Using Grazing-Incidence Small-Angle X-ray Scattering and Wide-Angle X-ray Diffraction Simultaneously to Analyze the Nanoscale Phase Separation of Poly(3-hexylthiophene) and [6,6]-Phenyl-C_{61}-butyric Acid Methyl Ester in Heterojunction Solar Cells

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The BL17B3 SWAXS instrument at the National Synchrotron Radiation Research Center (NSRRC), equipped with a SAXS area detector and a WAXS linear detector (in the meridian direction) connected to two data acquisition systems operated in master-slave mode, allows one to perform simultaneously in-situ SAXS/WAXS measurements for correlated changes of the crystalline structures and nanostructure of the P3Ht/PCBM thin films interested. With 10.5 keV X-rays, we aligned all the sample thin films (30 mm by 30 mm on Si substrate) for a small incident angle of 0.3° with an accurately of 0.005°. We monitored the changes of the SAXS and WAXS of the sample thin films with an in-situ temperature annealing between 80-200 °C, which were found to be more sensitive to annealing temperatures rather than heating process or heating rate.

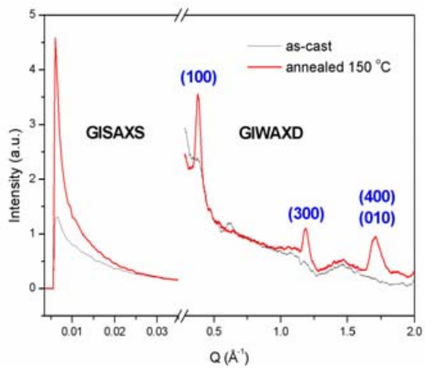

Figure 1. GISAXS/GIWAXD curves of as-cast and annealed (150 °C, 15 min) P3HT/PCBM films (not to scale).

Figure 1 displays the GIWAXD profiles of several P3HT/PCBM films. After annealing the P3HT/PCBM film at 150 °C for 15 min, a strong peak appeared representing the (100) reflections of the P3HT lamella layer structure along with two small peaks contributed by the (300) and (400) or (010) plane reflections of the P3HT lamella structure. In the low-Q range (ca. 0.006 $Å^{-1}$) of the GISAXS curves for the as-cast film, we observe a small scattering peak that is possibly attributable to the presence of PCBM in P3HT. For confirming this scattering peak, we have carried out control experiments by measuring GISAXS for both the pure P3HT and the P3HT/PCBM thin films (ca. 100 nm thickness; on Si substrate).

Figure 2 shows that the annealing at 150 °C for 15min does not affect the low-Q intensity of the GISAXS profile of the P3HT film, indicating that even if there is local phase separation inside the P3HT film, it does not contribute much to the intensity change in the low-Q region. Moreover, the GISAXS intensity of the as-cast or annealed P3HT/PCBM thin film is much larger than that of as-cast or annealed pure P3HT thin film, probably due to the large electron density difference between PCBM and P3HT (0.7 vs. 0.4 $e^{-}/Å^{3}$). Therefore, the GISAXS features in the low-Q region of P3HT/PCBM thin film are clearly dominated by PCBM, and we attribute the large GISAXS intensity change in the P3HT/PCBM thin film after annealing at 150 °C for 15 min to a significant growth of the PCBM aggregates. The PCBM scattering intensity increased dramatically as a result of the PCBM molecules diffusing out of the P3HT matrix and forming larger PCBM clusters.

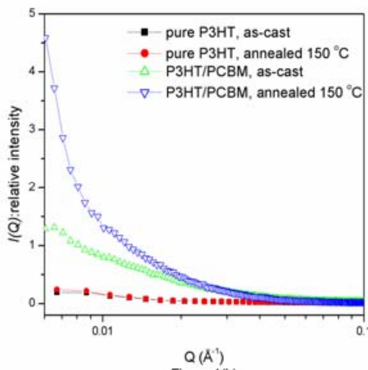

Figure 2. GISAXS curves of as-cast and annealed (150 °C, 15 min) P3HT and P3HT/PCBM thin films.

In summary, we applied GISAXS and GIWAXD simultaneously to study the morphologies of P3HT/PCBM active layers in bulk heterojunction solar cells annealed at various temperatures. This approach allowed us to investigate the effects of the sizes of the PCBM clusters and P3HT crystallites on the power conversion efficiencies of bulk heterojunction solar cells. It appears that improved power conversion efficiency requires the value of R_g of the PCBM clusters to be greater than 20 nm and the value of D_{100} of the P3HT crystallites to be greater than 16 nm for an active layer thickness of ca. 100nm.