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Substrate temperature dependence of the structure of polythiophene thin films obtained by Matrix Assisted Pulsed Laser Evaporation (MAPLE)

*V. Califano^{*1}, F. Bloisi^{1,2}, L. Vicari^{1,2}, M. Barra^{1,2}, A. Cassinese^{1,2}, E. Fanelli³, R. Buzio^{4§}, U. Valbusa⁴, A. Carella⁵ and A. Roviello⁵*

¹ CNR-INFM Coerentia c/o Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy. E-mail address: valeriacalifano@hotmail.com, Tel: 00390817682434.

² Dipartimento di Scienze Fisiche, Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy.

³ Department of Materials and Production Engineering, Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy.

⁴ Nanomed Labs, Department of Physics, Università of Genova and Advanced Biotechnology Center, Via Dodecaneso 33, 16146 Genova Italy.

⁵ Department of Chemistry, Università degli Studi di Napoli Federico II, Via Cinthia, 80124 Napoli, Italy.

§Present address: CNR-INFM LAMIA Laboratory of Artificial and Innovative Materials C.so Perrone 24 16152 Genova Italy.

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Short Title: Temperature dependence of the structure of polythiophene thin films obtained by MAPLE

* Author to whom any correspondence should be addressed

Abstract

Thin films of head-tail (H-T) regio-regular poly[3-(4-octyloxyphenyl) thiophene] (POOPT) were grown using the MAPLE (Matrix Assisted Pulsed Laser Evaporation) technique in which the target is a frozen solution of the polymer in chloroform. Target evaporation was obtained by laser irradiation at 1064 nm and substrates were kept at different temperatures. Information concerning the preservation of the polymer local chemical structure following laser irradiation was obtained by FTIR (Fourier Transform InfraRed) spectroscopy. Based on FTIR data, the chemical structure of the deposited polymer seemed to undergo little or no damage. From UV-Visible spectroscopic analysis, it turned out that the degree of order of the film is strongly affected by the substrate temperature: the polymer was deposited in a disordered form on the substrate at room temperature whereas on the hot surface we locally obtained the π -stacked structure characteristic of polythiophenes. Atomic force microscopy (AFM) images showed that the polymer formed aggregates of different dimensions ($<1\mu\text{m}$ to $5\mu\text{m}$) with a columnar shape and showed micrometric domains with sharp and apparently regular edges for the film grown on a hot substrate.

Electrical measurements performed by a standard two-probe technique confirm that the structural order degree strongly affects the film charge transport properties.

1 Introduction

Conjugated polymers are attractive materials because they potentially join the electrical properties of semiconductors with the easy processing of polymers. They have a framework of alternating single (σ) and double ($\sigma + \pi$) carbon-carbon bonds, which is responsible for their semiconducting properties. The separate sets of the π -bonding orbital energy levels and π^* antibonding orbital energy levels form the valence band and the conduction band,

respectively. The difference in energy between the two levels produces the band gap that determines the electrical properties of the material.

Among semiconducting conjugated polymers, polythiophenes have attracted much attention for their chemical stability and structural versatility. Furthermore, alkyl-substituted polythiophenes have self- π -stacking ability, and π -stacking structures are essential for the optical and electrical properties of these polymers.

Polythiophenes have found a wide range of potential applications as polymer light emitting diodes (PLEDs) [1,2], photodiodes for plastic solar cells (PVs) [3,4] and as active material for stimulated emission in lasers [2]. In these potential applications, it is essential to obtain thin films with (1) great regularity of the extended conjugated chain structure and/or the chain packing (π -stacking) to improve charge mobility and hence conductivity, (2) flat surfaces and minimum roughness to assure ohmic contacts, (3) a high control of the film thickness. Moreover, such devices often require multi-layer deposition. Solvent processing techniques, such as spin coating or drop casting, are not always suited, especially in terms of homogeneity of the film and thickness control. Furthermore, they are unsuitable for multi-layer deposition and patterning.

A promising technique for polymer thin film deposition, developed at the Naval Research Laboratory (Washington, DC) [5] and particularly appropriate for multi-layer deposition, patterning and thickness control, is MAPLE (Matrix Assisted Pulsed Laser Evaporation). It is derived from Pulsed Laser Deposition (PLD) and allows overcoming the problems related to the latter. In particular the photochemical decomposition produced by direct interaction of laser radiation with the material. In fact, even if some polymers have been successfully deposited with PLD, the mechanism of deposition, consisting in a pyrolytic decomposition followed by a re-polymerisation on the substrate, can work only with addition polymers [6].

In MAPLE, a pulsed laser beam impacts a target made of a dilute frozen solution of the polymer in a volatile and light absorbing solvent. The incident laser pulse vaporizes the frozen solvent when the absorbed laser energy is converted to thermal energy. The evaporation starts from a homogeneous expansion of the surface region overheated above the limit of its thermodynamic stability (explosive disintegration followed by expansion of the matrix). The vaporised solvent entrains the polymer molecules in the so-called plume [7-9]. The solvent molecules are pumped away by a vacuum system, the polymer molecules form a film on a substrate placed in the path of the plume.

MAPLE provides a softer mechanism of ablation than PLD allowing the deposition of intact polymer molecules. This can happen following one of two possible mechanisms. If the light absorption coefficient is higher for the solvent than for the solute most of the laser energy is absorbed by the solvent. If, as in our case, the solvent is almost transparent to laser radiation, which is absorbed by the solute molecules, due to low concentration of the latter, we have a highly non homogeneous light absorption. Laser evaporation of a frozen dilute solution of an absorbing solute in a transparent solvent can be assumed similar to laser ablation of a solution with spatially heterogeneous absorption [10]: the ablation efficiency of the heterogeneous solution is higher by more than one order of magnitude with respect to homogeneous absorption (as in PLD). This implies that using MAPLE technique it is possible to reduce laser pulse energy by one order of magnitude thus greatly reducing the negative effects of laser irradiation.

MAPLE has been used to deposit poly(3-hexylthiophene) films using orthoxylene as a solvent and a laser wavelength of 266 nm [11]. In this occasion it was shown that the substrate temperature influences film properties, even if only very small changes were observed.

For our MAPLE deposition, we used 1064 nm laser radiation wavelength and chloroform as solvent matrix since UV radiation often used in MAPLE [11-14] can produce both radical

dissociation of the solvent [14], giving rise to highly reactive species, and photochemical reactions with the polymers, particularly those containing strongly absorbing moieties [15]. For example, aromatic rings exhibit strong electronic transitions near 248 and 193 nm. The experimental procedure has been described in detail in previous works [16,17].

Here we study the dependence of the film properties on the substrate temperature for head-tail (HT) regio-regular poly[3-(4-octyloxyphenyl) thiophene] (POOPT) (chemical structure showed in figure 1), showing that MAPLE allows obtaining regio-regular H-T POOPT with different crystallization status. In particular we show that the characteristic π -stacked structure essential for its electronic and opto-electronic applications can be obtained by a hot substrate deposition procedure.

2 Experimental

2.1 Materials

Regioregular H-T POOPT with mean molecular weight $M_n = 16500$ was synthesised as specified elsewhere [18]. Chloroform solutions of POOPT (0.25% wt) were used as target solutions for MAPLE depositions. CHCl_3 (purchased from Sigma-Aldrich) of >99% purity was used as solvent.

2.2 MAPLE procedure

MAPLE depositions (deposition system is sketched in figure 2) has been carried out using a Q-switched Nd:YAG pulsed (7 ns pulse width) laser operating at $\lambda = 1064$ nm (laser fundamental harmonic). We operated with a laser fluence of 600 mJ/cm^2 and a repetition rate of 10 Hz. The laser spot on the target, which was elliptical because of the 45° laser incidence angle, was 0.32 cm^2 . The number of pulses delivered by the laser for each sample was 45000.

The vacuum deposition chamber contained a copper target holder of 2 ml capacity in thermal contact with liquid nitrogen contained in an external reservoir, so that it was possible to freeze the target *in situ*. The target holder was provided with a two-dimensional automatic movement system that allowed the full scan of a rectangular area on the target to avoid overheating and drilling. A flux of dry helium passed in the chamber throughout the pre-deposition operations in order to push off atmospheric moisture. As soon as the target was frozen, the helium flux was interrupted and the vacuum pump started operating. The final deposition parameters were pressure of about 10^{-5} Pa and target temperature of 103 K. The substrates were made of either a KBr pellet for allowing FTIR analysis or silica glass to allow UV-Visible analysis. Two sets of thin films were obtained with the substrate at room temperature (PTc and PTa) and another with substrate at 423 K (PTh). Samples PTa were post-annealed under vacuum at 423 K for 75 min (i.e. the time corresponding to a deposition of 45000 pulses at 10 Hz). The deposition parameters and features of the three set of samples are summarized in Table I. The thickness of the films was measured by a Tencor Alphastep IQ profilometer. The films are composed of gross particles dispersed on smoother layer. Hence the thickness was taken as the average of the smoother zones on more cuts.

2.3 Characterization

In order to detect possible chemical modification of the polymer, induced by its interaction with the laser, FTIR analysis was performed. FTIR elucidates the short-range structure of a material and allows identifying the possible chemical bonds and functional groups of a molecule. For polymers, FTIR measurements are primarily indicative of the basic repeat unit. FTIR absorption spectra of the films deposited on KBr pellets were recorded, in the 4000 - 400 cm^{-1} range, using a spectrometer equipped with a DTGS KBr (deuterated triglycine sulphate with potassium bromide windows) detector. A spectral resolution of 2 cm^{-1} was

chosen. The spectrum for each sample represented an average of 64 scans, which were corrected for the spectrum of the blank KBr pellet.

UV-Vis spectroscopy was used to investigate the structural order of the deposited polymer. In fact, there is a strong correlation between the electronic structure (and hence the optical properties) and the backbone conformation and packing of POOPT. UV-Vis spectra in the 250-800 nm range were recorded with a JASCO V560 spectrophotometer. Since the samples appeared rough, preliminary reflectance spectra were recorded in different points (not shown) in order to proof the optical homogeneity of the samples. No relevant differences were noted between the reflectance spectra of the different points for each sample.

To analyse the morphology of the deposited films, AFM measurements were finally carried out with the Explorer AFM by Thermomicroscopes-Veeco, operated in tapping-mode in ambient air.

The film electrical properties were investigated by performing current-voltage (IV) measurements, with a standard two-probe technique in which both the applied voltage and the measured current were controlled by a Keithley 487 picoammeter. To this aim, silver electrodes were sputtered on POOPT films, selecting active channels with length and width of 100 μm and 5 mm, respectively. All measurements were performed in air by using a probe station with metallic tips mounted on micrometric slide plates.

3 Results and Discussion

To establish whether the chemical structure of the polymer monomer unit underwent modifications or decomposition following irradiation by the laser, FTIR analysis of the three samples were performed and the results compared with the FTIR spectrum of a POOPT film obtained from casting of a drop of solution (figure 3).

The FTIR spectrum of the solution cast film shows a large number of bands, some of which are very characteristic of the polymer functional groups. In the range 1450-1650 cm^{-1} there are several bands, which arise from the contribution of both the main chain and the side chain. Polythiophene main chain has in fact two main bands at about 1460 and 1510 cm^{-1} , which arise from the symmetric and asymmetric ring-stretching mode respectively [19]. Besides, in the 1450-1650 cm^{-1} there are features of the phenyl ring of the side chains, corresponding to different stretching modes of the aromatic C=C bond. These bands are normally weak in unconjugated systems, but conjugation with any double bond causes a pronounced increase of their intensity. The very strong band appearing at 1245 cm^{-1} is characteristic of the =C-O stretching vibration of aromatic ethers [20]. A feature appearing at 830 cm^{-1} is due to the aromatic C-H out of plane deformation of the main chain [19]. Finally, in the high wavenumber region, two strong bands at 2925 and 2855 cm^{-1} are due to the asymmetric and symmetric C-H stretching vibrations of the methylene groups (CH_2), while the two weak shoulders at 2953 and 2868 are due to the asymmetric and symmetric C-H stretching vibrations of the methyl groups (CH_3).

MAPLE deposited samples show all spectra, which are very similar to the one of solution cast POOPT in terms of both peak positions and relative intensities. Furthermore, no additional bands due to decomposition appear. The three broad bands appearing between 3300 and 3560 cm^{-1} in the spectrum of PTc (trace d of figure 3) are due to water absorbed by the hygroscopic KBr pellet.

Hence, the irradiation of the POOPT target solution with infrared radiation produces the deposition of films with little or no damage in terms of monomer unit chemical structure.

The three films obtained appear different in colour, and in particular PTc is orange while PTh and PTa (the latter originally orange) are violet. This phenomenon is not new: Regioregular poly[3-(4-octylphenyl) thiophene] (POPT) is known to exist in two different forms; the

pristine form, obtained by spin casting, is red, and upon thermal treatment or in presence of vapour of chloroform irreversibly converts into a more crystalline form, purple, obtained also by solution casting [1,2,21]. This shift in absorption was explained as being caused by ordering of the polymer chains, involving a more planar conformation. Actually if the bulky side chains of the polymer are in a random coil rather than a planar conformation, they force the main chain out of planarity, decreasing the effective conjugation length (increasing the band-gap) of the polymer, thus giving a blue shift in absorption [1].

In figure 4 we report the UV-Vis absorption spectrum of the three samples deposited by the MAPLE technique compared with the spectrum of the solution cast film. All spectra have two main absorption bands, one in the visible region and another in the UV region.

The band in the UV region, located around 300 nm, is attributed to the absorption of the conjugated side chains [22-25]. Despite the fact that this band gives information about the side chains, in particular concerning their conformation with respect to the main chain, we will not discuss its variations (although evident) in this work, mainly because the spectra were acquired on glass rather than on quartz substrates, the absorption of which starts just under 300 nm, interfering with that of the film.

The band in the visible region is attributed to the π - π^* transition of the conjugated polymer main chain [26-29]. The values of the maximum λ_{\max} for the four samples are reported in table 2, together with the value of the optical band gap $E_g^{\text{opt}} = hc/\lambda_{\max}$.

Considering the spectrum of PTC sample deposited on the cold substrate (Figure 1, trace d), the maximum is located around 470 nm (≈ 2.6 eV). This value is commonly reported for polythiophenes in solution or in regio-random solid-state films [18,26].

The spectrum of the violet sample PTh deposited by the MAPLE technique on the hot substrate ($T \approx 423\text{K}$, trace b) shows a maximum at 560 nm (≈ 2.2 eV), with a red shift of around 70 nm with respect to the value shown for the PTC in the solid state and to the values

usually reported for the sample in solution.

This shift of the absorption maximum of conjugated polymers, that can range from as little as a few nm to around 100 nm, depends on the relative conformations of the polymer chains in the solution and solid-state phases. Its position depends on both the molecular conformation and supermolecular structure of the polymer, i.e. on the degree of π -stacking of the polymer molecules. If the polymer backbone is twisted so that the rings comprising the main chain are not coplanar, then the effective conjugation is decreased, the HOMO-LUMO gap is increased, and the polymer absorbs at shorter wavelengths [27-29].

We see in figure 4 that the maximum position of the PTh sample coincides with that of the solution cast film, also reported (Trace a). This last has already been reported and discussed in literature [18] for regio-regular POOPT. Alkyl-substituted aromatic or heteroaromatic polymers tend to crystallize in the π -stacked, lamellar structure, with the consequence that the main chain adopts a planar conformation with an increased effective conjugation length and longer wavelength absorption. We assume this to be indicative of the fact that the deposition on a hot substrate give rise to a π -stacked structure with a conjugation length similar to that obtained by solution casting, i.e. the polymer chains after laser irradiation preserve their length enough to give the same optical behaviour and this is important for the functionality of the material. The effect of the temperature is then to grant more mobility to the polymer chains, which have the chance to reach the semi-crystalline state, lower in energy with respect to the high entropy amorphous state.

On the other end the maximum around 470 nm of PTc sample seems to be indicative of a random coil conformation. Hence, the film deposited by MAPLE on the cold substrate was obtained in a disordered structure of coiled molecules. The deposition of a more disordered film with a blue shift in absorption is unusual for POOPT which, contrary to POPT, when deposited from solution, even with a fast technique such as spin casting, is always in the

planar π -stacked form [18].

Poly(3-hexylthiophene), structurally similar to POOPT, was already deposited by MAPLE and obtained directly in the π -stacked form, with results slightly depending on substrate temperatures [11]. The film obtained on the substrate at room temperature already resulted in a red shift, although smaller with respect to that obtained on the hot substrate. Nevertheless the difference observed was very small (≈ 13 -16 nm).

In figure 4 we report also the UV-Vis spectrum of the orange film (PTa sample, trace c) obtained by vacuum annealing of a cold deposited film for 75 min at a temperature of around 423K. Its maximum in the UV-Vis spectrum shifted towards the same position of the solution-cast film. However the maximum of absorption of this film had a smaller red shift with respect to solution cast film.

Another difference between the three spectra is that both PTa and PTh spectra show a rising of the absorption curve soon after the main absorption maximum on the shorter wavelength side, around 500 nm. This rising is more pronounced in the PTa sample, where it has a more evident aspect of absorption maximum. In the overall the region below 500 nm of the PTa and PTh sample resembles more closely that of the PTc sample than that of the solution cast film. This is evidence of the existence of two degrees of order in the films obtained by MAPLE both on the hot substrate and with the annealing procedure. Hence, in the PTh and PTc films there is the coexistence of two distinct phases of POOPT; one refers to the twisted POOPT chains, the other is the untwisted lamellar π -stacked structure. The coexistence of the two structures was already reported in the thermochromism of poly[3-(2'-(octyloxy)phenyl)thiophene in the solid state [26] and in the solvatochromism of POOPT in solution [30]. Hence in the MAPLE films the effect of the temperature, both for the hot substrate and the annealed samples, is not such to promote the complete transition of the random coil structure to the lamellar π -stacked structure (at least for the temperatures and

times used in this and similar [31] experiments we have carried out), the conversion being more incomplete for the PTa sample.

Solution cast, PTa and PTh sample, besides the maximum at about 560 nm, show two shoulders at 615 nm and 680 nm. The origin of these multiple peaks (commonly called vibronic “fine structure”) on the main π - π^* absorption peak is still a matter of some debate. It has been ascribed to absorption of polymer segments with different effective conjugation lengths [19], to vibronic coupling [32], to Davydov splitting of the exciton levels by inequivalent sites in the solid [33], and to combinations of Davydov splitting and the effects of exciton band density-of-state structure [34]. These peaks are only observed in regio-regular, conjugated polymers in the solid state (or in colloidal aggregates that have molecular packing similar to that of the semicrystalline solids), and then only when the size of the side chains allows for close approach of the π -systems on neighbouring chains (π -stacking) [35,36].

The presence of the vibronic fine structure in the solution cast film UV-Vis spectrum has been already reported in literature [18]; its presence in the spectrum of the PTh and PTa sample confirms the presence of a π -stacked structure and the value of the optical band gap points out a conjugation length of PTh sample similar to that obtained by solution casting, while the conjugation length of the PTa sample is somewhat shorter.

Finally, in the UV spectra of PTa and PTh sample an absorption tail extend far on the low energy side. The absorption spectra of amorphous materials sometimes show an extended tail of photon energy below the bandedge. These tails correspond to transitions from localized states in the valence band (defects or impurities) to the extended states in the conduction band [37].

In figure 5 we can observe AFM images of sample PTh, PTh and PTa on KBr disks. The disks appeared homogeneously coated by the polymer, but polymeric aggregates, of few microns down to few hundred nanometres in size, are clearly visible. The films appeared then very

rough and columnar structures are barely visible. The roughness of PTC is about 800 nm on $50 \times 50 \mu\text{m}^2$. For PTh and PTa film it was not possible to obtain information because they are too rough.

On the image of PTh sample we can observe micrometric domains with sharp and apparently regular edges surrounded by randomly rough smaller grains. This is a further evidence of the existence of crystalline domains in a two-phase structure composed of amorphous random coil POOPT and π -stacked lamellar chains. On the PTa image such domains are not visible, which would confirm the lower degree of order of the sample grown on a cold substrate and then annealed with respect to the one directly grown on the hot substrate.

The presence of aggregates on the three films can be caused by intrinsic properties of the MAPLE technique [7]. However, optimal results in terms of surface morphology have actually been obtained by MAPLE: thin uniform films (< 50 nm) of various materials, such as functionalized polysiloxanes and carbohydrates [5], were deposited. In our case improving the morphology of the PTh film could lead to an increase of the polymer regular structures, which seem to be confined within the particles.

As usually reported in literature, polymer films with improved structural order better support the charge carrier transport, thanks to a stronger and more effective π - π inter-molecular interaction. This basic scenario is in good agreement with our studies, as prompted by figure 6, where IV measurements for PTh and PTa samples are reported.

At low electric fields ($E < 10^4$ V/cm), the current dependence on voltage is linear and the conductivity σ value can be extracted by the basic ohmic law. In this way, σ has been estimated to be about $2 \cdot 10^{-8}$ S/cm for the PTh film, which well agrees with the value evaluated for a spin coated film of the same polymer [38]. This conductivity value is only slightly smaller than that estimated for spin-coated films of the same material. Accordingly to this result, the assessed electrical performances of the deposited films are not limited by the

film quality. On the contrary, the conductivity value is almost one order of magnitude lower in the PTa case. At high fields, both curves show a super-linear behaviour, likely related to the presence of space charge effects and trapping mechanisms. No significant currents (lower than few pico-amperes which is the noise level of our experimental set-up) have been found in similar measurements carried out for PTc samples.

4 Conclusions

Regio-regular poly[3-(4-octyloxyphenyl) thiophene] was deposited as thin solid film by matrix assisted pulsed laser evaporation. FTIR spectroscopy indicates that no degradation of the polymer occurs during the deposition in terms of monomer unit chemical structure. The UV-visible absorption spectrum of the films is characteristic of a random coiled polymer for deposition on room temperature substrate and of a two-phase structure composed of random coiled polymer and π -stacked lamellar structure for deposition on a hot substrate, where the π -stacked chains have effective conjugation length similar to that of solution cast film. On annealing, the cold deposited film reorganized its structure towards a similar but somehow more disordered two-phase structure. AFM investigation of films morphology revealed quite rough surfaces: further work is needed to improve this aspect, even if it does not sensibly affect electrical properties. The presence of micrometric and apparently regular domains surrounded by randomly rough smaller grains seems to confirm the existence of a two-phase structure in the PTh film.

Electrical measurements reveal a difference of at least three orders of magnitude between the conductivity of samples deposited on room temperature and hot substrate and one order of magnitude between the sample grown on the hot substrate and the one grown on the cold substrate and then annealed.

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Figure Captions

Figure 1. Chemical structure of poly[3-(4-octyloxyphenyl)thiophene].

Figure 2. MAPLE set up, top view. The target movement is in the yz plane, where z-axis is normal to the xy plane.

Figure 3. FTIR spectra of (a) solution cast and MAPLE deposited (b) PTa (c) PTh and (d) PTc films of POOPT.

Figure 4. UV-visible spectra of (a) solution cast and MAPLE deposited (b) PTa (c) PTh and (d) PTc films of POOPT.

Figure 5. AFM images acquired on (a) PTc film. The white bar corresponds to 780 nm. (b) PTh film. White bars are: 5 μ m (top) and 2.5 μ m (bottom); red arrows indicate micrometric domains with sharp and apparently regular edges surrounded by randomly rough smaller grains. (c) PTa film. The white bar corresponds to 5 μ m.

Figure 6. Typical IV measurements for PTh and PTa samples

Table Captions

Table 1. POOPT thin films obtained by MAPLE deposition, deposition temperature and visible features of the films.

Table 2. Values of the maximum absorption and of the band-gap of the POOPT thin films obtained by MAPLE deposition.

Figure 1

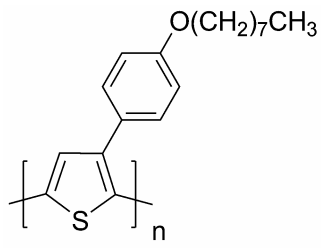


Figure 2

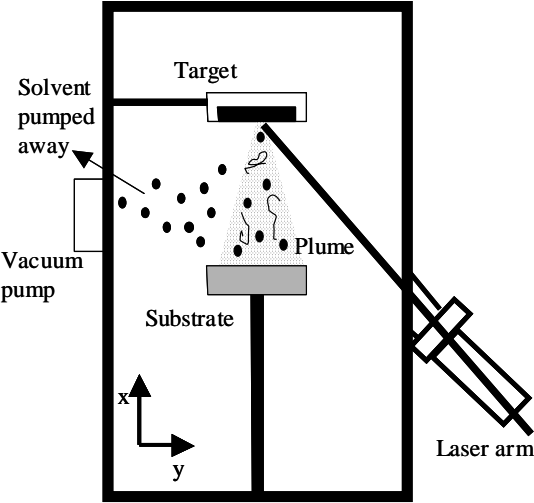


Figure 3

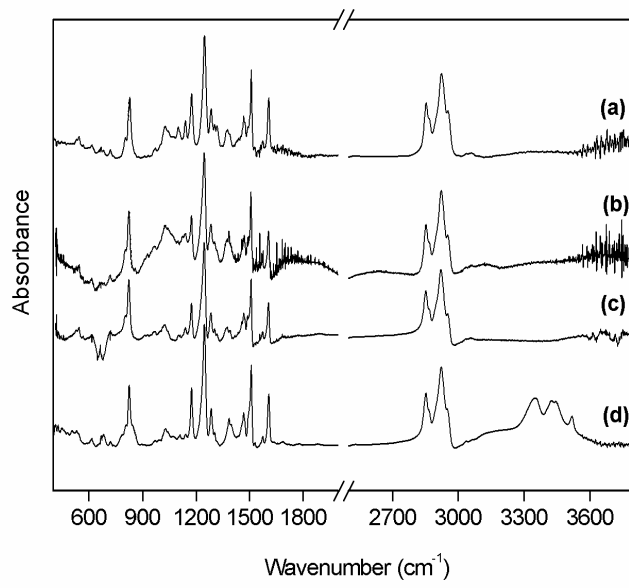


Figure 4

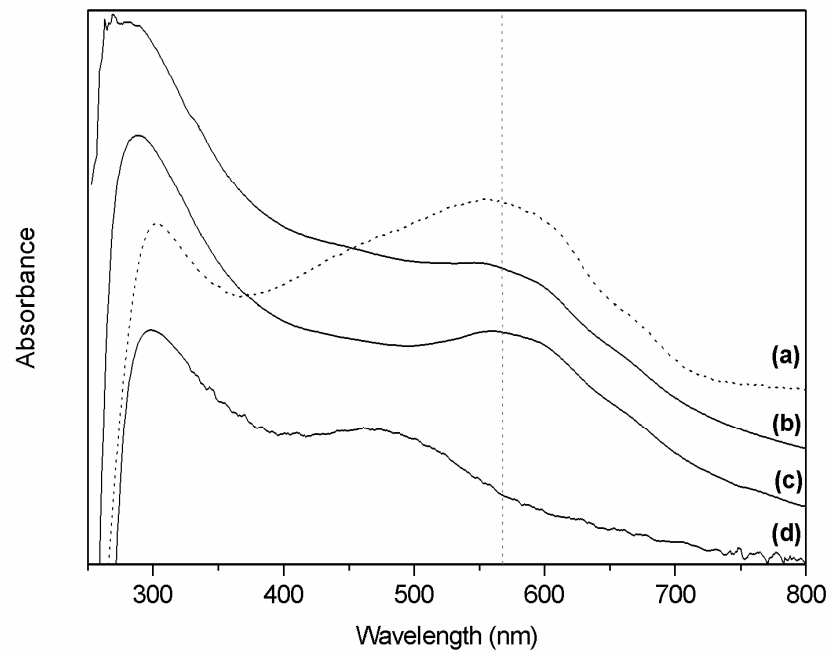


Figure 5

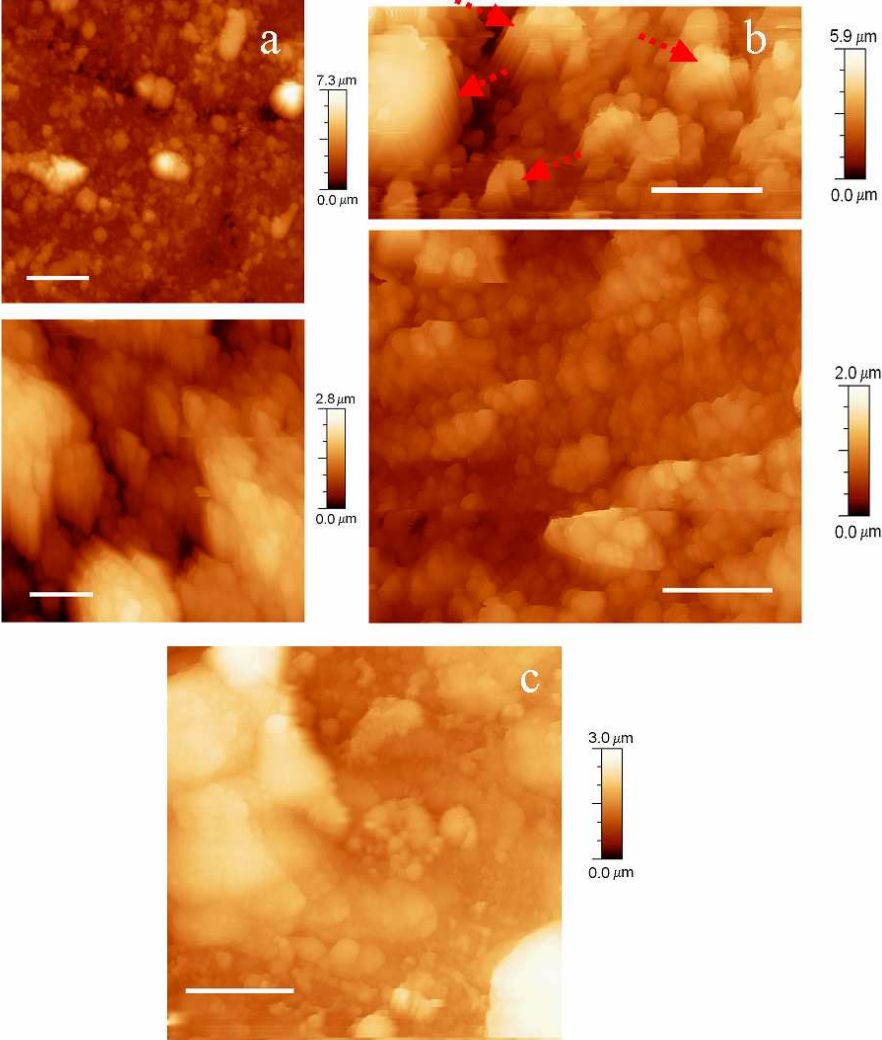


Figure 6

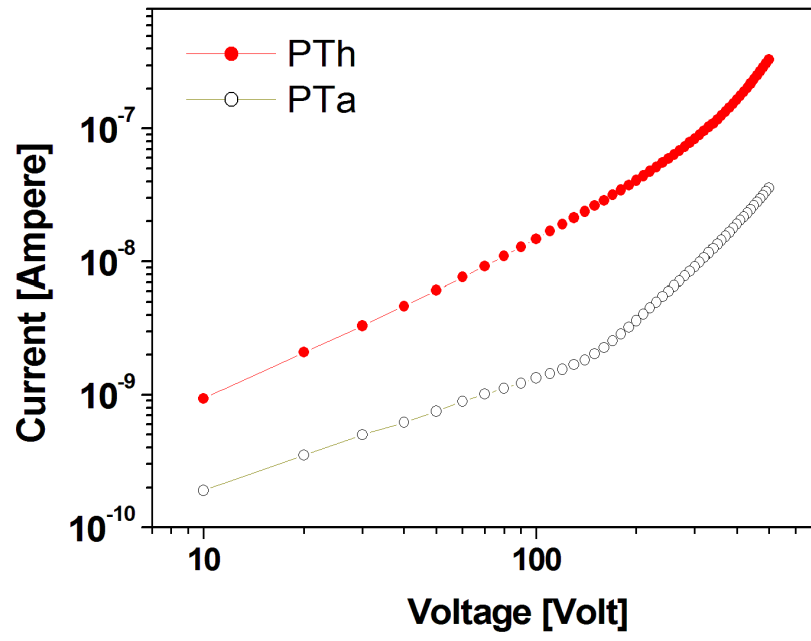


Table 1

Sample	Substrate T (K)	Nr of pulses	Post-treatment	Film colour	Film thickness (μm)
PTc	293	45000	-	Orange	1.0
PTh	423	45000	-	Violet	0.5
PTa	293	45000	293K for 75 min	Violet	0.6

Table 2

Sample	λ_{\max} (nm)	E_g^{opt} (eV)
Solution cast	560	2.21
PTh	560	2.21
PTa	550	2.25
PTc	470	2.64