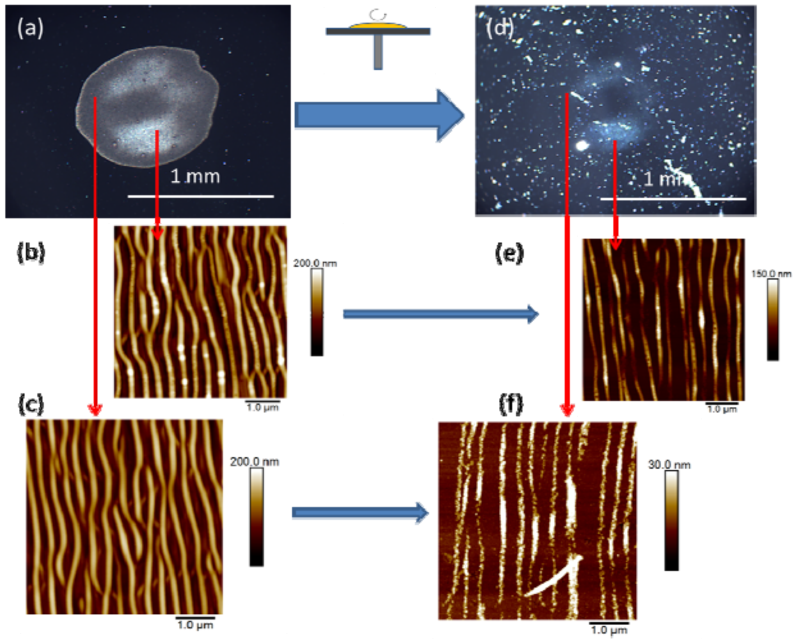

Figure 1. (a) Optical micrography of the fingerprint let by the laser after irradiation λ=532 nm on spin-coated $PC_{71}BM$ with 3600 pulses at a fluence of $F=17.2 mJ/cm^2$.(b and c) AFM topographic images in the indicated positions. (d) Optical micrography of the laser fingerprint after washing with chlorobenzene.(e and f) AFM topographic images of the washed sample at the selected positions.

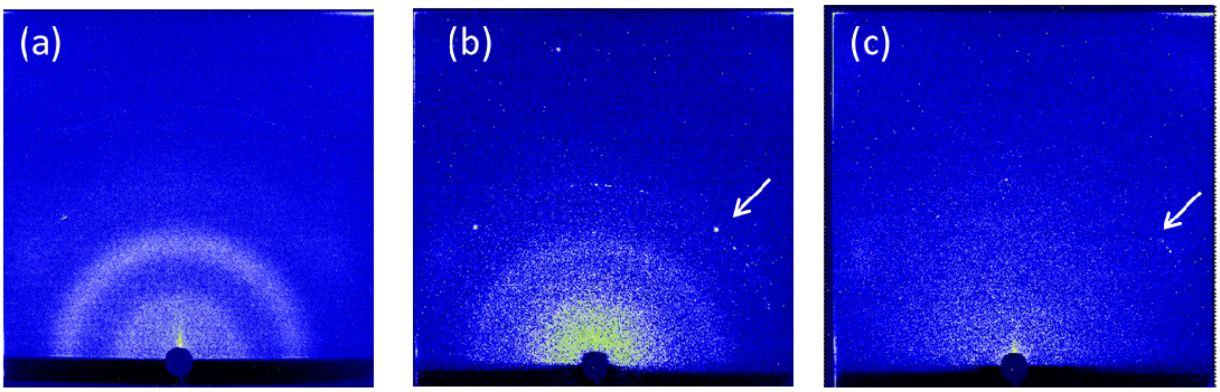

Figure 2. GIWAXS pattern of: (a) a spin-coated $PC_{71}BM$ sample, (b) of the same sample after irradiation at λ=532 nm with 3600 pulses at a fluence of $F=17.2 mJ/cm^2$ and (c) of the chlorobenzene washed sample. The arrows indicate the new dotted ring appearing upon irradidiation.

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[4] Sanchez, L.; Otero, R.; Maria Gallego, J.; Miranda, R.; Martin, N. Chemical Reviews 2009, 109, 2081. (29)
[5] Staniec, P. A.; Parnell, A. J.; Dunbar, A. D. F.; Yi, H.; Pearson, A. J.; Wang, T.; Hopkinson, P. E.; Kinane, C.; Dalgliesh, R. M.; Donald, A. M.; Ryan, A. J.; Iraqi, A.; Jones, R. A. L.; Lidzey, D. G. Advanced Energy Materials 2011, 1, 499.