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Report:

The aim of the experiment is an *in-situ* observation of the aignment procedure of the polymer film F8T2 due to temperature treatment. F8T2 films are deposited on a rubbed polyimide layer (prepared on a silicon substrate) which induce uniaxial order due to heat treatment at around 550K. By *ex-situ* investigations it is observed that the polymer backbone alignes along the rubbing direction of the polyimide surface.

The temperature dependent investigations were performed by using a commercial available heating chamber (DHS900, Anton Paar GmbH). During the experimental procedure the change of the sample position (vertical translation in z-direction and angular tilt of the sample) was investigated as a function of the temperature of the heating chamber. In the used temperature range the vertical position is linear and reprocible with the temperature as shown for sample B in Figure 1. The position marked with the arrow gives the z-position of the sample after a heating run, the solid line gives a linear regression through the observed z-positions of the sample surface. The angular tilt of the sample is below 0.02 degrees and negligible for the experimental performance.

Figure 2 gives a characteristical diffraction pattern of an F8T2 film in the as-prepared state with typical diffraction features at $q = 0.3 \text{ Å}^{-1}$ and 1.4Å^{-1} . An optimization of the angle of incidence for the experiment was performed close to the angle of total external reflection of the silicon substrate and it was found than an angle of 0.18 degrees gives the highest diffraction signal of the F8T2 film.



Fig. 1: Movement of samples due to heating of the sample at the heating stage. Vertical sample translation in absolute values (left) and tilting of the samples in relative values (right).



Fig. 2: Diffraction pattern of an F8T2 film in the as-prepared state taken at an angle of incidence (α_i) slightly below the critical angle of total reflection of the substrate (left) and q_{xy} line scans at different α_i taken at $q_z = q_c$ (q_c = critical wave vector transfer.

After the alignment of the F8T2 film, the diffraction pattern became anisotropic dependent on the direction of the primary beam relative to the F8T2 polymer chains (= the rubbing direction of the polyimide surface) as it is depicted in the left part of Figure 3. The *in-situ* investigations reveal a change of the the diffraction feature at q = 1.4Å⁻¹ but the shift of the diffraction peaks due to alignment of the polymer chains or of the polymer backbone sidechains cannot be separated from the peak shift due to the temperature itself (expansion of the lattice). So no clear conclusion can be given from the demperature dependence of the peak at q = 1.4Å⁻¹. However, the peak development of the q = 0.3Å⁻¹ feature shows a clear development due to the temperature treatment and the irreversibility of the alignment process can be clearly observed between the diffraction pattern of the as-prepred film and after heat treatment at 343K (Figure 3, right).



Fig.3: The wide angle diffration features of an 20nm thick aligned film of F8T2 investigated with the primary beam along the rubbing direction ($\rightarrow \equiv$) and perpendicuar to the rubbing direction ($\rightarrow \parallel \mid$) (left). The diffraction feature at small angles and their evolution with temperature from an as-prepared film via heat treatment to an uniaxially aligned film (right), the curves are shifted for clarity.

The main result of the experiment is the intensity development of the diffraction peaks as a function of temperature during cooling of the sample after the heat treatment. The diffraction peak at $q = 1.35 \text{Å}^{-1}$ increases with temperature up to 373K and remains constant below that temperature; the diffration feature at $q = 0.35 \text{Å}^{-1}$ shows saturation at 440K (compare Figure 4). It can be concluded that the two different order temperatures arise from two different types of order in the polymer film, it can be suggested the the order of the polymer backbone arises at larger temperatures than the order in the sidechains of the polymer.



Figure 4: Development of intensity as a function of temperature during the cooling of the F8T2 film after annealing taken at $q_{xy} = 1.35 \text{\AA}^{-1}$ (left) and $q_{xy} = 0.35 \text{\AA}^{-1}$ (right)