Observation and analysis of flat-lying molecular layer via scanning probe microscopy

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Summary

The analysis of the formation of ultra-thin organic films is a very important issue. In fact, it is known that the properties of organic field effect transistors are strongly affected by the early growth stages. For instance, in the case of sexithiophene deposited on thermal SiOx, the presence of domains made of molecules with the backbone parallel to the substrate surface has been indirectly evidenced by photoluminescence spectroscopy and directly imaged by Ultrasonic Force Microscopy. On the contrary, photoluminescence spectroscopy have failed to observe sexithiophene deposited on native SiOx. In this paper, we show how Scanning Probe Microscopy techniques combined with post-annealing process are able to identify a flat-lying molecular layer on the native SiOx. By using Lateral Force Microscopy and Atomic Force Microscopy in Intermittent Contact we investigate its mechanical properties and, by using Ultrasonic Force Microscopy, we directly identify the structure of flat-lying molecular layer. Finally, we show how the post annealing process can address the growth of organic materials towards a “driven layer-by-layer growth” to both improve the surface coverage and reduce the domain boundaries effects in organic field effect transistor.

Key words: scanning probe microscopy, organic growth, α-Sexithiophene, flat-Lying molecules, annealing.

Introduction

In organic electronics, conjugated oligomers represent an important class of molecules besides conjugated polymers (Malliaras, 2005). While polymers are generally more amenable to processing, the oligomers, having lower molecular weight, can be deposited in a much more controlled fashion down to the molecular scale. As a consequence, the oligomer film morphology is easier to characterize and to relate with physical properties such as molecular conformation and organization, crystallinity, grain size and orientation (Pope, 1998). This provides an important path to identify and explore key issues necessary for improving organic electronic properties such as charge conductivity and recombination (Fraboni, 2009). In particular, the interface between the organic film and the dielectric substrate has turned out to be vital for the performances of organic transistors and the morphological properties of the first Monolayer (ML)* have been correlated to the conduction properties of these devices (Dinelli, 2004 a, b). This is particularly important for the fabrication of electroluminescent devices where it is necessary to combine two organic films providing, respectively, paths for electron and hole conduction (Hepp, 2003).

Therefore, in the past few years, the initial growth stages (i.e. at a sub-monolayer coverage) have been intensively studied by both X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM). Whereas it has provided accurate details on the crystallinity (i.e. unit cell size and molecular orientation) and grain size distribution, XRD is applicable to relatively thick samples when at least the first ML is complete (Moulin, 2006).

**A coverage of one Monolayer (1 ML) is defined as the amount of material needed to cover the substrate with one layer of T6 molecules having the backbone perpendicular to the surface.*

On the other hand, AFM represents the key approach linking XRD data and film morphology in the real space, as well as providing access to local information with nanometer scale spatial resolution rather than averaged over a large sample area (Annibale, 2007).

In particular, when conjugated oligomers are deposited on chemically inert and flat SiOx surfaces, firstly form stable nucleus of few molecules. Subsequently, nucleus evolve as islands during the deposition and coalesce one each other to form a continuous organic layers (Wu, 2007). The film growth is characterized by two contemporaneous molecular configurations: the upright configuration of the islands and the flat-lying configuration in between of them. During the film's growth, these flat-lying molecules can affect islands coalescence in two ways: if they remain flat, an empty space in between islands is created; otherwise, if they are collected from islands, the interfacial disorder between islands is increased (domain boundaries).

These flat-lying molecules are observed in the case of sexithiophene (T6) sub-monolayer films deposited on thermal silicon dioxide (SiO_2) surfaces. Photoluminescence spectroscopy (PS) has revealed crucial information on the molecular organization allowing to identify a significant population of domains made of T6 molecules lying flat in direct contact with the substrate (Loi, 2005). PS has allowed for the first time to provide insight into the initial growth stages of organic films in reason of the T6 J-aggregates formed on thermal SiO_2 (Da Como, 2006). Authors observed that besides the upright configuration with molecular axis normal to the sample surface, T6 molecules can also arrange themselves in a flat-lying configuration. Recently, these T6 flat-lying aggregates on thermal SiO_2 are directly imaged by Ultrasonic Force Microscopy (UFM) (Dinelli, 2011).

To extend the T6 *J*-aggregates investigations, PS measurements have been repeated on chemically treated SiO_x to correlating it with the surface physical/chemical properties (Dinelli, 2006). PS had failed to image flat-lying molecules on native SiO_x. This experimental result allows to infers that such T6 aggregates are formed in reason of the hydrophobic nature of the thermal SiO_2. In reason of the result, further investigation are necessary to investigate how T6 molecules are organized on the native SiO_x.

In this paper, we present an investigation carried out by means Scanning Probe Microscopy (SPM) techniques to identify and analyse the T6 flat-lying aggregates when T6 molecules are deposited on native SiO_x. In particular, T6 films in sub-monolayer regime are investigated by using AFM operating in Contact Mode (CM), Intermittent Contact Mode (ICM) and in the Ultrasonic Force Microscopy (UFM) configuration (Kolosov, 1993). By controlling carefully the experimental conditions of the growth, we have indirectly observed the physical properties of an homogenous layer of flat-laying molecules which covers the native SiO_x surface in between T6 islands. In addiction, this homogenous layer can be re-organized through a short post-annealing process (not exceeding 1 hour). When a sub-monolayer film is deposited on an heated substrate, this process supplies exceeding energy able to move flat-lying molecules. In reason of their weak bond with the substrate they can move towards islands (which are energetically favoured) increasing the island's size. In such way we have realized a *quasi*-complete monolayer film.

Materials and Methods

T6 molecules, purchased in powder from Sigma Aldrich®, were vacuum sublimated on Si substrates (*p*-type, ρ=2 - 10Ωcm) with native SiO_x. The amount of molecules deposited on the SiO_x substrate and the deposition rate *r* were kept constant to 50 ng and 5 ng/min, respectively. They are measured through a Quartz Micro-Balance (QMB) placed near to the substrate to monitor the amount of deposited molecules with 1ng of sensitivity. To avoid thermal drift effects in the QMB measurements, it is cooled by a water cooler to keep its temperature constant (20°C). This sensitivity allow us to estimate the surface coverage with an error lower than the 1%. T6 molecules deposited on SiO_x substrates form rounded islands covering approximately the 30% of the SiO_x surface (sub-monolayer regime).

To implement the post-annealing process, films are grown with the substrate kept to 80°C and 100°C. These temperature are chosen in reason of the negligible amount of molecules re-evaporated from the heated substrate ("complete condensation" regime) (Venables, 1984). Conversely, for

120°C the 90% of the total deposited molecules are re-evaporated, so this temperature is useless for our research aims. After the molecules deposition, the substrate is kept for 1 hour at the same temperature (post-annealing process – 80°C or 100°C), while the sample and the Knudsen cell shutters are closed. In this period, the temperature of the T6 powder in the Knudsen cell is decreased from 230°C to 180°C, to avoid the sublimation of molecules. After the post-annealing process, the substrate has been cooled to RT with the same temperature decay time (approx. 10 minutes) and removed from vacuum through a Fast Entry Lock (FEL).

The morphologies of sub-monolayer T6 films and the mechanical properties of the flat-lying molecular layer have been observed by using several SPM techniques: 1) ICM used in attractive and repulsive regimes (Garcia, 2002); 2) CM measuring the later deflection of the cantilever, namely Lateral Force Microscopy (LFM) (Sundararajan, 2000); 3) UFM which is a technique based on a standard AFM operating in CM with the additional application of an ultrasonic vibration to the substrate, well above the AFM cantilever resonance. In this way, the friction force can be eliminated because the tip-sample contact is broken several times while the tip is laterally moved during the imaging process (Dinelli, 1997).

Results and Discussions

In order to investigate the flat-lying molecular layer, firstly we study the effect of the post-annealing process. The averaged surface coverages $\langle\Theta\rangle$ has been calculated for each temperature (80°C and 100°C) and without (or with) the post-annealing process. We define $\langle\Theta\rangle$ as the mathematical average of three coverages measured from three AFM topographic images (20 μm x 20 μm) of three different surface regions. Figure 1 shows the $\langle\Theta\rangle$ results.

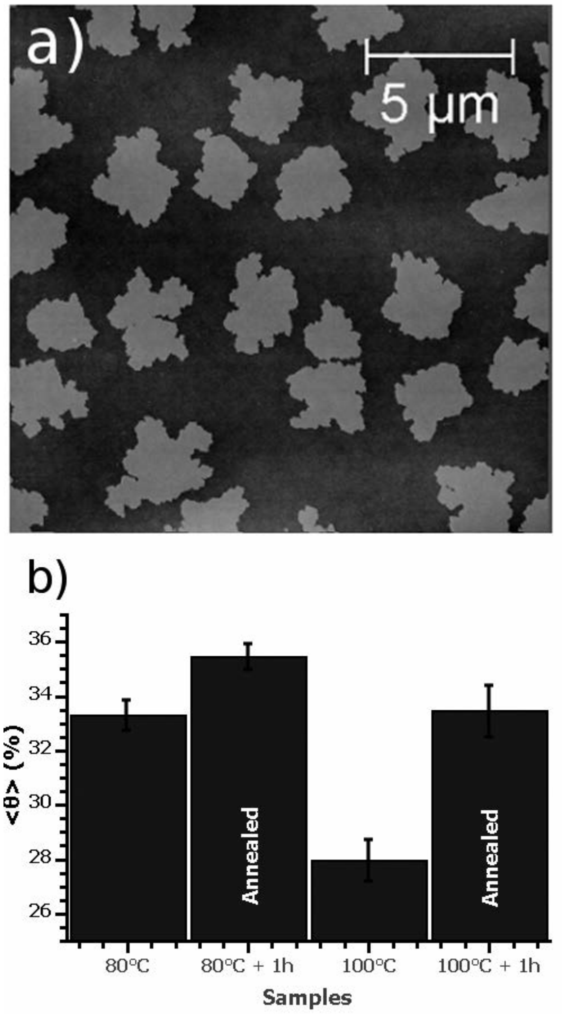

Figure 1. a) AFM topographic image of T6 islands grown on native SiO_x. Islands are red labelled through the threshold process by means of islands are selected through their height (upright molecules are 24 Å long) and $\langle\Theta\rangle$ is calculated. b) Averaged surface coverage $\langle\Theta\rangle$ (in percentage) vs. the sample type. A coverage of 100% corresponds to a surface completely covered by upright T6 molecules.

The statistical analysis of $\langle\Theta\rangle$ shows clearly that the post-annealing process increase the islands size. For 80°C, $\langle\Theta\rangle$ (expressed in percentage of the surface covered by T6 islands) runs from 33% to 36% (+3%), while for 100°C it increases from 28% to 34% (+6%). $\langle\Theta\rangle$ values for samples grown at 80°C and 100°C (without post-annealing) suggest a slightly re-evaporation of T6 molecules during the deposition (-6%) but can be considered negligible respect to the 90% observed for 120°C.

These results indicate that some molecules (not visible in AFM topographic image) are present in between islands and they are re-organized through the post-annealing process. In particular, the heat (energy) provided 1 hour after the deposition gives energy and time to move the not-organized molecules towards islands thus increasing their size. This is particularly evident in the 100°C case, where the size is increased up to 6% while, in the 80°C case, molecules have not enough energy to be collected by islands (just 3% more).

The surface coverage $\langle\Theta\rangle$ is an indirect measurement of the re-organization effect induced by the post-annealing process. Now, it is important to turns out these experimental observation by using SPM techniques which give high spatial resolution and local physical information. Assuming a flat-lying molecular layer in between islands (even after the post-annealing process), it is clear that a molecular layer on bare SiO_x change its friction property.

To investigate friction we used LFM technique that is extensively used to study friction of various samples with ultralow loads (few nN) and scan range from tens of micrometer down to the atomic scales. In general, the LFM technique is a contact technique, i.e. the tip is permanently in contact with the surface. During the surface scan, the microscope feedback system use the vertical movements induced by the cantilever deflection (laser spot is moved up and down on the photodiode – Normal forces F_n) as signal for measuring the surface topography. At the same time, due to the friction forces F_f between the tip and the surface, the cantilever is slightly twisted (friction signal). The cantilever torsion is measured by the lateral movements (left and right) of the spot on the photodiode. During friction measurements, the friction signal from both forward and backward scans are needed in order to understand the origins of the observed friction forces. It is well known that when an AFM tip is scanned across a sample surface, the measured friction forces (or lateral forces) are generated by both material effects as well as topography-induced effects (Sundararajan, 2000). Those effects are independent to the scan direction, hence they are eliminated subtracting the friction data of the backward scan from that of the forward scan, leaving only material-induced effects (friction forces) (Muller, 1997).

The surface friction is well described by the friction coefficient μ, which is a dimensionless scalar value that describes the ratio of the force of friction between two bodies (F_f) and the force pressing them together (F_n). In general, $\mu = \mu_S + \mu_k$ but the static friction is usually larger than its kinetic counterpart, so $\mu \approx \mu_S$. In first approximation, F_f and F_n are proportional to the torsion and the deflection differences (as measured from the photodiode - nA). The deflection difference (ΔD) is measured as the difference between the cantilever deflection when the tip doesn't interacts with the surface and the set-point deflection. On the other hand, the torsion difference (ΔT) is measured as the difference between the lateral position of the laser spot when the tip doesn't interacts with the surface and the statistical torsion values (Gaussian distribution) measured from the lateral force images. For our measurements we used soft cantilever (NT-MDT CSG10, k = 0.11N/m) and we apply low load (4 nN at most). In such conditions, we can evaluate the friction coefficient as $\mu^* = F_f$

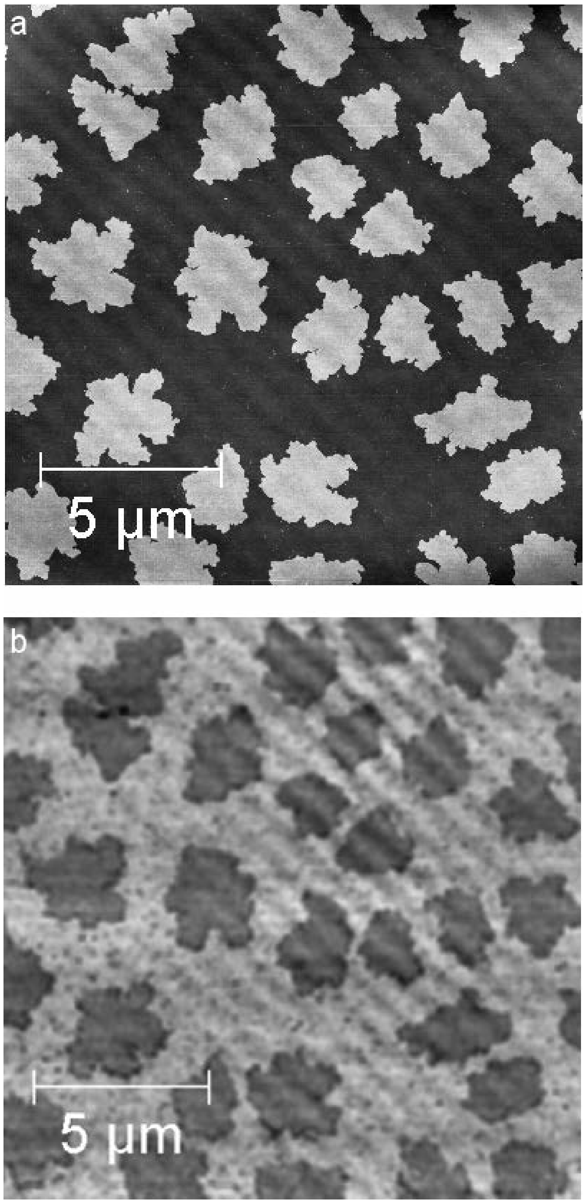

Figure 2. a) AFM topographic image of T6 islands grown on native SiO_x. b) Friction image obtained by subtracting the friction data of the backward scan from that of the forward scan.

/ $F_n \propto \Delta T/\Delta D$, where μ^* indicates the friction coefficient when the cantilevers are not calibrated. It is useful to study the trends the surface's friction vs. substrate temperature and post-annealing process. Figure 2 shows the friction image subtracting friction data in backward and forward scans. Topographical artefacts were eliminated and two regions are clearly visible: bright regions (substrate) and dark regions (T6 islands). Afterward, μ^* has been evaluated from the statistical analysis of friction images of T6 samples compared to the friction image of bare SiO_x (Figure 3).

The evolution of friction coefficient confirms the presence of a flat-lying molecular layer which increase the friction force between tip and sample. As expected, the sample grown at 80°C shows higher friction force (lower thermal energy, higher amount of molecules in between islands), that decreases with the increases of the substrate temperature and the post-annealing process. This trend sustains two hypothesis: a) an homogenous flat-lying molecular layer exists in between islands; b) the post-annealing process promote the re-organization of these molecules. Notably, the sample grown at 100°C, and annealed for 1 hour, shows the same friction coefficient of the bare SiO_x suggesting a complete re-organization of the molecules.

In order to both confirm the results obtained up to now and reach high spatial resolution images, we performed AFM measurements in ICM. It is a less invasive technique respect to the CM technique so, in principle, a proper setting of the working conditions for phase contrast in ICM should allow one to identify the flat-lying molecular layer with high spatial resolution. When ICM works with a high amplitude set-point (i.e. small reduction of the free cantilever oscillation amplitude, namely attractive regime (Garcia, 2002)), the averaged tip-sample force $<F_{ts}>$ is about a few hundreds of pN (Holsher, 2006). On the contrary, when the amplitude set-point is decreased, $<F_{ts}>$ is increased up to 20 nN (namely repulsive regime). Figure 4 shows a topographic and phase images in attractive (A) and repulsive (R) regimes for the 80°C sample (the sample with the higher amount of molecules in between islands).

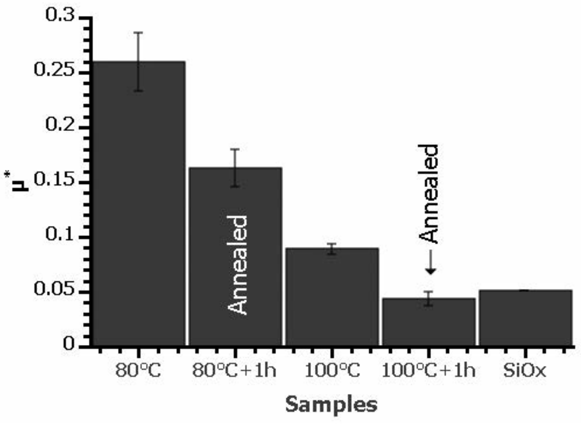

Figure 3. Evolution of the friction coefficient μ^* vs. substrate temperature and post-annealing process, compared to the bare SiO_x.

By looking the phase images in attractive regime, the substrate shows a modulation of the contrast as if it be composed by mounds. Conversely, in repulsive regime the contrast is flattened and mounds are replaced by dark regions rounded by brighter edges. This qualitative observation can be investigated by comparing the average roughness R_q of the interstitial regions surrounding the T6 islands measured in both regimes. In attractive regime, $<F_{ts}>$ is about 400 pN and R_q is (2.7±0.5) Å while in repulsive regime, where $<F_{ts}>$ is about 16 nN, R_q become (1.9±0.3) Å. This R_q variation indicates the presence of a compliant molecular layer on the SiO_x substrate, which can be compressed when $<F_{ts}>$ increases. The presence of this compressible layer is also confirmed by the height distribution measured on the substrate in both regimes (Figure 5a – up). The height peak shift of 2.5 Å passing from attractive to repulsive regime. In repulsive regime the number of counts for lower height is notably increased to represent a surface flattening when $<F_{ts}>$ increases. As comparison we have measured the height distribution in both regime for bare SiO_x (Figure 5a – down). Here, the height peak shifts less (1 Å) therefore a variation of 2.5 Å is understandable only if we consider the surface coated by a soft and compressible layer.

As shown in Figure 4, for ICM we have also measured the shift of the cantilever oscillation. Its absolute value shows the operating regimes: Attractive (phase value >90°) or Repulsive (phase value <90°) (Garcia 2002). However, even in the phase contrast no clear structure appears in the images, suggesting that the flat-lying molecular layer is homogenously distributed. As described by Garcia (Garcia 2002), the phase is correlated to the energy provided by the tip and dissipated into

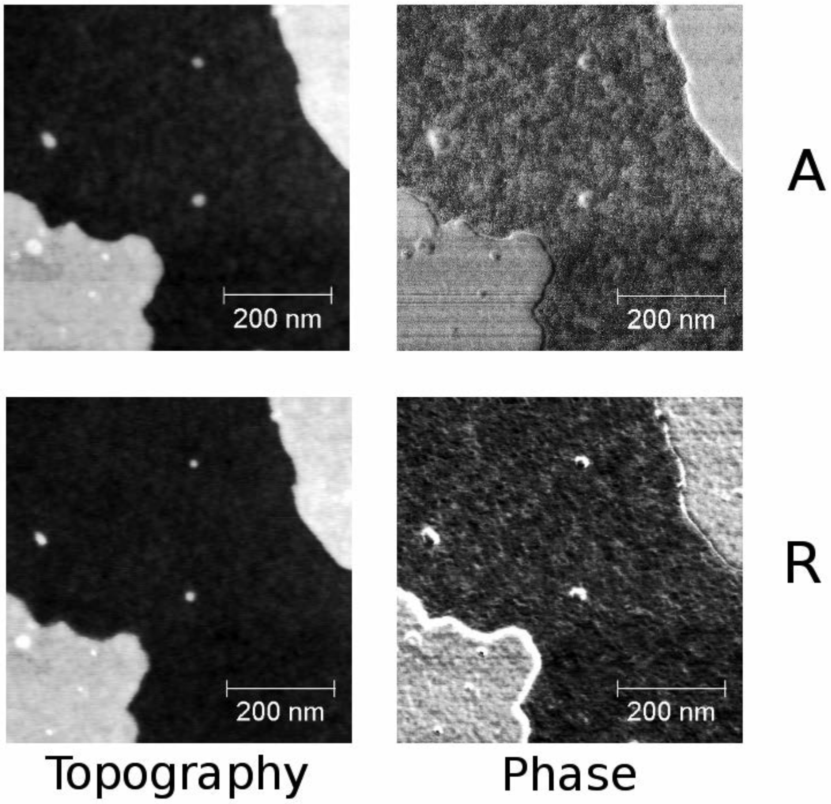

Figure 4. AFM topographic (left) and phase (right) images in attractive (A-up) and repulsive (R-down) regimes. In the attractive regime, the tip interacts with the surface through the van der Waals forces. On the contrary, in repulsive regimes it interacts through the Hertz repulsion forces.

the contact region of the surface, through the following relationship:

$$E_{diss} \approx \frac{\pi \cdot k \cdot A_{SP}}{Q} \cdot \left(A_0 \sin\phi - A_{SP}\right)$$

where k and Q are the elastic constant and the quality factor of the cantilever, respectively, A_0 is the free amplitude oscillation, A_{SP} is the set-point amplitude oscillation and ϕ is the phase value.

As shown in Figure 5b, the energy dissipated into the substrate increases with the increasing of the substrate temperature and the post-annealing process. This trend is in agreement with the presence of a soft layer over the SiO_x, i.e. less damping of the cantilever oscillation (less energy dissipated) is expected for softer samples (with Young's modulus $E \leq 10GPa$) (Tamayo, 1996). The high dissipated energy onto the sample grown at 100°C of substrate's temperature and post-annealed for 1 hour, validates this observation because the AFM tip interacts with the bare silicon oxide ($E \approx 130GPa$). The same energy trend is observed for attractive and repulsive regimes where the tip interacts with the sample through the van der Waals force and the Hertz repulsive force, respectively (Tamayo, 1996). In the repulsive regime, cantilever's damping is due to the viscoelastic properties of the material so, with the re-organization of the molecular layer, the energy dissipated (damping) is increased. The same behaviour is observed in attractive regime where the long-range range adhesion hysteresis is responsible to the high dissipated energy (Gomez, 2010).

CM and ICM have shown indirectly the presence of a flat-lying molecular layer and its mechanical properties, but they are too much invasive to image it with high spatial resolution. For such reason we used Ultrasonic Force Microscopy (UFM) (Kolosov, 1993) that provides both the nanometer scale spatial resolution and the material sensitivity necessary to identify both upright and flat-laying molecular layer in the initial stages of T6 film growth. It is based on a standard AFM operating in

CM with the additional application of an ultrasonic vibration to the substrate by means a modified sample holder. It is composed by a piezoelectric disk with resonant frequency of 2MHz, glued to a standard metallic sample holder. The samples under investigations are then directly attached to the top of the piezoelectric disc via a thin layer of ultrasonically transparent and replaceable binder, namely phenylsalicilate. Ultrasonic vibration (2MHz) is well above the AFM cantilever resonance. In this way, the friction force can be eliminated because the tip–sample contact is broken several times while the tip is laterally moved during the imaging process. Any possible damage to the sample or the tip is thus minimized. Additionally, UFM is material sensitive (Briggs, 2010), so we are able to differentiate where the flat-lying molecular layer isn't homogenous, imaging it with unprecedented spatial resolution.

Figure 6 shows topographic (a-left) and ultrasonic (a-right) images of the sample grown with 80°C of substrate temperature. The ultrasonic contrast on the substrate is homogeneous (most of the surface is bright) besides some dark spots uniformly distributed. By zooming on a SiOx surface region where no topographical features are present (Figure 6b-left), it is clear that the surface is covered by an homogenous layer (gray coloured) with black spots (two of them are indicated by white arrows). This observation is confirmed by the statistical measurements of the contrast on that region (Figure 6b-right); it is a convolution of two Gaussian distributions, one centred on (5.14±0.12)V (lower statistical weight) and the other one centred on (5.26±0.12)V (higher statistical weight). In reason of the high material sensitivity of the UFM technique, that contrast can be associated to the SiO$_x$ substrate (lower value) and to the flat-lying molecular layer (higher value).

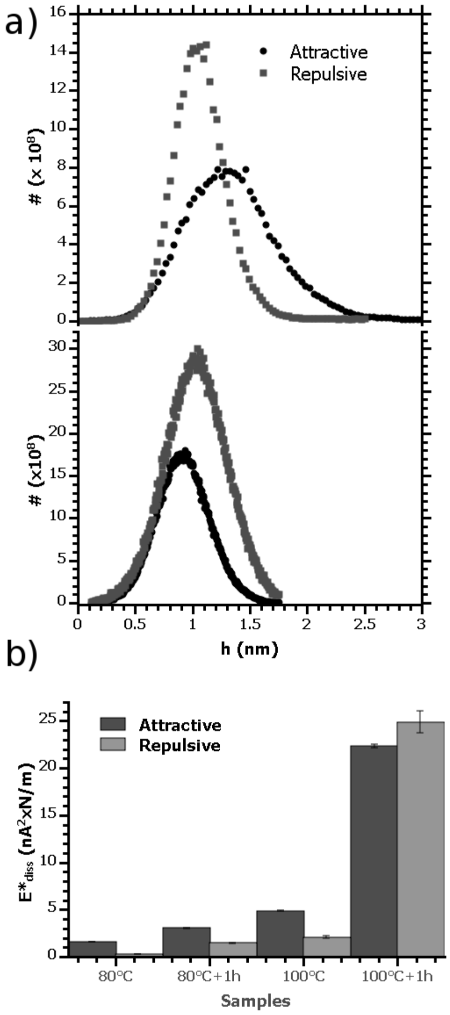

Figure 5. a) Cumulative height plots for the sample grown at 80°C (up) and the bare SiO$_x$ (down). The height peak correspondent to the substrate is shifted when the tip-sample interaction pass from the attractive (black spots) to the repulsive (grey spots) regime. b) Energy dissipated vs. substrate temperature and post-annealing process where *E^*_{diss}* indicates the energy dissipation for not-calibrated cantilevers, as described for the friction coefficient.

Table 1. Ultrasonic Deflection ud (in V) measured on both the substrate and the T6 islands, and their difference. An increase of the ud difference value corresponds to a more stiff substrate. In fact, the calculated difference (last column) shows that the post-annealing process free the substrate from the flat-lying molecular layer increasing the ud difference. All measurements were made with cantilevers with spring constant of 0.9 N/m, with the exception of the measurement signed by * which is done with a cantilever stiffer (3N/m). To be compare with the other measured, the measured ud value should be multiply roughly for the spring constants ratio, i.e. 3/0.9.

Samples	*Substrate (V)*	*6T islands (V)*	*Difference (V)*
80°C → RT	5.4748	4.1666	1.3082
80°C → 1h → RT	3.0214	2.5415	1.4397*
100°C → RT	1.1389	0.7326	0.4063
100°C → 1h → RT	1.5230	0.9622	0.5608

Besides the sample grown at 80°C, all the other samples are investigated by UFM. Table 1 summarizes the obtained results which confirm what observed by using CM and ICM: a flat-lying molecular layer in the interstitial regions between T6 islands exist and it is re-organize by means the post-annealing process.

Conclusions

T6 films with sub-monolayer coverage are grown with different substrate temperature (80°C and 100°C) and constant amount of deposited molecules. Afterwards, they are submitted (or not submitted) to a post-annealing process.

Samples are investigated by using Scanning Probe Microscopy techniques. They have shown that a flat-lying molecular layer exists on the SiO_x surface and it can be re-organized by means the post annealing process. It shows an homogenous distribution of flat-lying molecules compared to the mound distributions observed on thermal SiO_x. This suggest that the PS contrast elsewhere observed is due the hydrophobic nature of the thermal SiO_x. In addiction, the sample grown at 100°C and post-annealed for 1 h have shown a complete molecular re-organization as proved by the decreasing of the friction force (LFM), the increasing of the dissipated energy (ICM) and the material contrast observed by ultrasonic contrast.

In perspective, this method can address the growth of organic materials towards a “driven layer-by-layer growth” which will be able to both improve the surface coverage and reduce the domain boundaries effects (in reason of the improved molecular organization) which are detrimental for the electrical performances of the organic devices.

Acknowledgements

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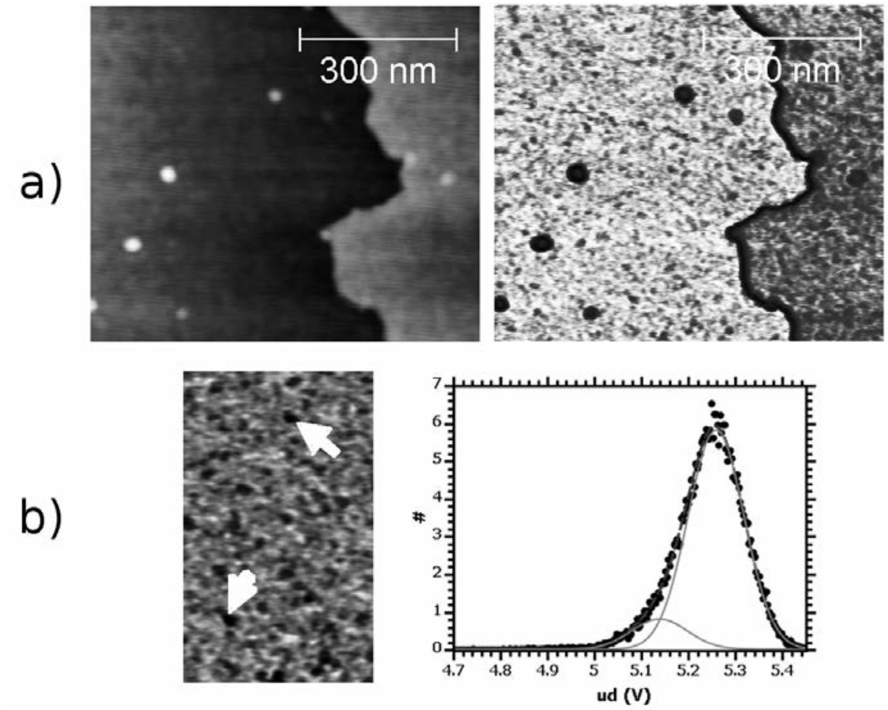

Figure 6. a) Topographic (left) and ultrasonic (right) images of the 80°C sample; b) Ultrasonic image of a substrate region free of topographic features (left) and correspondent statistical distribution of the ultrasonic deflection ud (expressed in volts) that is induced on the cantilever by the piezoelectric plate (right). White arrows show two dark spots correspondent to the SiO_x substrate.

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