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Structure and morphology optimization of poly(3-hexylthiophene) thin films onto silanized silicon oxide

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ABSTRACT

The influence of the preparation conditions, including substrate functionalization with common silanizers, onto structure/morphology of the overlying poly(3-hexylthiophene) thin films has been investigated by using both grazing incidence X-ray diffraction and atomic force microscopy. The factors determining the formation of spin-coated films suitable for applications in field effect transistors, i.e. concentration, spin-speed, and thermal treatment are addressed. We have established, by a tuning of the preparation and post-deposition treatments, the optimal conditions to get films with the required structural/morphologic features. Moreover we have shown that the macromolecules orient and organize at the interface zone ($\leqslant$10 nm from the interface) better than in the upper layers, i.e. far away from the interface.

1. Introduction

Conjugated polymers, specifically poly(3-hexylthiophene), represent a valid alternative to amorphous silicon for large area and low cost applications, e.g. in organic field effect transistors (OFET), light emitting diodes (LED), and solar cells (PV); the molecular structure and orientation of the active layer, together with its morphology constitute the topic of the huge number of studies dedicated to this system [1,2,4–43]. In this frame structural investigations – using XRD, ED, and NEXAFS – we have widely demonstrated that P3HT layer consists of a sequence of π–π interacting macromolecules essentially in an edge-on configuration with respect to the substrate thus forming morphological units, lamellae or fibrils according to molecular weight (MW) range, as evidenced by AFM analysis [5,9,12,15,18,19,21,32,34,35,41–44]. The shape and length of these features vary as a function of several factors, namely MW, deposition techniques and conditions, solvent and post-annealing treatments, and the substrate functionalization. This latter can be realized by means of substituted silane molecules having the terminal residues of the alkyl chains of different polarity and length. The silane molecules form a self-assembled monolayer (SAM) which acts as a sort of template influencing the structure and morphology of the overlying P3HT layer [40,44]. Films of different quality in terms of both crystallinity and molecular orientations are obtained, depending on the preparation conditions, typically using spin- or dip-coating and cast techniques.

The structural evolution of P3HT films upon thermal treatment have been extensively studied and related to OFET, LED, and PV device performances [33,35,36,38–40,42], yielding stringent evidences concerning amorphous presence, macromolecule orientation, crystallite dimensions, lattice parameter changes, as evidenced in [35,38–40,42]. Moreover the recent work of Salleo et al. [45] on the origin of gap states related to the charge transport has shed light onto intimate mechanisms of charge transport in P3HT-based OFETs. Also a mechanical treatment (e.g. ultrasound irradiation) has been shown to strongly affect both structure and morphology and eventually the charge mobility [41].

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Nonetheless, the effect of film preparation (namely solution concentration, spin speed, and thermal treatment) onto morphology/structure has not been yet completely addressed, as the control of competing thermodynamic and kinetic effects in semicrystalline polymeric systems is achievable under stringent conditions only.

From the electronic point of view, at least two studies [6,8] have demonstrated that in P3HT-based FET the charge carrier transport occurs at all over the whole film thickness (typically 25–30 nm thick), but mainly confined in the first layers (~5 nm) immediately in contact with the substrate interface, identified as the effective active layer (EAL). In this regard, the knowledge of the structure/morphology of the P3HT layer at the polymer/substrate interface (⩽10 nm) and its dependence from the silanizer constitutes the keystone to understand the corresponding SAM effect on the electrical response. The influence of SAM on the P3HT structure/morphology does not persist all along the film thickness (typical 25 nm), rather it is confined into an interface region (⩽10 nm from the substrate) [40]. It is thus necessary to selectively study the P3HT properties of layer close to the interface (~5–10 nm), distinguishing them from those of the more external ‘bulk’, in order to establish if the higher hole mobility definitely relates to any structural, orientational, or morphologic features of the polymer. In the aim of exhaustively characterizing the thin layers used in the devices, two requirements have to be satisfied:

- the determination of structural features of films – 25/30 nm thick – using techniques capable to distinguish polymer at interface and in the upper layers, typically depth-resolved grazing incidence X-ray diffraction (GIXD) [40].
- the acquisition of detailed morphology – using atomic force microscopy (AFM) – on samples of different thickness to detect upper layer condition, extrapolating the results to buried interface of thicker films.

The comparison of both GIXD and AFM data can allow one to put forward the variations of both morphology, structure, and orientation of P3HT layers, as exemplified in Fig. 1.

The goal of this work is to describe the structure/morphology of ultra thin layers (UTL) compared to thicker layers and to find possible effect of two typical SAMs, i.e. hexamethyldisilazane (HMDS) and octadecyltrichlorosilane (OTS), onto corresponding UTL structure/morphology. The structural and morphological investigation is focused onto the interface zone between P3HT layer and SAM. To this end, spin coating rate, solution concentration, and thermal treatment have been varied.

The above mentioned factors affecting the layer formation have to be disentangled in order to drive the film structural and morphologic characteristics optimal for OFET applications. To this purpose a peculiar range of number average molecular weight (Mn) (15–16 KDa) with related dispersivity (⩽1.7), and high regio-regularity (~98%) have been selected to avoid the residual presence of low-Mn (<7 KDa). In this way the presence 3D phase [30] with a different structure is prevented and the chain folding of the backbone [26], which possibly augments the semi-crystalline character of the polymer, minimized. Hence the structural/morphological investigation is focused onto the interface zone between P3HT layer and the two aforementioned SAMs. The P3HT crystal structure considered in the following is the one proposed by Brinkmann [37].

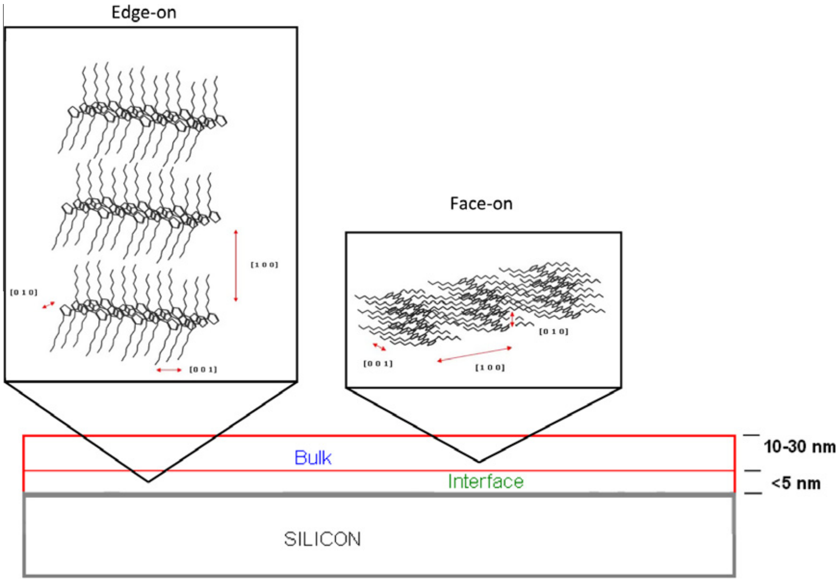

Fig. 1. Sketch of P3HT film viewed along the thickness, the main crystallographic direction of the monoclinic unit cell are indicated in the two orientations, which are predominantly present in bulk (face-on) or at the interface (edge-on).