

Scientific background and results of preliminary work

Solar cells provide energy sustainably, with a low carbon footprint, and in 2007 the industry had a market value of over \$10 billion [1]. Although solar cells currently contribute less than 0.1% to the global electricity supply, the industry has an annual growth rate of 30-40% [1] and this, coupled with the vast magnitude of the global solar resource, should ensure that solar cells make an ever-increasing contribution to global energy needs. While solar cells based on inorganic materials such as Si are well known, the past decade has seen increasing interest in solar cells in which the photoactive constituents are organic semiconductors. These organic photovoltaics (OPVs) are an exciting prospect for harvesting solar energy, due to their many beneficial features such as mechanical flexibility, extremely light weight, and compatibility with low cost manufacturing routes (e.g. printing).

OPVs fall into two distinct classes: (i) those based on polymeric materials, which generally can be processed by solution, and (ii) those utilising discrete small-molecule organic semiconductors, which can sometimes be processable both by solution and evaporation. Solution-processable materials have the greatest commercial potential in relation to low cost printing technologies. On the other hand, evaporative processing offers more controlled deposition and is more technologically advanced due to its key role in the development of inorganic PV devices.

Small molecule-based OPVs are a key research focus currently. One small-molecule organic semiconductor that has been shown to function well in OPVs is 7,14-bis((triisopropylsilyl)ethynyl)dibenzo[b,def]chrysene (TIPS-DBC, Figure 1) [2]. Importantly, this compound can be processed both by solution and by thermal evaporation in vacuum. TIPS-DBC is therefore an ideal candidate for studying the differences between OPVs fabricated using the two processing methods.

Typical TIPS-DBC devices are shown in Figure 2. They consist of: (i) a transparent conducting substrate (glass/ITO), (ii) a polymeric hole conducting layer (PEDOT:PSS), (iii) the TIPS-DBC photo-active electron donor layer deposited either via spin-coating or evaporation (30 nm), (iv) an evaporated C60 electron acceptor layer (30 nm), (v) an evaporated exciton blocking layer (BCP) and (vi) electrode materials (e.g. 20 nm Ca followed by 100 nm Al). A bulk heterojunction (BHJ) device can also be fabricated, in which the TIPS-DBC/C60 bilayer is substituted with a spin-coated 1:1 blend of TIPS-DBC and C60.

Our results to date indicate that TIPS-DBC/C60 devices perform differently depending on the method by which they are prepared. Bilayer devices in which TIPS-DBC is evaporated exhibit efficiencies around 2%, while the performance of bilayer OPVs in which TIPS-DBC is spin-coated is observed to be lower by up to one third. Interestingly, BHJ devices show similar performance to evaporated bilayer devices, despite their different thin film structure. It is important to understand the correlations between processing conditions, structure and performance (e.g. efficiency and longevity) of these OPVs. It has been recognised that interfacial morphology is critical to device performance, since it is the interfaces at which charge separation occurs. We have examined the surface of TIPS-DBC layers by AFM (Figure 3) and found that spin-coated and evaporated films exhibit different surface morphologies. In addition, SEM analysis reveals more defects in the C60 layer deposited on top of spin-coated TIPS-DBC films (Figure 4).

Previous neutron and X-ray reflectivity studies have examined buried interfacial structures in polymer-, but not small molecule-, based OPV systems. Parnell et al. [3] used neutron reflectometry to study the depth-dependent composition of a polymer BHJ device, and found evidence for different layers at the film/substrate and film/air interfaces. Kiel et al. [4] studied

the same system and proposed a layer close to the film/air interface that was shown to be detrimental to device performance. Paci et al. [5] used X-ray reflectivity to investigate the same polymer blend, and was able to gain insights into ageing and degradation processes in the photoactive layer. **Simulated reflectivity** profiles (Figure 5) indicate that neutron reflectometry will be a sensitive probe of the TIPS-DBC/C60 interfacial region.

Aim of proposed experiments

The aim of these experiments is to use neutron reflectometry to examine the structure and interfacial morphology of films containing PEDOT:PSS, TIPS-DBC and/or C60 deposited on polished Si wafers, in order to better understand the differences in performance of spincoated, evaporated and BHJ OPV devices. We will also undertake X-ray reflectometry to provide complementary data and aid model fitting.

Detailed description of experiments

Samples will be deposited on polished Si wafers to provide suitable smoothness for reflectivity measurements. Half of the samples will be deposited directly onto Si, while the remainder will be deposited onto 10 nm of PEDOT:PSS on Si, since it is anticipated that the TIPS-DBC layers may deposit differently on these different substrates. TIPS-DBC layers will be either spin-coated or evaporated, and C60 layers will be evaporated on top.

Deposited directly on Si substrates

Sample 1: 10 nm PEDOT:PSS

Sample 2: 30 nm TIPS-DBC (spin-coated)

Sample 3: 30 nm TIPS-DBC (evaporated)

Sample 4: 80 nm 1:1 TIPS-DBC/C60 (spin-coated BHJ layer)

Sample 5: 30 nm TIPS-DBC (spin-coated) + 30 nm C60

Sample 6: 30 nm TIPS-DBC (evaporated) + 30 nm C60

Deposited on 10 nm PEDOT:PSS

Sample 7: 30 nm TIPS-DBC (spin-coated)

Sample 8: 30 nm TIPS-DBC (evaporated)

Sample 9: 80 nm 1:1 TIPS-DBC/C60 (spin-coated BHJ layer)

Sample 10: 30 nm TIPS-DBC (spin-coated) + 30 nm C60

Sample 11: 30 nm TIPS-DBC (evaporated) + 30 nm C60

Platypus measurements: 11 samples, 6 hr each (including time for sample alignment).

Accounting for set-up and direct beam measurements, 5 days of beam time are requested.

X-ray reflectometry: Estimated 2 hr per sample. Allowing for set-up, 3 days are requested.

Reasons for choice of requested instrument

The molecules used in these devices have modest X-ray contrast but very good contrast in neutron SLDs without the need for deuteration (TIPS-DBC $\sim 1.2 \times 10^{-6} \text{ \AA}^{-2}$ and C60 $\sim 5.3 \times 10^{-6} \text{ \AA}^{-2}$). Neutron reflectometry is therefore ideal for probing the buried interfacial region between TIPS-DBC and C60. Although these devices are also being studied by XPS depth-profiling and TEM cross-sectional analysis, these methods may cause damage to the samples resulting in interlayer mixing and morphological changes. Hence, non-destructive analyses based on neutrons and X-rays are highly desirable as corroborating techniques.