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Helium Ion Microscopy to Study Bulk Hetero Junction Polymer Solar Cell Materials

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The helium ion microscope (HeIM) uses secondary electrons (SEs) to image surfaces, similarly to scanning electron microscopes (SEMs). However, in HeIM instead of using an electron beam, helium ions provided by a gas field ionization source [1] are used to generate SEs, with advantages described in [1]. With an estimated ultimate resolution of 0.25 nm for imaging [2] we anticipate to resolve the structures expected to be present in copolymer bulk hetero junctions used for solar cells. As it was suggested that the HeIM may cause less damage in otherwise very beam sensitive specimens such as polymers [3], the HeIM seems to be an ideal imaging tool for such polymer structures. However an initial investigation on such solar cell materials [4] did not yield much detail about their structure.

We have carried out a study on P3HT:PCBM (1:0.7) material during which we found that plasma cleaning carried out in the HeIM prior to imaging can reveal the nanostructure much more clearly. The top row in Fig. 1 contains HeIM (Zeiss Orion PlusTM) images of P3HT:PCBM (1:0.7) as spin cast (on a silicon substrate), and after annealing for 10 minutes in a nitrogen atmosphere at two different temperatures. When imaging the fresh specimens, the detailed structure is barely visible in the top row images in Fig 1, a result similar to that reported in [4]. This is despite variations in SE emission for the two pure materials as demonstrated in Fig 2. Unlike transmission electron microscopes that are commonly used for these materials but deliver a 2D projection of the 3D structure, the HeIM images are obtained only from the topmost few nanometers of the surface of the specimen. While this eliminates problems experienced in the interpretation of transmission images, most surfaces contain contamination layers. To remove such layers, plasma cleaning, generating oxygen radicals to remove hydrocarbon was employed. Images taken after plasma cleaning for 8 min (Evactron from Xei Scientific) are shown in the bottom row of Fig 1. These images reveal clear intensity differences, depending on their annealing treatment. The as-cast specimen clearly stands out through the absence of distinct large scale brightness variations found in the annealed specimens where the brighter areas seem to form a network. Images taken at very low magnification allowing simultaneous imaging of pure PCBM and P3HT spin cast on silicon (Fig. 2) exhibit a substantially higher intensity for P3HT compared to that obtained from PCBM for both fresh specimens and after plasma cleaning. We therefore expect the darker areas in Fig 1 to correspond to PCBM rich areas. In Fig 1 the structure found after annealing at the higher temperature (170°C) is not substantially different to that annealed at the lower temperature (130°C).

After annealing at 130°C, the lower magnification image in Fig 3 reveals inhomogeneities on the length scale of a few 100 nm, which are marked by white lines in Fig 3 and resemble more the “as cast” structure than the “annealed structure”. A cross-section of the blend annealed at 170°C is

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shown in Fig 4. The bright line on the bottom is the silicon/blend interface indicating that there is a step. The large black areas may suggest an increased PCBM concentration. There is an intensity variation across the thickness of the film with the top layer appearing brighter. However this is most likely to be a topography effect rather than the result of an increased P3HT content as neutron scattering experiments do not show a depletion of PCBM at the surface when the specimen is annealed [5]. This and the absence of the structure resembling that found in Fig 1 suggest that a different cross-section sample preparation approach may be needed.

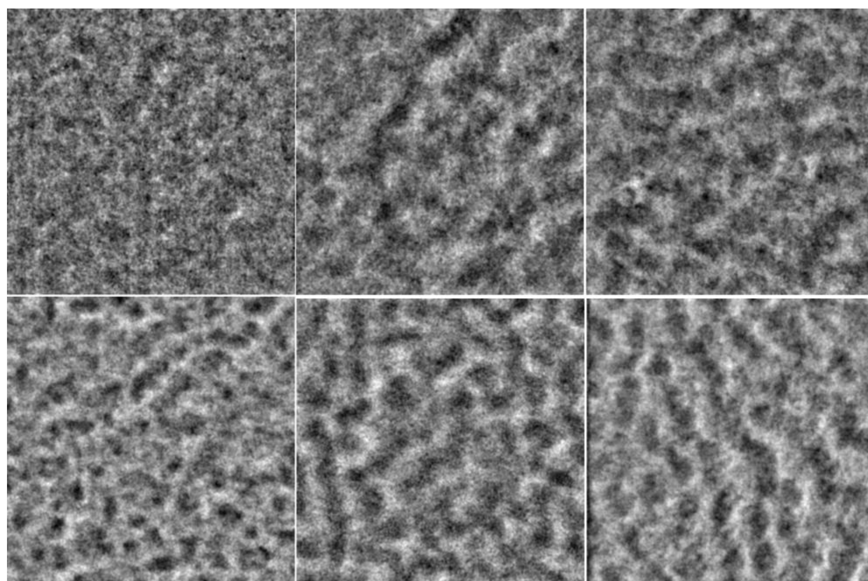

Fig.1. HeIM images: Top row: as received; bottom row: after 8 min plasma cleaning. Left: as cast; center: annealed at 130°C; right: annealed at 170°C. Field of view (FOV): 140 nm.

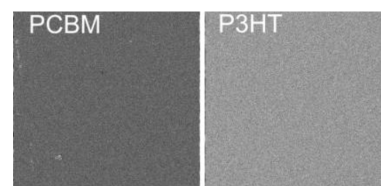

Fig.2. Low magnification HeIM images taken at identical microscope settings for pure PCBM and P3HT, fresh. FOV: 300 µm.

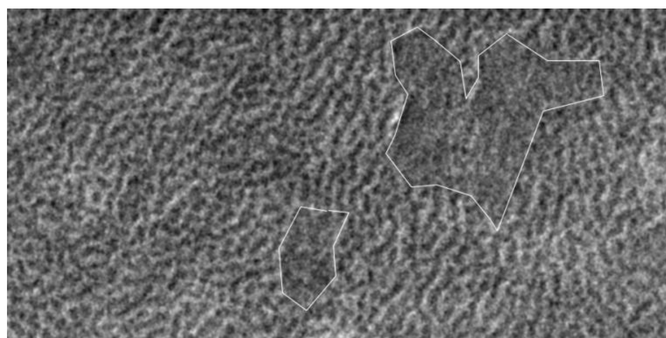

Fig.3. HeIM image of blend annealed at 130°C after 8 min plasma cleaning FOV: 800 nm × 400 nm.

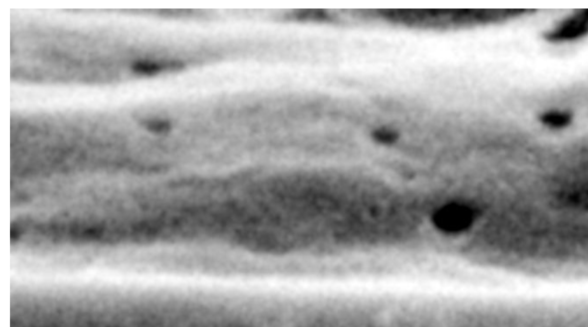

Fig.4. HeIM image of cross-section of blend annealed at 170°C after 8 min plasma cleaning. Specimen was cleaved after cooling in liquid nitrogen. FOV: 200 nm × 110 nm.

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