Low-energy electron transmission measurements of thin polymer films in a scanning electron microscope

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Low-energy scanning transmission electron microscopy (STEM) is applied to analyze and quantify thickness and composition of irradiation-sensitive polymer films. The experiments were carried out with a dual-beam FEI Strata400S microscope. A standard STEM detector with several ringlike segments was used which is positioned below the polymer samples. High-angle annular dark-field (HAADF) images originating from electrons transmitted in a hollow cone between 0.2-0.7 rad show composition-sensitive contrast [1].

Thin films of semiconducting polymers employed in organic solar cells are examined in this work. The research focuses on the morphology of the absorber layer, which contains of a blend of the fullerene derivate PCBM ([6,6]-Phenyl C61-Butyric Acid Methyl Ester) as acceptor and the donor-doped material P3HT (Poly(3-Hexylthiophen)). The degree of decomposition of these two materials is crucial for the performance of the photovoltaic device, because the excitons generated by the incident photons can only be separated at the interface between electron- and hole-conducting regions. On the other hand the regions with the two phases have to be large enough to allow charge transport to the electrodes.

Analyses were performed at low energies (< 30keV) to overcome the difficulty of discerning different phases of low average atomic number ($Z_{(P3HT)}$=6.8; $Z_{(PCBM)}$=9.5), density ($\rho_{(P3HT)}$=1.1 g/cm³; $\rho_{(PCBM)}$=1.5 g/cm³) and therefore similar electron scattering properties. The challenge in imaging thin polymer films is to distinguish if the contrast is caused by thickness variation or different composition. Hence measurements were compared with Monte Carlo simulations performed by the NISTMonte-package [2], which uses Mott cross sections to model elastic scattering and the energy loss formula of Joy and Luo [3]. The simulations require the density and the mean atomic number of the constituents. The influence of the semiconductor detector on the intensity like the gain and the charge collection efficiency was also taken into consideration [4].

As seen in Fig.1 the simulated fraction of the transmitted electrons shows a maximum for a specific specimen thickness. The maximum of the intensity depends also on the electron energy (Fig.2). This enables the precise determination of film thickness by measuring the transmitted intensity for different acceleration voltages. For the validation of the Monte Carlo model, FIB (focused ion beam) sectioning is used to cut cross-sectional trenches into the polymer film, which is protected by a thin Pt layer, to measure the thickness (Fig.3).

Monte Carlo simulations (Fig.1) also yield information about the optimum electron energy for imaging the phase separation in the PCBM:P3HT composite. For film thicknesses and electron energies corresponding to the intersection point of the two curves no material contrast of the constituents will be observed. All contrast at this voltage indicates thickness variations and composition analyses should be made at parameters away from this intersection point. The signal should be as high as possible and the distance between the two curves maximized. To minimize the influence of local thickness variations low slopes of the curves are necessary. As an example a HAADF-STEM image of a PCBM:P3HT film of

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105nm thickness is shown in Fig.4 which shows regions with different brightness. Present evaluations indicate that material contrast correlates partially with contrast caused by thickness variations. Nevertheless, EDX measurements confirm material contrast because the bright regions contain a slightly higher concentration of sulfur as expected for P3HT.

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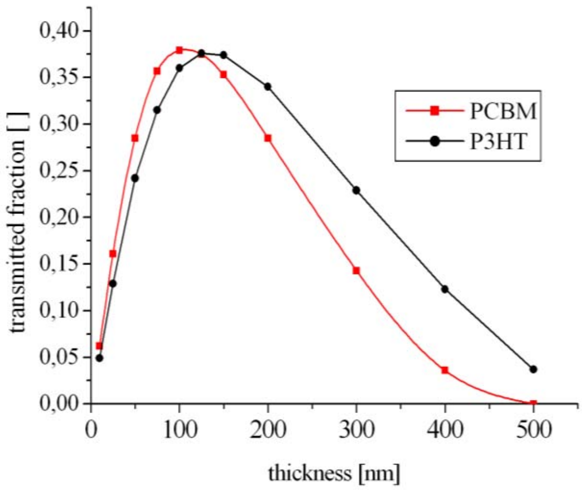

Figure 1. Monte Carlo simulation of the STEM-HAADF image intensities for 6 keV electrons

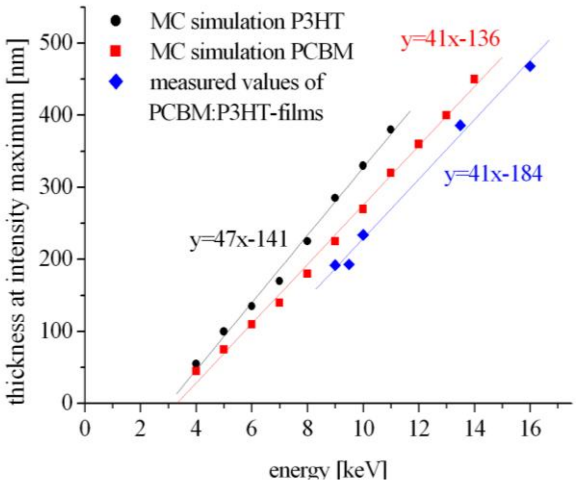

Figure 2. Dependence of the thickness at maximum intensity on the electron energy

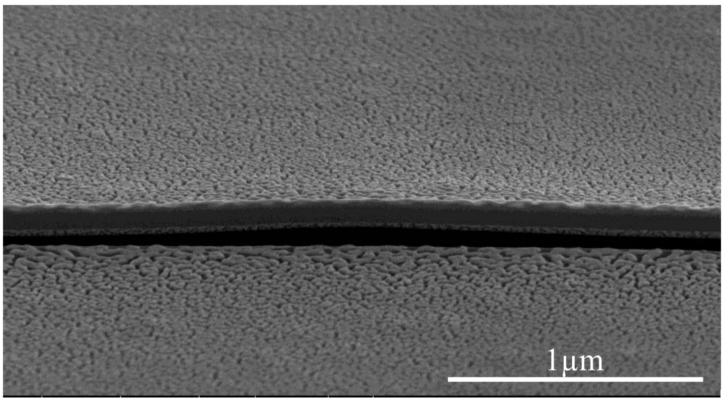

Figure 3. FIB cut in a PCBM:P3HT absorber layer with a thin Pt protection layer

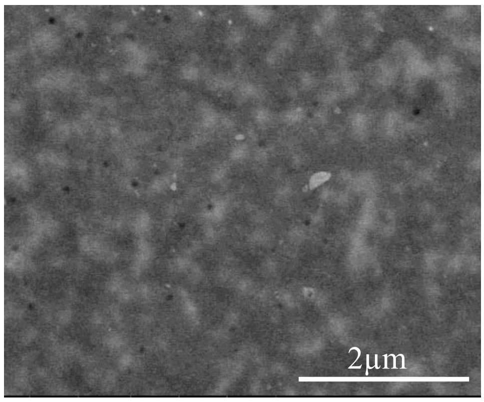

Figure 4. STEM HAADF image of a P3HT:PCBM film (mixing ratio 1:0.9) at 6keV

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