

## 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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

### ***Reports supporting requests for additional beam time***

Reports can now 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.



	<b>Experiment title:</b> Grazing incidence SAXS-WAXS of polymer photovoltaics	<b>Experiment number:</b> <b>28-01-857</b>
<b>Beamline:</b> BM28	<b>Date of experiment:</b> from: 13 May 2009 to: 19 May 2009	<b>Date of report:</b> 6 Nov 2009
<b>Shifts:</b> 18	<b>Local contact(s):</b> Paul Thompson	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists):  <b>J E Macdonald*</b> , <b>S Lilliu*</b> , <b>M Hampton*</b>  School of Physics and Astronomy, Cardiff University, 5 The Parade, Cardiff CF24 3YB, UK  <b>J Nelson and T Agostinelli*</b>  Department of Physics, Imperial College, London SW7 2AZ, UK		

## Report:

Organic photovoltaic (PV) devices promise considerable benefits over their Si-based counterparts due to the potential capability for cheap, large area processing on flexible substrates. Their efficiencies have increased dramatically over recent years. Most organic PV devices are based on thin films comprising an electron accepting component (such as a fullerene derivative) and an electron donating component (usually a conjugated polymer) between two electronically different electrodes. Efficient conversion of absorbed photons into photocurrent relies upon sufficiently intimate mixing of the two components, so that photo-generated excitons are capable of diffusing to an interface where charge separation can occur, and on the existence of continuous networks of each component, so that separated charges can be conducted to the electrodes. For most efficient operation, a certain degree of phase separation is required: larger domains reduce the rate of interfacial charge recombination and enable more ordered molecular packing within the domains, leading to enhanced charge mobilities. In addition, vertical segregation of components so that, e.g., the electron acceptor is concentrated near the electron collecting electrode, is expected to enhance the efficiency of charge collection.

The primary aim of the experiment was to perform GI-WAXS studies of thermal annealing in blends of regioregular poly-3-hexylthiophene (P3HT) with the methanofullerene, phenyl C<sub>61</sub> butyric acid ester (PCBM). This is the material system that has produced some of the highest power conversion efficiencies (around 5-6%) and the most studied. A wide range of experimental studies have demonstrated that variations in polymer regioregularity, blend film composition, solvent, deposition conditions, and post deposition treatments such as thermal and vapour annealing lead to variations in organic photovoltaic device performance, apparently as a result of variations in blend film morphology [2-7]. A second aim was to investigate the feasibility of GI-SAXS during in-situ annealing to follow the morphology changes to complement the GI-WAXS study of crystallisation.

GI-WAXS studies were successfully performed during in-situ annealing of P3HT/PCBM blends for 30%, 50% and 70% PCBM. Considerable care was taken in optimising the PID settings, thermocouple calibration both for the sample surface and the heater and in suppressing any background scattering. Samples were heated rapidly to the anneal temperature 140°C with an overshoot of 0.5°C, rapidly achieving stability of better than

0.1°C. Images were taken with the MAR detector with acquisition times of 10 sec (and 5 sec readout) continuously during the conventional anneal time of 30 minutes. Surprisingly, the significant crystallisation occurred in the first 3 minutes, with little change thereafter (Fig. 1). Peak fitting showed that the main change during the early stages of the anneal involve crystallisation of P3HT (fig 2).

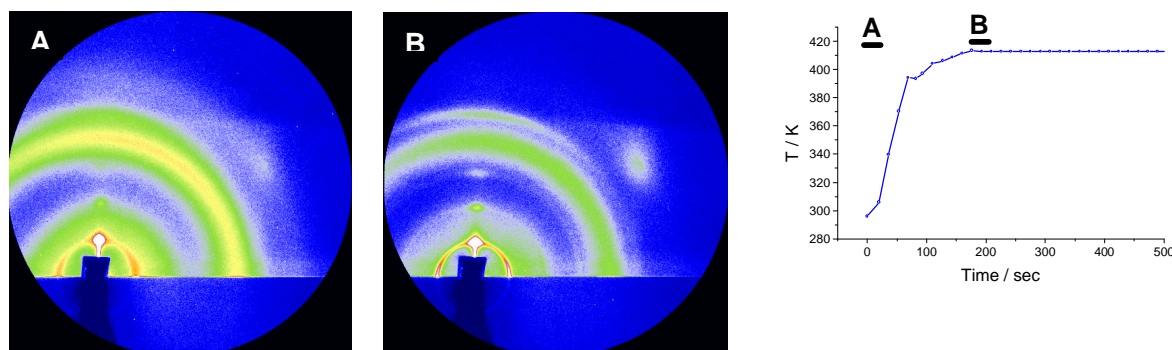


Fig.1 GI-WAXS from P3HT:PCBM (50%) at the start of the anneal (A) and after 180 seconds (B), as indicated on the temperature profile during the anneal. Each image is of 10 seconds acquisition time. The peaks are labelled for B, with Miller indices referring to P3HT crystalline peaks.

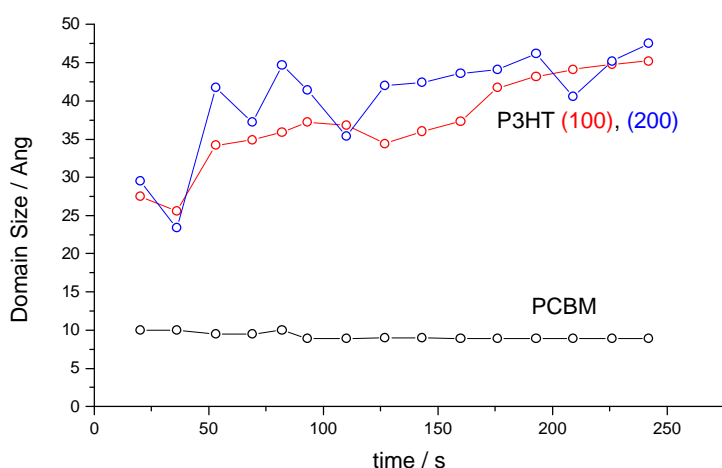


Fig. 2 Domain sizes for P3HT and PCBM as a function of anneal time during the first four minutes of annealing.

There is limited evidence that the most dramatic increases in device efficiency also occur during the first few minutes of the anneal. We are currently performing more extensive device studies to determine the inter-relationship of device performance and crystallisation. Data analysis for the GI-WAXS is now almost complete and we have started writing a draft paper for submission in December or January.

We also spent a day setting up and testing in-situ GI-SAXS measurements. The results showed very little change during the thermal anneal. We have since discussed with M. Toney, who have unpublished data on GI-SAXS from P3HT/PCBM blends. He confirmed that they also observed little change in the GI-SAXS on annealing. As a consequence, we are intending to concentrate on GI-WAXS in coming experiments on photovoltaic blends.

## References

- [1] A.C. Mayer et al, *Materials Today* 10, 28 (2007)
- [2] F. Padinger et al., *Adv. Funct. Mater.* 13, 85 (2003)
- [3] Y. Kim et al., *J. Mater. Sci.* 40, 1371 (2005)
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- [6] G. Li, *J. Appl. Phys.* 98, 043704 (2005)
- [7] Y. Kim et al., *Appl. Phys. Lett.* 86, 063502 (2005)