In-situ GIWAXS - Ellipsometry Study of Molecular Arrangement of Conducting P3HT Films

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Thin conducting photoactive polymer films have become of great interest over the last decade. This is mainly due to their various possibilities of application in electronic devices such as organic solar cells (OSCs), organic light emitting devices (OLEDs) or organic field effect transistors (OFETs). They combine mechanical flexibility, optical adjustability and many more device design possibilities with production advantages such as solution processability and cheap manufacturing cost.

One very promising material is poly(3-hexylthiophen-2,5-diyl) (P3HT), which has especially proven its suitability for the fabrication of organic solar cells. In combination with n-type F8TBT high efficient all-polymeric solar cells have been already successfully manufactured by McNeill et al. [1]. Interestingly the efficiency of P3HT:F8TBT solar cells could be increased by almost a magnitude due to post production annealing of the device. This is contributed to the strong tendency of P3HT to crystallize, which is also favored by heat treatment above the glass transition temperature ($T_g = 130°C$). Such thermally induced highly crystalline P3HT thin films have also shown electrical conductivities magnitudes higher than untreated thin films.

Grazing incidence wide angle X-ray scattering (GIWAXS) can be used to probe the molecular order of polymer chains in photoactive thin films [2]. In combination with optical ellipsometry, which additionally reveals the film thickness and offers information about the refractive index $n$ and the absorption coefficient $k$, a full study of the thin film properties can be achieved. Figure 1(a) shows the in-situ set-up which was installed at the BW4, HASYLAB (Hamburg). The ellipsometer and the micro-focused X-ray beam ($40 \times 20 \, \mu m^2$) are oriented to each other in such a way that the same sample area was addressed by both methods. The sample-detector-distance was chosen to be 97.1 mm and the wavelength was set to 1.38 Å. A characteristic GIWAXS signal of a pure P3HT film spin-coated on a solid silicon support is shown in figure 1(b). The scattering along the $\alpha_f$ -direction indicates the ordering parallel to the support, whereas the maxima along $\theta$ are given by the orientation of the polymer chains vertical to the support (illustrated also by the insets).
For the heat treatment five different temperature steps are chosen: 25 °C, 90 °C, 120 °C, 150 °C, and 180 °C. Also the transition back to 25 °C was monitored. The temperatures were chosen to be well below and above the glass transition temperature of the polymer. For all different steps the temperatures were kept constant during the GIWAXS and the ellipsometric measurements.

Figure 2: (a) Out-of-plane cuts taken along exit angles $\alpha_f$ and (b) corresponding ellipsometric data probed at different annealing temperatures.

Figure 2(a) shows integrated cuts along the $\alpha_f$ -direction for all probed temperatures. For all stages prominent maxima at the (100), (200), and (300) Bragg peaks are visible. In addition, at higher temperatures the positions are shifted to smaller q-values indicating increasing lattice constants. Interestingly, the (010)-peak visible at larger angles is in comparison to the (100)-peak and its corresponding higher orders only slightly shifted. Also a strong tendency of the polymer chains to orient in a perfect lattice can be seen from the increasing acuity of the observed peaks. Whereas the untreated sample shows broad peaks indicating a wide orientation distribution, the annealed samples reveal a much better molecular ordering. After cooling down the lattice constants relax to the as-prepared values, but the ordering perfection remains constant as for the heated samples. This saved embedded ordering of the polymer chains finally leads to an increased electrical conductivity along the carbon backbone.

The simultaneous obtained ellipsometric measurements, shown in figure 2(b), exhibit a strong variation in the characteristic $\Delta$- and $\Psi$-values. The $\Delta$-values correspond to the relative amplitude ratio, whereas the $\Psi$-values give information about the relative phase shift. Both values can be fitted with an optical model which finally depends on the film thickness, the refractive index, and the extinction coefficient. In the data the minimum position of the $\Psi$-value is shifted to smaller angles of incidence with increasing annealing temperature and the shape of the $\Delta$-curves is flipped around at the glass transition temperature of the polymer. These characteristics already indicate a similar morphological change as observed with GIWAXS leading to altered absorption coefficients. In order to extract the full information the data analysis of the ellipsometric measurements is still ongoing.

References
