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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 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.

ESRF	**Experiment title:** Crystallisation kinetics at a buried polymer interface	**Experiment number:** 28 01 746
Beamline: BM28	**Date of experiment:** from: 10 May 2006 to: 16 May 2006	**Date of report:** 2 Sept 2008
Shifts: 18	**Local contact(s):** Dr. Simon Brown	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

J E Macdonald*, A Das*, H Thomas*, H Simmonds*

School of Physics and Astronomy, Cardiff University, 5 The Parade, Cardiff CF24 3YB, UK

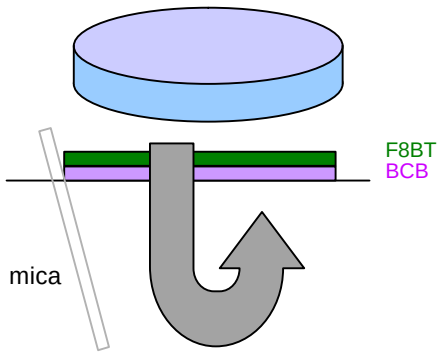
H Sirringhaus

Optoelectronics Group, Cavendish Laboratory, J J Thomson Avenue, Cambridge CB3 0HE, UK

Report:

A fundamental understanding of the influence of free surfaces and buried interfaces on the properties of thin polymer films is important in many applications. Near interfacial boundaries, surface and interface effects may lead to physical properties that significantly differ from those in the bulk, such as the chain conformation, chain dynamics and the demixing of multicomponent blends. A combination of surface- and finite-size effects may also influence the character and location of the crystallisation and glass transitions. Crystallisation at the surface of a semi-crystalline polymer thin film may be affected by both changes in chain conformation near the surface, and by differences in chain dynamics between surface and bulk. Two material systems were studied in this experiment: the poly(ethylene terephthalate) (PET)-polystyrene (PS) interface and the poly(9,9-di- n-octylfluorene- alt-benzothiadiazole) (F8BT) - divinyltetramethylsiloxane-bis(benzocyclobutene) (BCB) interface. This latter interface is a key system for n-type conduction in organic field-effect transistor (FET) structures, with relatively good electron mobilities [1].

PET-PS could be spin-coated directly onto silicon substrates: PET was first spin-coated from a ortho-chlorophenol solution, followed by PS coating from a toluene solution, since PET does not dissolve in toluene. However, such an approach could not be employed for F8BT-BCB since there are no such suitable orthogonal solvents. The BCB dielectric is deposited onto silicon and is cross-linked by rapid thermal annealing at 290°C for 15 seconds prior to spin-coating of the semiconducting polymer. However, the electron density of the upper semiconductor layer is larger than that of the BCB, thus precluding depth-dependent studies of the buried interface. This was solved by preparing the BCB/F8BT structure on a mica substrate and then gently translating the mica downwards, at a shallow angle, through the surface of clean deionised water to float the polymer layers onto the water surface. These were then transferred onto a Si/SiO_2 substrate by bringing the



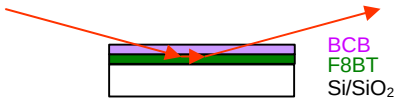


Fig. 1 (a) Depositing the bilayer onto silicon by flotation from a mica substrate (b) Diffraction from the interface for α_c (BCB) < α_c (F8BT)

substrate vertically downward onto the floating film giving a Si / SiO_2 / 50nm F8BT / 30nm BCB structure (fig. 1).

Depth-resolved diffraction was performed by taking area detector images for a range of incident angles α covering the three critical angles for BCB, F8BT and SiO_2. Fig. 2 shows the diffraction pattern from a sample annealed at 300°C followed by a slow cool to 200°C and sections through the images for a range of critical angles. The F8BT peaks can be seen to develop with increasing α. Sharp peaks from mica are also observed from the surface, whose integrated intensity is significantly weaker than for the F8BT. The sharpness of these mica peaks indicate that there are very small localised traces of mica on the BCB surface arising from the flotation process, which could not be seen visually and that were not detected in AFM scans. The F8BT peaks do not correspond to the only reported unit cell parameters for crystalline F8BT (monoclinic cell with a = 14.65 Å, b = 5.3 Å, c = 16.7 Å, c-axis at 98° to the a-b plane [2]). Our peaks indicate a c-axis which is a factor of 2 greater than this published value and a different crystalline arrangement in our samples. Refraction from the buried F8BT-BCB interface could not be clearly observed, indicating a rather diffuse interface. Reflectivity scans to probe the diffuseness of the interface were inconclusive, fitting being complicated by the mica traces on the top surface. As a result it was difficult to draw definitive conclusions regarding the gate dielectric-semiconductor interface from this challenging experiment.

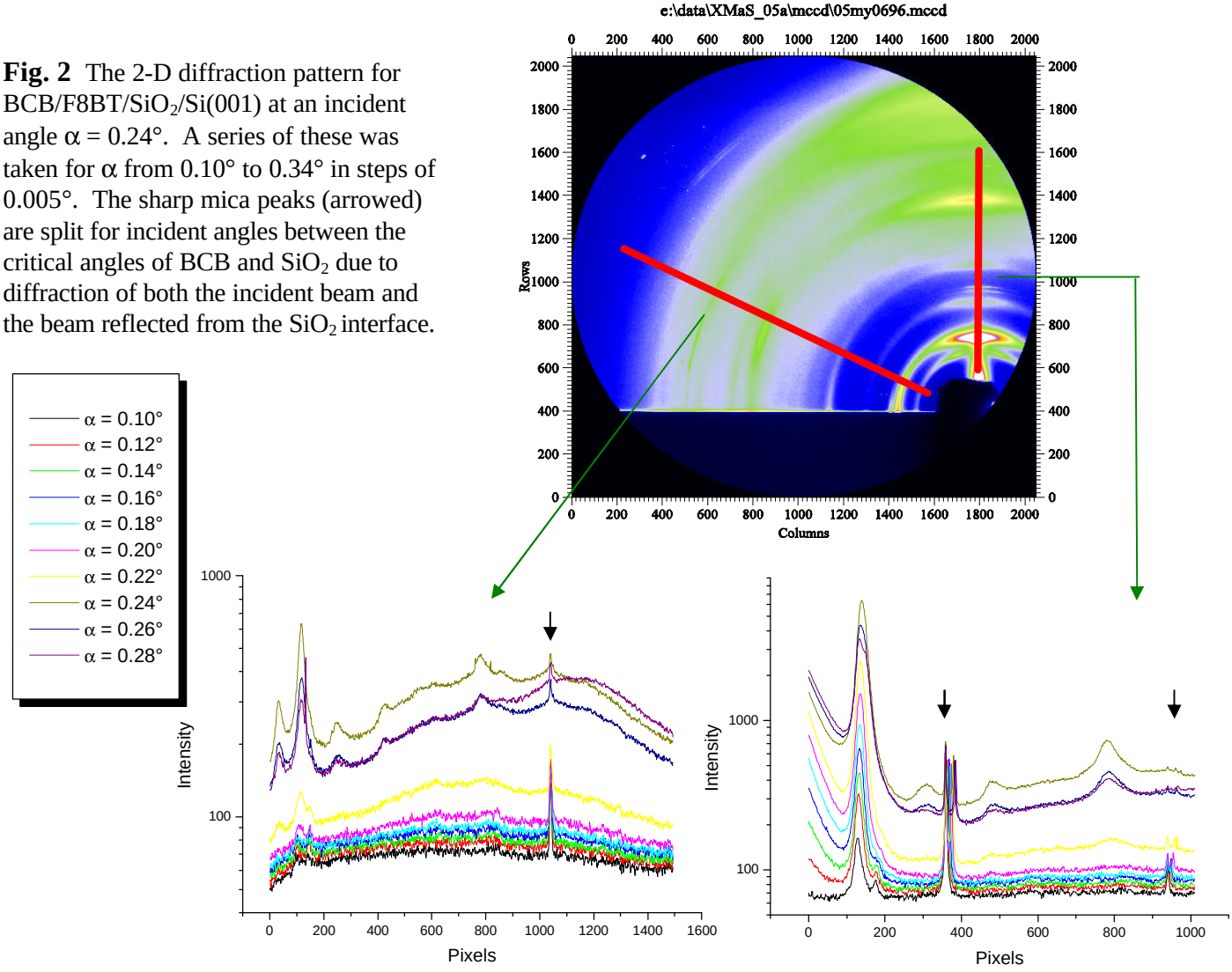


Fig. 2 The 2-D diffraction pattern for BCB/F8BT/SiO_2/Si(001) at an incident angle α = 0.24°. A series of these was taken for α from 0.10° to 0.34° in steps of 0.005°. The sharp mica peaks (arrowed) are split for incident angles between the critical angles of BCB and SiO_2 due to diffraction of both the incident beam and the beam reflected from the SiO_2 interface.

References

[1] L-L Chua, J Zaumseil, J-F Chang, E C-W Ou, P K-H Ho, H Sirringhaus and R H Friend, Nature 434 (2005) 194-199

[2] C.L. Donley et al, J Am Chem Soc 125 (2005) 12890-12899