

# EFFECT OF SUBSTRATE ROUGHNESS ON CRYSTALLINITY AND DOS STRUCTURE OF POLY(3-HEXYLTHIOPHENE) THIN FILM

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## 1. Introduction

The characteristics of organic materials for electronic applications like FET and photovoltaics are strongly dependent on their ability to form crystalline structures. Individual steps in process of preparation of these self-assembly systems therefore influence their final physical properties. In order to optimize this process to reach the desired features it is necessary to identify the effects of all the technological steps during preparation on the electrical properties.

One of the commonly used materials in the field of photovoltaics are the poly(3-hexylthiophene)s (P3HT). They are thiophene backbone polymers with six carbon long side alkyl group. Due to their well-known properties they are ideal for purposes of examination of effects of sample preparation steps [1]. Concerning the crystalline structure of thin films, commercial availability of P3HT with high regioregularity is of great advantage. This parameter strongly affects geometry of polymer chain and overall ability to crystallize [2].

In this paper we focus on structural changes of P3HT film due to effect of the substrate roughness and the influence of these changes on the density of states (DOS) function of the material. The crystalline structure was investigated by Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) and the mapping of DOS in the band gap region was obtained by energy resolved electrochemical impedance spectroscopy (ER-EIS) [3]. The investigation of P3HT layers was supplemented with photoluminescence (PL) measurements to obtain information about optical nature of DOS.

## 2. Materials and sample preparation

Material under investigation was commercially available P3HT from Sigma-Aldrich. This P3HT polymer has molar mass of  $4.5 \times 10^4$  g/mol and the regioregularity of 99.9 %.

Thin films were prepared by spin coating from 1,5 wt % solutions dissolved in dichlorobenzene (DCB). Two different types of substrates were used: glass substrate with thin ITO/glass and p-type heavily doped crystalline silicone (p+ c-Si) substrates. Both substrates were cleaned in acetone and isopropanol and treated for 10 minutes in ozone. Before P3HT deposition silicone substrates were also etched in hydrofluoric acid to remove silicon dioxide layer. Spin coating parameters of P3HT layer were adjusted to 30 rps for 50 s, which gave the thickness of about 60 nm. After spin coating the samples were left to dry in solvent vapors and subsequently thermally annealed at 110 °C for 5 minutes.

### 3. Method

The GIWAXS is the reciprocal-space technique widely used for the structural characterization of organic thin films. In this technique, the monochromatic and collimated X-ray beam impinges on the sample surface at small angle of incidence (usually  $\alpha_{\text{inc}} = 0.2^\circ - 1^\circ$ ). The periodicity in ordered domains of the organic molecules such as polymer chains is manifested in the GIWAXS pattern by a diffraction maximum. The GIWAXS measurements on the P3HT thin-films were performed on a commercial device Nanostar (Bruker AXS, Germany) with the liquid Ga metal-jet X-ray source (Excillum, Sweden).

The DOS functions were measured by ER-EIS method. This technique is based on the impedance measurement of organic film/electrolyte interface [3]. The method was recently applied for elucidation of the chemical defect-related DOS in P3HT by Gmucová et al. [4] and UV irradiation induced defect states in polysilanes [5]. The impedance/gain-phase analyzer Solartron analytical, model 1260, was used in the configuration described in our previous paper [3]. The frequency was set to 0.5 Hz, the amplitude of AC voltage to 100 mV, and the sweep rate of the DC voltage ramp to 10 mV/s.

PL measurements were performed on the P3HT thin-films using Horiba Jobin-Yvon Fluorolog-3 device with 450 W Xe lamp and Hamamatsu R928P photomultiplier tube with the integration time 0.1 s and the integrated reference Si photodiode. The emission and excitation spectra were obtained in 90 degrees arrangement at the incident angle of 30 degrees on the P3HT layers. Bandpass of the excitation and emission monochromator was 2.5 nm.

### 4. Results

The GIWAXS analysis was based on the most intense  $100$  diffraction peak from P3HT crystals. Its intensity distribution along  $q_z$  axis at  $q_y = 0 \text{ nm}^{-1}$  exhibits for ITO substrate an asymmetry, which was deconvoluted into two Gaussian peaks. This fact implies that the higher roughness of the substrate stimulates growing of two different crystallization phases. On the other hand only one crystalline phase is observed in the P3HT layer on p+ c-Si.

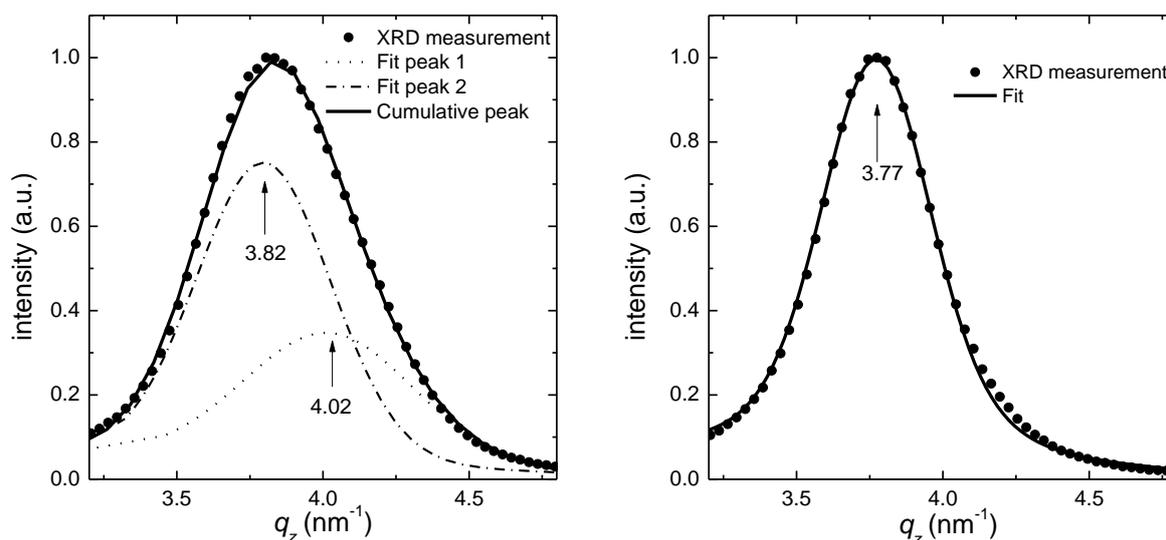


Fig. 1. The intensity distribution along  $q_z$  axis taken at  $q_y = 0 \text{ nm}^{-1}$  within  $100$  diffraction peak from P3HT crystal measured on ITO (left) and p+ c-Si (right) substrates. The asymmetric peak of ITO substrate was deconvoluted into two distinct Gaussian peaks: dominant peak 1 and minor peak 2.

The diffraction peaks along  $q_z$  axis of the GIWAXS measurements with peak deconvolution are shown in Fig.1 for ITO (left) and p+ c-Si (left) substrates. The maximum position  $q_{\max}$  of the diffraction peak provides the spacing between the adjacent organic molecules via equation  $d = (2\pi)/q_{\max}$ . Space distances between P3HT molecules in the observed crystalline phases are 1.65 nm (maximum positions at about  $3.80 \text{ nm}^{-1}$ ) and 1.56 nm (maximum position at  $4.02 \text{ nm}^{-1}$ ).

The comparison of measured DOS for P3HT on two different substrates using ER-EIS is shown in Fig. 2. On the left graph the  $g(E)$  is shown in linear scale. This depiction allows to determine the width of the bandgap, which is 2.22 eV for both samples. Logarithmic scale (right graph in Fig. 2) reflects the fine DOS structure in the bandgap. As can be seen the main difference between the layers on ITO and p+ c-Si substrates is the satellite peak below the HOMO. The difference in the DOS at the energy -4.9 eV with respect to the vacuum level is more than one order of magnitude. Taking into account the structural results in Fig. 1, this effect is the result of the second crystalline phase of the P3HT sample on ITO evoked by the roughness of the substrate surface. The mean roughness of the ITO layer on a glass substrate is about 7 nm while for the p+ c-Si substrate this value is below 1 nm. We believe that higher protrusions of ITO surface modify crystallization process of P3HT during solvent and thermal annealings, which result in two crystalline phases in comparison to flat p+ c-Si substrate where only one dominant crystalline phase is formed. The presence of two different crystalline phases can give rise to additional intermolecular interactions resulting in the appearance of the narrow band below the HOMO.

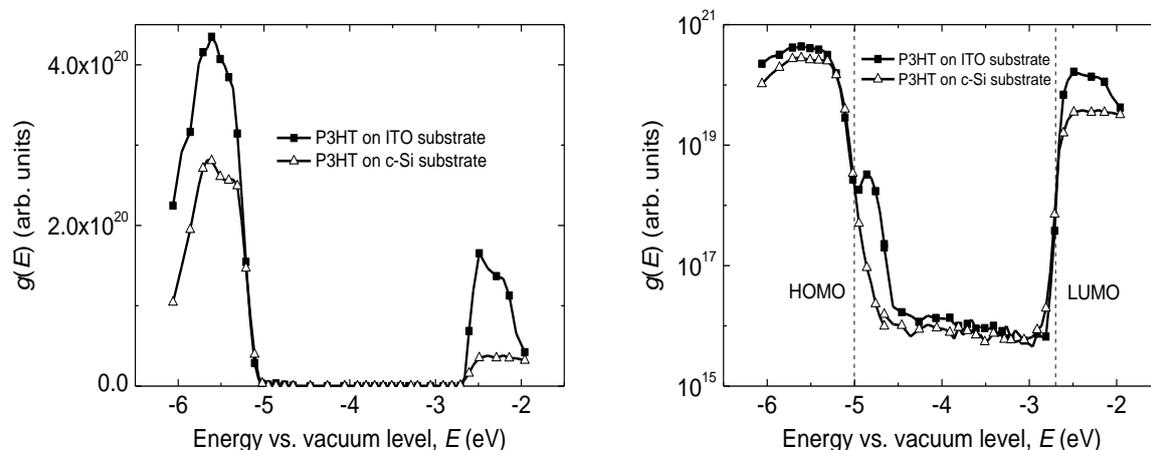


Fig. 2. Measured  $g(E)$  in HOMO/LUMO region of P3HT on crystalline silicon and glass covered ITO substrate in linear (left) and logarithmic (right) scale.

The presence of different crystalline phases and induced band of defect states above the HOMO is also reflected in the fluorescence characteristics of two samples under investigation. The fluorescence spectra of P3HT layers on ITO and p+ c-Si substrates are shown in Fig. 3. We can see a decay of the peak shoulder at long wavelengths for ITO substrate. The energy corresponding to wavelength range of this decay is around 1.85 eV, which is in a good agreement with the energy position of the defect-state band with respect to the LUMO (see in Fig. 2). We suppose that this band acts as a non-radiative recombination centre for excitons. In case of p+ c-Si substrate with the presence of one crystalline structure and absence of the defect-state band, higher intensity of the shoulder indicates that excitons recombine in this energy range radiatively.

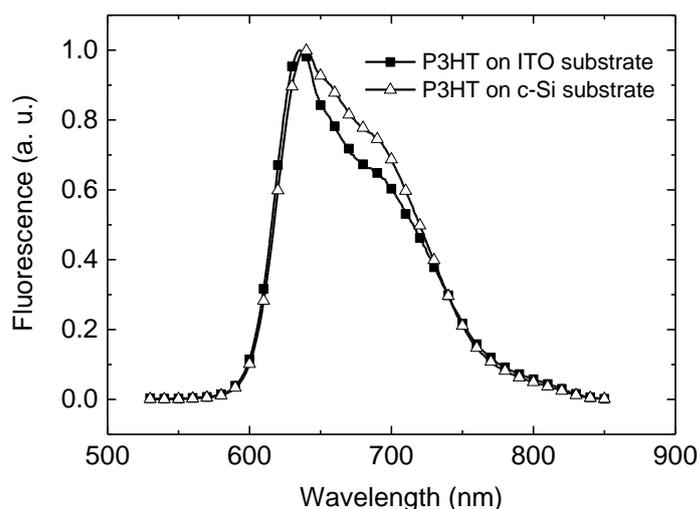


Fig. 3. Fluorescence emission spectra of P3HT layer on ITO and  $p+$  c-Si substrates for excitation wavelength of 522 nm.

## 5. Conclusion

We demonstrated the sensitivity of structural features of P3HT polymer films on the roughness of the substrate surface. Even small variance in the surface roughness can result in the formation of various crystal phases, which induces change in the DOS distribution. We found out that P3HT layer grown on ITO substrate with the surface roughness of 7 nm shows two crystalline phases. The first phase, observed also in P3HT layer on  $p+$  c-Si, corresponds to the interchain stack distance  $s$  of 1.65 nm. The second crystalline phase with 1.58 nm separation between stacks introduces a defect-state band above the HOMO. PL measurements revealed that this band acts as a nonradiative recombination centre of excitons which can adversely affect solar cell performance.

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## References

- [1] R.L. Elsenbaumer, D. Spiegel, Y. Kim, D. Hota, A.J. Heeger, *Synth. Met.*, **28**, C419 (1989).
- [2] H. S. O. Chan, S. C. Ng, *Prog. Polym Sci.*, **23**, 1167 (1998).
- [3] V. Nádaždy, F. Schauer, K. Gmucová, *Appl. Phys. Lett.*, **105**, 142109 (2014).
- [4] K. Gmucová, V. Nádaždy, F. Schauer, M. Kaiser, E. Majková, *J. Phys. Chem. C* **119**, 15926 (2015).
- [5] F. Schauer, M. Tkáčová, V. Nádaždy, K. Gmucová, L. Tkáč, J. Chlpík, *Polym. Degrad. Stabil.* **126**, 204 (2016).