（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。 ）

MLF Experimental Report	提出日 Date of Report 20^{th} May 2013
課題番号 Project No. 2012B0200 実験課題名 Title of experiment Diffusion Kinetics in Organic Solar Cells 実験責任者名 Name of principal investigator Prof. Ian R. Gentle 所属 Affiliation The University of Queensland, AUSTRALIA	装置責任者 Name of responsible person Norifumi YAMADA 装置名 Name of Instrument/（BL No.） BL16 実施日 Date of Experiment 8^{th} Feb 2013 – 13^{th} Feb 2013

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

The following chemicals were used during our experiments at BL 16 SOFIA in the MLF:

PCDTBT – poly[N-9’’-hepta-decanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole] $(C_{43}H_{47}N_3S_3)_n(C_6H_5)_2$

P3HT – poly(3-*n*-hexylthiophene) $(C_{10}H_{16}S)_n$

60-PCBM – [6,6]-phenyl C_{61} butyric acid methyl ester ($C_{72}H_{14}O_2$)

70-PCBM – [6,6]-phenyl C_{71} butyric acid methyl ester ($C_{82}H_{14}O_2$)

ICBA – indenyl C_{60} bis adduct ($C_{78}H_{16}$)

TAPC – 1,1-bis-(4-bis(4-methyl-phenyl)-amino-phenyl)-cyclohexane ($C_{46}H_{46}N_2$)

MoO_x – sublimed molybdenum oxide thin films

ZnS – sublimed zinc sulfide thin films

Ag – sublimed silver thin films

ZnO – sublimed zinc oxide thin films

Samples were prepared on silicon wafers. Organic thin films were prepared with various combinations of materials by spin casting from solution: PCDTBT/60-PCBM, PCDTBT/70-PCBM, PCDTBT/ICBA, P3HT/60-PCBM, P3HT/ICBA. The inorganics were deposited by thermal evaporation as stacks of MoO_x/Ag/MoO_x and MoO_x/Ag/ZnS on silicon and MoO_x was also deposited on top of the organic layers P3HT/60-PCBM and PCDTBT/70-PCBM.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

The aim of this experiment was to investigate the evolution in vertical film structures employed in organic photovoltaic cells due to interdiffusion of the active components under annealing. The first part of the investigation focussed on combining the amorphous polymer PCDTBT with the fullerenes 60- and 70-PCBM under a variety of deposition conditions. Bilayer structures were formed by depositing the PCBM phase onto PCDTBT films in a variety of solvents. The change in vertical phase structure under annealing was then examined initially using SOFIA in single-frame mode and annealing the samples outside of the beamline. Time-resolved measurements were performed with the reflectometer in double-frame mode and the samples annealed *in situ*. Samples were prepared under three sets of deposition conditions with 60- and 70-PCBM. The films formed using 70-PCBM were found to be rougher and gave poor reflectivity profiles unless an additional cosolvent was used in its deposition. The films formed with 60-PCBM gave more intense reflections and modeling of the neutron data revealed diffusion of the overlying PCBM phase into the polymer rich layer upon annealing (Figure 1). The processing of the data collected is nearing completion and a manuscript is being drafted that will include the corresponding solar cell device data.

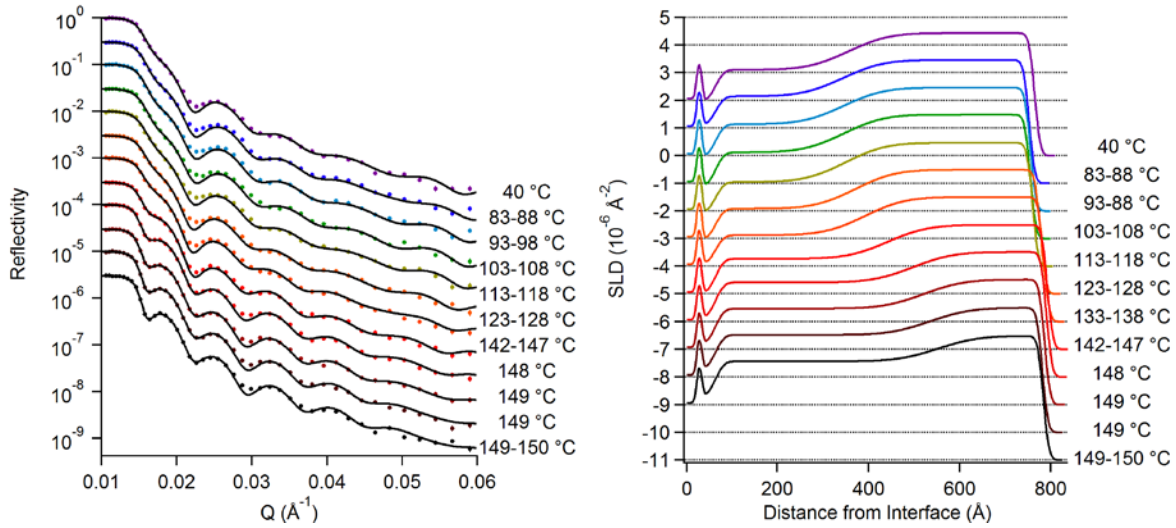

Figure 1 Time-resolved reflectivity data and model SLD *vs* thickness for PCDTBT/60-PCBM bilayer as the annealing temperature was increased from 40 to 150 degrees C

The second part of this study focused on the influence of metal oxide/sulfide thin films commonly employed to improve solar cell efficiency on the vertical phase profile of the underlying organic layers. Initially the behavior of MoO_x/Ag/MoO_x and MoO_x/Ag/ZnS stacks used as charge collection layers in organic photovoltaics was investigated and then the behavior of P3HT/60-PCBM and PCDTBT/70-PCBM organic layers underneath MoO_x was tested. Again steady-state reflectometry was used to elucidate any changes occurring upon annealing and then time-resolved reflectometry was used to monitor the changes occurring *in* situ under heating. Modelling of the data collected is proceeding and initial observations indicate that the thickness and scattering length density of the MoO_x layers change upon annealing in a manner consistent with densification of the MoO_x layers (Figure 2).

2. 実験方法及び結果（つづき） Experimental method and results (continued)

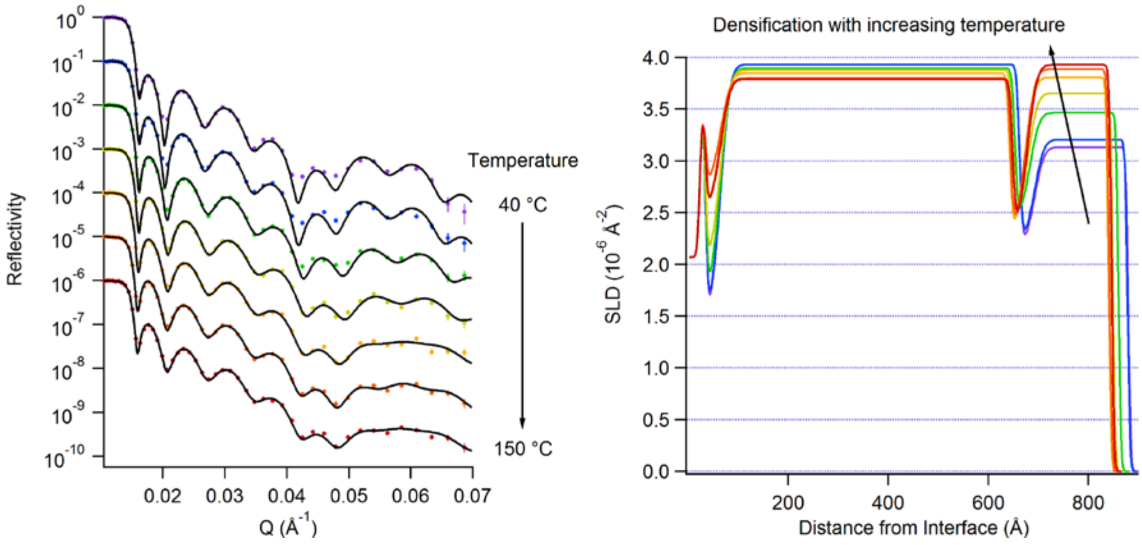

Figure 2 Time resolved neutron reflectivity profiles and model SLD *vs* Thickness plots for a MoO_x thin film atop a PCDTBT/70-PCBM blend layer upon thermal annealing.

Modelling of this data is ongoing and we hope to publish a manuscript in the near future based on the behavior of inorganic/organic interfaces used in plastic solar calls under thermal load.

The final aim of the work was to determine if using a processing additive or a new fullerene acceptor ICBA in thin films with P3HT and PCDTBT yielded any vertical phase separation in the resulting films. The data collected for the P3HT films was of poor quality and it was found that coating the large area silicon substrates under the same conditions as used in solar cell manufacture led to the films being uneven across the area examined. As a result the only data modelled was for a PCDTBT/ICBA blend film that gave a reflectivity profile consistent with a single layer of uniform SLD.

All samples brought to J-PARC were tested as planned, a full complement of steady-state reflectivity data was initially collected to ascertain which films were susceptible to morphology changes on annealing. Time-resolved reflectivity data was collected on all samples exhibiting a change in their reflectivity profiles upon thermal annealing providing a wealth of data relating to the dynamic properties of these systems at elevated temperatures.