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## Report:

Recent research of organic semiconductors is directed towards highly ordered molecular structures in the solid state. Especially conjugated polymers have become a topic of intense research in the context of organic field-effect transistors (OFETs) fabrication. The backbone as well as the side chain lengths and the processing conditions strongly affect the packing of the structure and contribute therefore to the optoelectronic properties of the film. The size, type and regioregularity of poly-3-hexylthiophene (P3HT) polymer films have been explored extensively aiming for the optimization of the electronic properties. The molecular weight has also been shown to have a significant effect on ordering and transport properties [1,2]. Traditionally, starting from the pioneering work of Bao [3] and Sirringhaus [4] till nowadays (see, for example, [2,5]) structural and electrical characterizations have been performed separately. Our preliminary laboratory experiments have shown that there are structural changes in the active polymer layer during operation of an OFET. However, applying voltage to source and drain gold contacts in combination with in situ x-ray investigations on small polymer channels (0.1mm -2mm) in is not a trivial task due to small channel width and strong background scattering from the gold contacts. Therefore, we have performed an experiment of in-situ x-ray characterization of the basic component of an OFET, namely a thin active P3HT layer under applied voltages up to 200V using a synchrotron radiation source.

The depth resolved x-ray diffraction of the thin polymer films was carried out at the beamline ID10b at ESRF at the energy of 9.987 keV and utilising a PSD with 1024 channels (70 channels correspond to 1°). All in-situ x-ray measurements under applied electrical field were performed under inert gas atmosphere using a custom made domed stage build at Graz University of Technology especially for that purpose. The applied voltage was varied in the range from -200 up to 200V. By tuning the angle of incidence with respect to the sample surface, below or above the critical angle of total external reflection $\alpha_c$, the penetration depth of the x-ray beam into the sample was controlled. In particular, we used in- and out-of-plane grazing incidence x-ray diffraction for orientation dependent depth-resolved structural analysis. For both grazing incidence geometries we found several diffraction peaks of (h00) series which are associated with the alkyl side chains and the (020) peak of the conjugation direction in the case of spin coated films. Typically, spin coated films provide mixed orientation due to the fast fabrication procedure. In opposite, drop casted films are proved to be preverentially oriented with the conjugation direction parallel and alkyl side chains lying almost perpendicular to the thin film surface. All samples

were measured at the channel lenght of 2 mm. At the same voltage the current through the film was found to be few orders of magnitude higher for drop casted films.

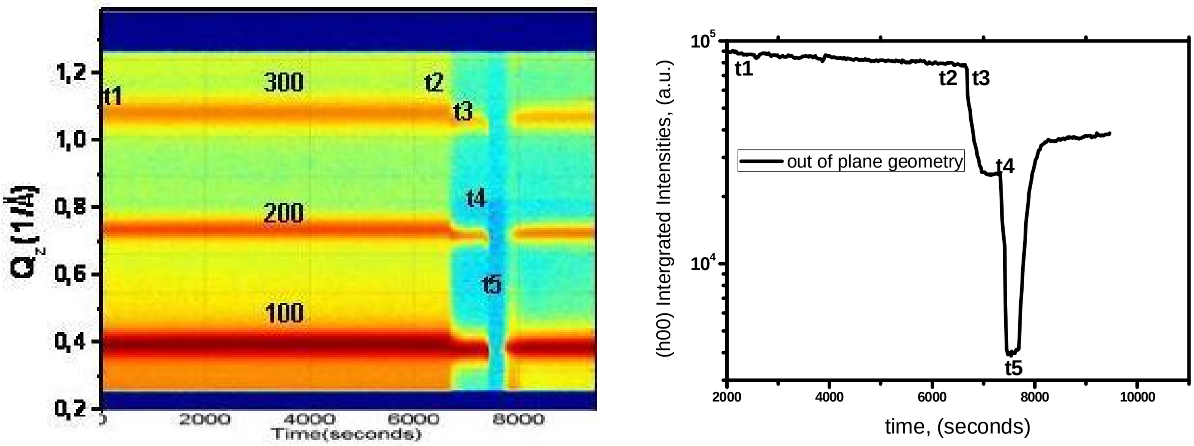


Figure 1. Electric field induced melt of (h00) planes at -200 V as a function of time

Drop casted samples display a well pronounced periodicity normal to the surface. Electric field induced melting of out of plane (h00) peaks is shown in figure 1. In the time span between t1 to t2 where a voltage is gradually increased up to 200V crystalline structure remained unchanged. Straigth after changing the polarity to -200V the peak intensites decrease by factor of three within 10 min (interval t3-t4) folllowing by complete melt within 2 min (t4-t5). Interestingly, after switching off voltage the out-of-plane crystalline structure particularly recovers within about 10 min to an intensity about half of the initial one.

Structural melting under electric field looks similarly to thermal induced melting because it is accompanied by a shift of the peak positions to the smaller Q values indicating expansion of the interplanar distances (not shown). Due to this relation our finding could be explained by impact of Joules heating by the electrical current. However, this model cannot explain why the melting starts at a change of the polarity of the voltage. The answer to this question needs further experiments.

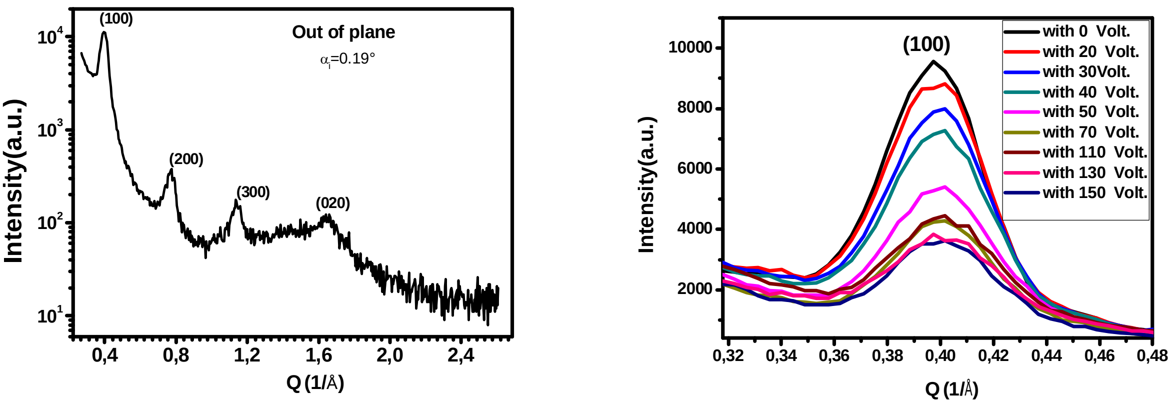


Figure 2. Out of plane scan of spin coated film (left), fist order (100) peak under electric field (right)

Typical out of plane line scan of spin coated films is shown in Fig. 2 (left). Together with (h00) series for the higher Q values one can resolve a (020) peak on the top of a broad amorphous halo. Fig. 2 (right) shows the decrease of the (100) out of plane peak as a function of voltage. Increase of voltage induces monotone decrease of structural peak intensity. However, even at 150V crystalline structure partially remains.

Different behaviour of the structural modification under applied voltage was found for in plane direction. The in plane (020) peak revealed a higher sensitivity to the applied voltage. In contrast to out of plane peaks the in plane (020) peak decreases faster in intensity and disappears already at 110V whereas 10% of the (100) intensity still is visible (see Fig. 3). The strong influence at the (020) suggests the assumption that electrical transport takes place mainly along the $\pi-\pi$ stacking direction. Interestingly,

repeating the cycle of stepwise increase of voltage a second time the change in intensities was less strong compared to the first cycle. For the first cycle the structural ordering decreases with increasing voltage for all reflections but at second circle the peak intensities of both (100) and (020) peaks decrease to about 40% at 110V.

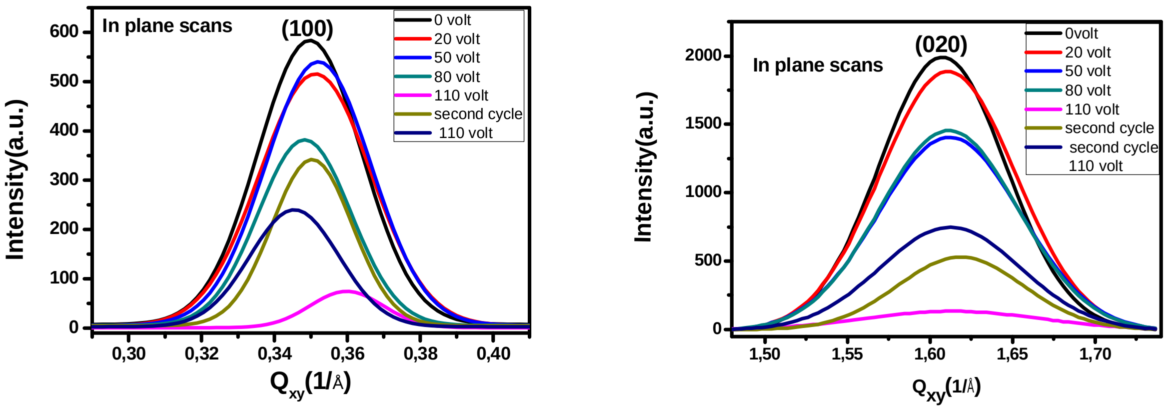


Figure 3. Out of plane scan of spin coated film (left), fist order (100) peak under electric field (right)

In conclusion, in-situ characterization of the thin P3HT films allows monitoring of the structural changes under electric field. In-plane direction reveals to be stronger affected in comparison to out of plane one applying the voltage. Within in-plane direction a strong modification takes place for (020) planes indicating the strongest interaction of electric filed along π-π conjugation.

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