



## Morphology and orientation of thin poly(3-hexylthiophene) (P3HT) films on differently silanized silicon oxide

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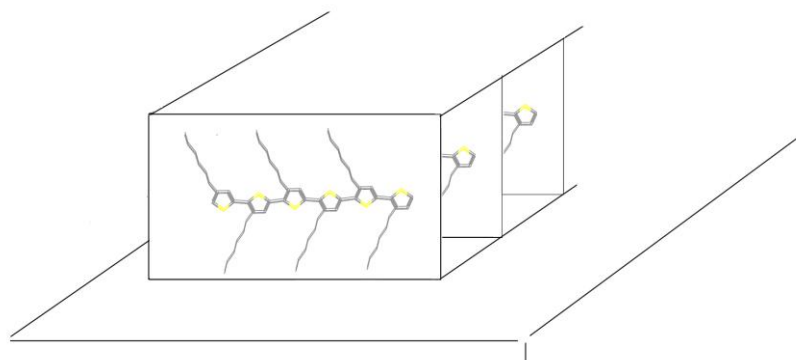
**Abstract:** The morphology and structure of the overlying poly(3-hexylthiophene) (P3HT) layer onto differently silanized silicon oxide has been studied by Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD) techniques. By increasing the silanizer alkyl chain length, the layer morphology evolves from a filament like to globular needle like as a consequence of the different SAM organization, while the P3HT conformation remains *edge-on*. For each case the effect of the annealing temperature has been studied. For all the cases a particular attention has been paid to the first thin layers close to the interface P3HT/SiO<sub>x</sub>. The effect of a polar substituent and presence of aromatic ring has been also studied.

### Introduction

Conjugated polymers such as poly(3-hexylthiophene) (P3HT) are presently used as active layer in the field effect transistors (OFET) [1-9]. A relevant problem to be solved for these materials is represented by their stability especially during operation. In order to improve both this property and the device performance the knowledge and optimization of both the crystalline structure and orientation of the P3HT molecules becomes crucial [2, 10]. In particular, according to XRD investigations, the P3HT macromolecules organize themselves into a sequence of  $\pi$ - $\pi$  interacting molecules with their backbone essentially *edge on* oriented with respect to the substrate as shown in Figure 1a. [6-15] thus giving rise to a filament morphology [6-13]. The model used to explain these morphological structures has been presented by Sirringhaus [6] and Salleo [16].

The fibrillar structures and consequently the electronic behaviour (mobility) is sensibly influenced by several variables such as molecular weight (MW) and regioregularity of the polymer, deposition method, solvent boiling point, solution concentration, substrate functionalization, and into post-treatment conditions. [11, 14, 15, 17-21]. Besides, an appropriate choice of the substrate could be fundamental in determining the edge-on face-on configuration. One typical substrate for OFET is represented by silicon oxide functionalized with silane molecules. The use of reactive alkyl substituted silane allows for the improvement of the interaction between the P3HT layer and the substrate and consequently the active layer performances [22-24]

The silane chains, generally perpendicular to the SiO<sub>x</sub>, mutually interact producing self assembled monolayer (SAM) that can influence through the modulation of the polar/apolar character of the substrate surface the overall morphology of P3HT layer, via specific interaction polymer/SAM. [24]. In any case most of the typical silanization processes give rise to edge-on configuration for the overlying P3HT even if with a different morphology.



**Fig. 1.** Model for the perpendicular (*edge-on*) configuration for P3HT on silicon oxide. The sequence of the  $\pi$ - $\pi$  interacting *edge-on* P3HT macromolecules leads to the formation of the typical filament morphology.

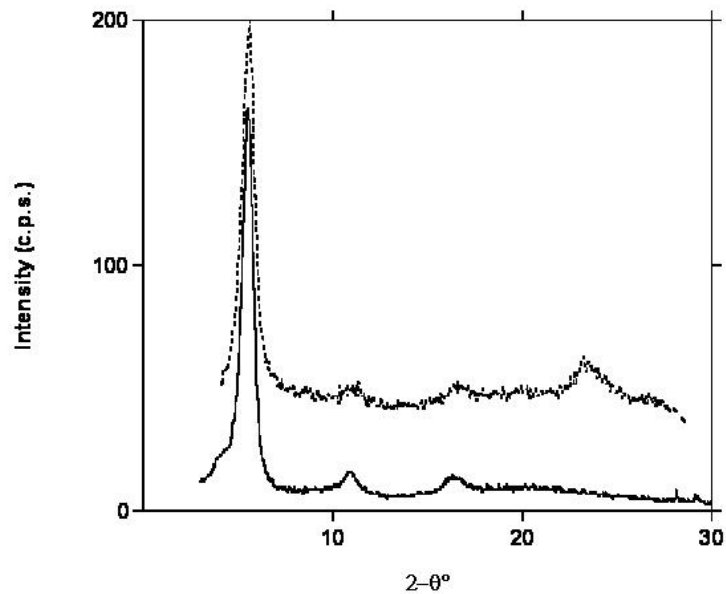
In the present work, the effect of the silanizer's alkyl chain length onto the overlying P3HT layer has been investigated for two limit cases i.e. methyl (DMDS) and octadecyl (OTS) and a modelling of the relative morphological features is presented. Besides the influence of the phenyl group (phenyltrichlorosilane) and a polar aminopropyl group with respect to the propyl case has been considered. In order to investigate the inner P3HT layers, i.e. closer to the interface, a peeling procedure has been carried using polydimethylsilane (PDMS) [25].

## Results and discussion

### *XRD investigations*

Thin films of different thickness, ranging from 5 nm (peeled samples) to 25 nm, were examined under nitrogen flux at 25 °C in Bragg-Brentano geometry; the presence of [1 0 0] peak was revealed, while no evidence of [0 1 0] intensity could be observed, both in the *as-deposited* case and after the proper annealing procedure. As an example, Fig. 2 shows the XRD patterns of films and powders -after proper annealing- taken in Bragg Brentano geometry to observe out of plane reflections. It is evident the essentially total edge-on orientation of the chains as expected, in fact the [0 1 0] reflection at 23.4 ° ( $2\theta$ ) is present only in powder spectrum (top in the Figure). In all cases, regardless to the underlying SAM, edge-on chain-orientation (see the model in Fig. 1) is dominating.

From line profile analysis [26], the crystallite size along with the long spacing, [1 0 0] direction, is derived to be less than 9 nm; while after a suitable thermal treatment, such size increases up to 20 nm. Therefore the molecular arrangements are improved by the annealing treatment.

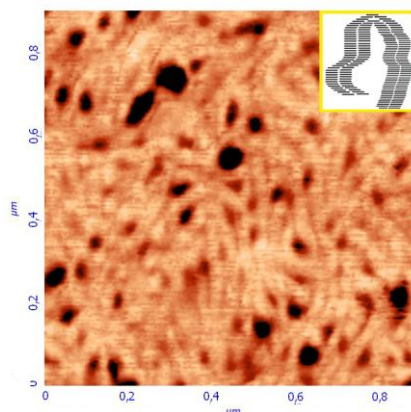


**Fig. 2.** XRD patterns of P3HT in Bragg Brentano geometry: powder (top) and films (bottom), after proper annealing to enhance the crystallinity. The spectra are slightly shifted in intensity for clarity.

### AFM results

#### -Effect of the silanizer alkyl chain length

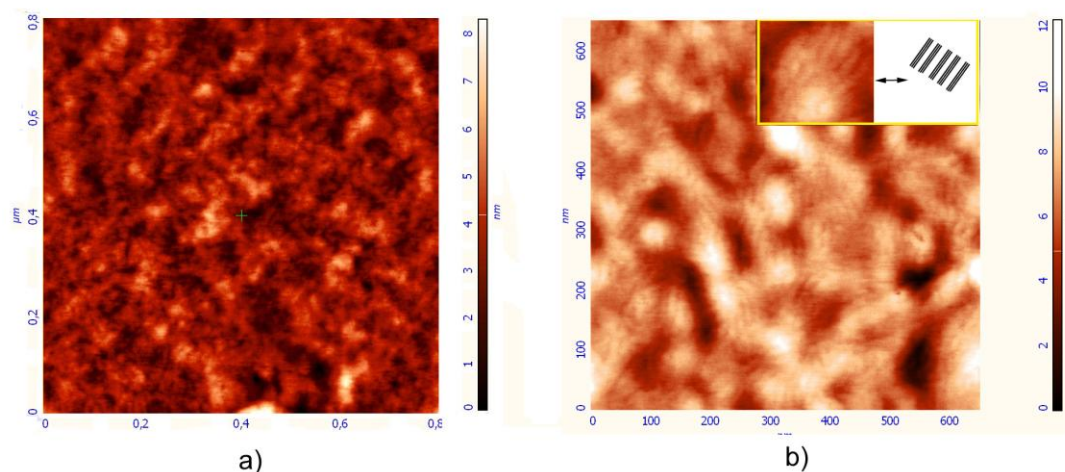
Figures 3-4 show the P3HT morphology corresponding to two different silanizations where the silanizer alkyl chain length is varied i.e. methyl and octadecyl.



**Fig. 3.** P3HT layer deposited onto methyl silanized silicon oxide after annealing. (AFM phase image). In the inlet, a sketch of the filament model is presented.

The increase of the chain length produces an evolution from the typical filament-like morphology (Figure 3) to a globular morphology where the fundamental units are

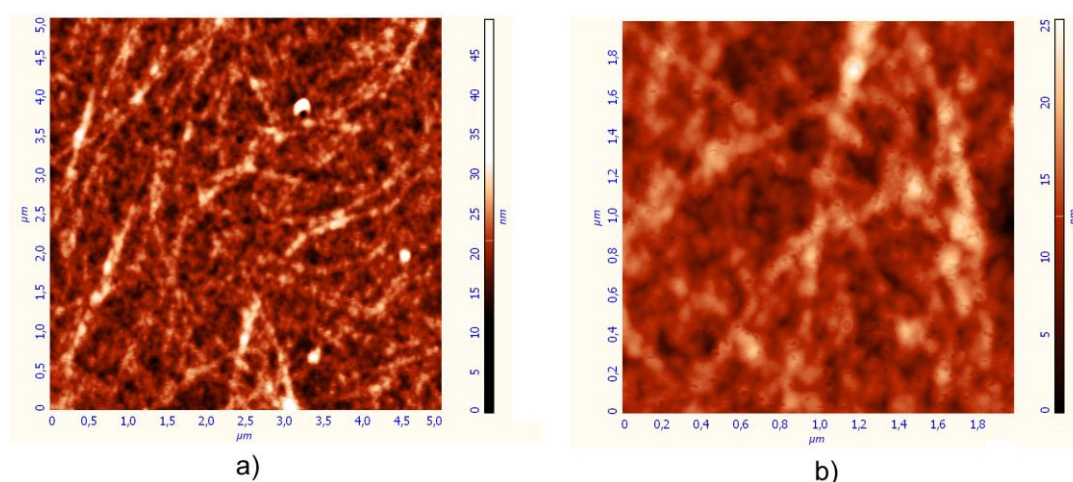
represented by needle-like structures (Figure 4). For both the filaments and needle features a model where a sequence of P3HT macromolecules  $\pi$ - $\pi$  interacting occurs perpendicularly to the substrate surface as shown in Fig. 1. However, while in the methyl case the sequence forms long filaments (order of micron) (see inset Figure 3), in the octadecyl case, the sequence is limited to 20 macromolecule units [27] thus giving rise to needle like units (see inset Figure 4b). In both the cases the layers have been annealed in order to improve the macromolecule order (see XRD experiments). The effect of the annealing is to improve the image contrast hence the evidence of morphological features. Figure 4 shows the P3HT/OTS before (a) and after (b) annealing as an example.



**Fig. 4.** P3HT morphology corresponding to OTS silanization before (a) and after (b) annealing, respectively. In the inset of Figure 4b, a detail of needle-like structures and the corresponding simplified model sketch is shown.

#### -Phenyl case

The silanization with PhTS introduces phenyl groups perpendicular to the SiO<sub>x</sub> surface.



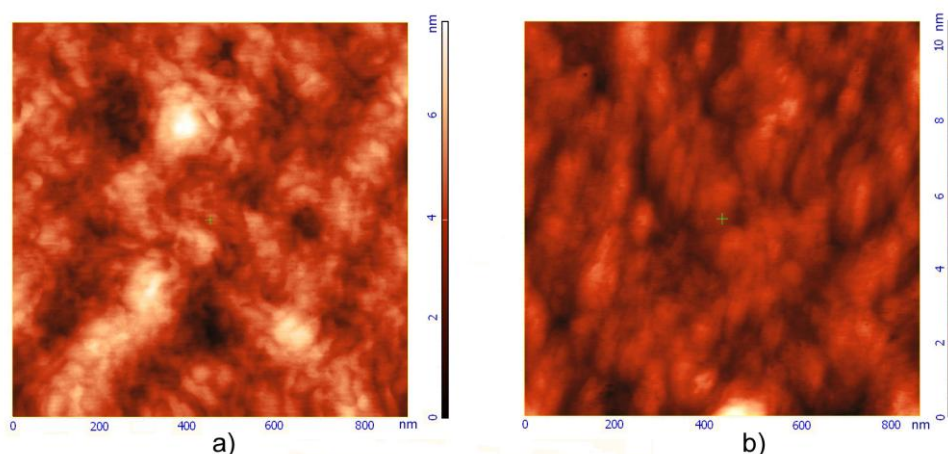
**Fig. 5.** Effect of the silanization with phenyl silane onto the P3HT layer. b) a magnification of a).



According to Figure 4, the P3HT organizes into curved filaments as in the methyl case even if the filaments are less packed and with a bigger curvature radius. For both the cases a difference with respect to the straight filaments corresponding to non silanized case occurs.

#### -Effect of the silanizer polarity

In Fig. 5 the P3HT morphology corresponding to a propyl and amino propyl silanization is presented. For propyl, a globular structure similar to the OTS case occurs for the overlying P3HT layer while the presence of a terminal amino group in the propyl chain induces a preferential orientation of the rod-like units.



**Fig. 6.** Comparison between P3HT morphologies corresponding to silanizations with propyl silane a) and aminopropyl silane b).

### Conclusions

The influence of the silanization of the silicon oxide substrate onto a P3HT thin layer morphology (average thickness: 20 nm) and chain orientations have been investigated by varying the silanizer substituent in terms of alkyl length (comparison between methyl, octadecyl silane, presence of aromatic ring (phenyl) and polarity (3-aminopropyl compared with propyl silane). The usual aptitude for straight filament formation, in which  $\pi$ - $\pi$  interacting P3HT macromolecules face together in edge-on conformation, is tuned by the different silanizers. While the methyl silane induces the formation of P3HT bent filaments, a longer chain gives rise to short term needle-like structures where P3HT molecules involved in the  $\pi$ - $\pi$  interaction are no more than 20 units. The substitution of methyl groups with phenyl rings as silane substituent maintains the filament morphology even if in the phenyl case the P3HT filaments are less bent and more elongated. Finally the insertion of a polar amino group in the propyl substituent produces a better orientation of the needle-like units. Also for this case, XRD results indicate an edge on conformation even for the layers closer to the surface (5 nm), in agreement with the recent investigation on P3HT thin films [28]. On these bases, a different conformation only for the first layer as claimed by Kim [24] cannot be ruled off. To shed light on this aspect a very detailed study on ultrathin films using synchrotron radiation is in progress. Indeed, the morphology of underlying SAM layer due to the SiO<sub>x</sub> silanization has an influence in determining the final P3HT morphology. In order to correlate the TFT electron mobility with morphological/structural features a very detailed work has been

performed, allowing for the description of a reliable electron mobility mechanism [27].

## Experimental part

### *Sample preparation*

P3HT used was Merck product having  $\cong 98\%$  regioregularity, as determined by  $^1\text{H}$  NMR investigations. The molecular weights were evaluated by gel permeation analysis (GPC) relative to polystyrene standards. The measurements were carried out by using a SEC System Waters GPCV 2000 apparatus equipped with a differential-refractometer 410 on line detector and Waters Styragel columns at room temperature using THF as an eluent. A MW value of 25 KDalton and a polydispersivity of 1.7 were derived, corresponding to an average polymer length of 33 nm, assumed in extended chain conformation. DSC analysis revealed a melting point close to 215 °C.

Silicon oxidation has been performed by using a water solution of  $\text{H}_2\text{O}_2/\text{HCl}$  at 80 °C for 10 minutes (mean oxide thickness: 200 nm). The fabrication of SAMs was performed for the different cases by immersing Si (001) into the following solutions:

-Dimethyldichlorosilane (DMDS): solution of 1cc of DMDS into 10 cc of chloroform for 30 minutes.

-Octadecyltrichlorosilane (OTS): a OTS/ hexadecane solution of an order of magnitude of 1mM has been used for 15 h.

-Phenyltrichlorosilane (PhTS): solution of 1cc of PhTS into 10 cc of chloroform for 30 minutes.

-Propyltrichlorosilane (PTS): solution of 1cc of PTS / 10 cc of chloroform for 30 minutes.

-Aminopropylsilane (APS) was prepared according the procedure reported in ref. 22.

P3HT was deposited from a toluene solution (8 mg /cc toluene) by spin coating at a speed of 3000 rpm giving a thickness of 20-25 nm on the average. Annealing has been carried out for each case in a dry box under nitrogen flux at temperatures from 80 °C to 200 °C for ten minutes then slowly cooled down to room temperature. In order to make the P3HT layer even thinner, a peeling method was used by using polydimethylsilane (PDMS). The procedure consisted of a deposition of few drops of the corresponding monomer onto the P3HT layer to be removed and subsequent annealing at 80 °C allowed for the polymerization and the following wrench. [25]

### *AFM measurements*

Morphological characterization has been carried out with commercial AFM NT-MDT in non-contact force modulation mode. Both height images and phase images was contemporarily taken. The typical parameters used were 50-60% of the original modulation amplitude as reference signal at the cantilever resonance. Thickness measurements have been performed by mechanically removing a portion of the polymeric layer and measuring with AFM the corresponding step height.

## XRD measurements

XRD experiments were carried out on films at room temperature by using Cu-K $\alpha$  radiation. A computer controlled Siemens D-500 diffractometer equipped with Soller slits, graphite-monochromator, and a Vortex detector to enhance the signal/noise ratio, in Bragg–Brentano geometry were used.

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