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Growth of polyalkylthiophene films by matrix assisted pulsed laser evaporation

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Abstract

Films of regio-random and regio-regular poly(3-hexylthiophene) were grown by matrix assisted pulsed laser evaporation (MAPLE), where the target is a frozen solution of the polymer in orthoxylene. Analysis by MALDI mass spectroscopy confirms that the deposition does not result in any degradation of the polymer. UV–visible absorption spectroscopy and AFM images show that the structure of the films strongly depends on the temperature of the substrate during deposition. Best results are obtained when the substrate is held at low temperature.

Keywords: Thin solid films; Pulsed laser deposition; Conducting polymers; Organic electronic devices

1. Introduction

Materials used in organic electronic devices (OEDs) such as organic light-emitting diodes (OLEDs), organic thin film transistors (OTFTs) or organic photovoltaic cells (OPCs) include polymers and small molecules. These two classes differ by several characteristics, among which the way they are processed into thin layers to be incorporated in OEDs. As a rule, polymer films are processed by casting (e.g., dip and spin casting) while small molecules are deposited from the vapor phase. Each of these techniques presents advantages and drawbacks. Spin casting is easy and cheap, but it is not suited to most patterning techniques. Advantages of vapor deposition are easy control of the thickness, and possibility of monitoring parameters such as growth rate and substrate temperature, which gives access to a control of the structural organization of the film.

Pulsed laser deposition (PLD) has undergone intense development during the past years. More recently, this technique has been extended to various organic materials. Many of them are small molecules, including molecules of interest in OEDs [1,2]. PLD of polymers have also been reported.

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Addition polymers, such as polytetrafluorethylene (PTFE) or polymethyl-methacrylate (PMMA) are particularly well suited to this technique. According to Blanchet and coworkers [3] film formation occurs by way of pyrolytic decomposition, followed by repolymerization on the substrate. The use of PLD to deposit conjugated polymers used in OEDs is hampered by the fact that their structure cannot be subjected to the decomposition and reconstruction process that works with addition polymers. An alternative technique has recently been developed at the Naval Research Laboratory: Matrix assisted pulsed laser evaporation (MAPLE) [4]. Briefly, the target is a frozen matrix made of a dilute solution of the polymer in a volatile solvent. The solvent and solution concentration are chosen so that most of the laser energy is absorbed by the solvent and not by the solute. The former evaporates and is pumped away, thus inducing desorption of the later and its transfer to the nearby substrate. The low absorption of laser light by the solute prevents bond dissociation thus preserving its chemical integrity. MAPLE has been claimed to allow the deposition of homogeneous films of high molecular weight organics without damage. The technique has been applied to fragile compounds such as carbohydrates and biological materials.

In this communication, we apply MAPLE to regio-random and regio-regular poly(3-hexyl-thiophene) (RRa-P3HT and RR-P3HT, respectively).

2. Experimental

2.1. Materials

Regio-random P3HT (RRa-P3HT) was purchased to Aldrich and used as received. The Grignard metathesis method was used to prepare the regio-regular polyhexylthiophene (RR-P3HT). In a typical procedure, 2,5-dibromo-3-hyxylthiophene is converted to the 4-hexyl-5-bromo-2-thienyl magnesium bromine, which is polymerised using Ni(dppp)Cl_2. The polymer was precipitated in methanol and isolated by centrifugation. The resulting polymer was purified by Soxhlet extraction with methanol, hexane and chloroform. The yield of chloroform soluble fraction is 20%. The MALDI MS spectrum of the polymer in methylene chloride shows peaks between $m/z = 3324$ and $m/z = 6648$ in close agreement with data reported in the literature [5].

2.2. Film deposition

MAPLE was carried out in a vacuum chamber equipped with an optical window for laser illumination. The ablation targets were prepared with around 5 ml of 0.8 wt.% polymer solutions in orthoxylene. They were dipped into liquid nitrogen before being introduced in the vacuum chamber. A frequency-quadruple Nd:YAG laser (266 nm) was used for the desorption process. The laser beam was focused on the target (spot size 2–3 mm^2) under an incidence angle of 45°. The pulse duration was 5 ns with a repetition rate of 10 Hz. The energy density per pulse was 0.2 J/cm^2.

Prior to deposition, the chamber was evacuated to a background pressure of 10^{-6} mbar. The frozen target was held at around −70 °C by means of a flow of liquid nitrogen. (The melting point of orthoxylene is −25 °C.) Films were grown on silicon and sapphire substrates located at 35–40 mm from the target. During deposition, the pressure raised to around 10^{-4} mbar.

2.3. Characterization of the films

UV–visible absorption was recorded on films deposited on sapphire with a Varian CARY 500 differential spectro-photometer. The thickness of the films was determined with a Dektak 3 (Veeco) profilometer. Analytical matrix assisted laser desorption–ionization mass spectrometry (MALDI-MS) was performed at the Laboratoire de Chimie Structurale Organique et Biologique (University Pierre et Marie Curie, Paris VI).

AFM images were acquired at the Laboratoire des Milieux Nanometriques (Université d'Evry Val d'Essonne). In this case, the substrates were silicon wafers with a roughness of a few tenths of nanometer.

3. Results

3.1. Absorption spectra

The electronic absorption spectra of RRa-P3HT in solution and film are shown in Fig. 1. The spectra present a wide structure peaking at 428 nm for the solution and 429 nm for the film. The strong resemblance between the spectra is indicative of a highly disordered film, as can be expected from the irregular character of the polymer.

Turning to the regio-regular polymer, Fig. 2, we observe a drastically different behavior. The spectrum of the solution strongly resembles that of the regio-random polymer, with only a moderate red shift of the peak position (452 nm). Four films were made with RR-P3HT: one was spin-coated and the three others deposited by MAPLE on substrate held at −30, 20 and 80 °C, respectively. The spectra of the films present a substantial red shift, together with a structure where one can discern three different peaks. Both features are attributed to an increased coplanarity, leading to a higher degree of conjugation [6]. This can be viewed as an intra-chain effect promoted by the side chain regularity [7]. The absence of red shift in the regio-random polymer corresponds to an absence of coplanarity. We also note that full coplanarity is very unlikely, because the polymer is never fully regio-regular, and because most polymer films are mixtures of ordered and disordered domains. The amount of red shift can therefore be used as a qualitative indicator of the amount of coplanarity in the film. The position of the maximum absorption peak of each film is given in Table 1. According to that criterion the film can be arranged in decreasing order of coplanarity as follows: Spin-coated film, MAPLE@−30 °C, MAPLE@80 °C and MAPLE@20 °C.

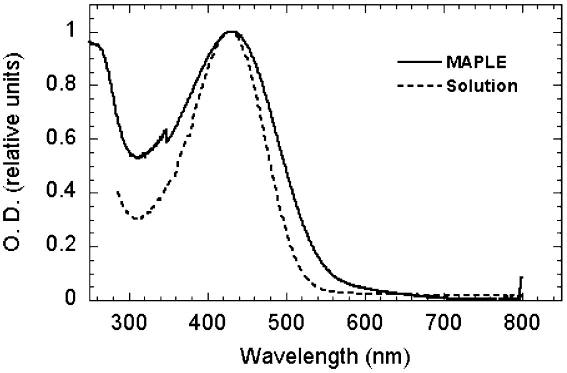

Fig. 1. UV–visible absorption spectra of regio-random poly(3-hexylthiophene) in solution and MAPLE film.

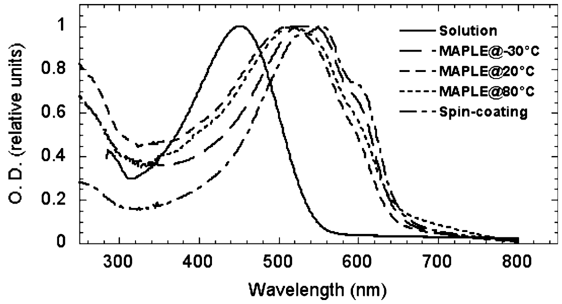

Fig. 2. Same as Fig. 1 for regio-regular P3HT. Films are deposited on substrates held at various temperatures. A spin-coated film is shown for comparison.

The thickness of the films is also indicated in Table 1. It is worth pointing out that the absorbance of the spin-coated and MAPLE@−30 °C films scales nicely with their respective thickness. This is not the case with the MAPLE@20 °C film, which seems to present a higher absorption. A possible explanation would be that the absorption coefficient of coplanar chains is less than that of non-coplanar ones. This would thus confirm the classification made above.

3.2. MALDI-MS

The MALDI-MS spectrum of a solution of RR-P3HT in methylene chloride is shown in Fig. 3(a). We estimated the average molecular weight to 4654 (around 28 monomers) and the polydispersity index to 1.05, which compare nicely with that published by other groups [5]. Note that the average molecular weight measured by MALDI-MS strongly depends on the solvent, and that the technique is poorly sensitive to high molecular weights. Accordingly, it can be expected that the data given by MALDI-MS underestimate the actual molecular weight.

To measure the spectrum of a film, we dissolved it in a small droplet of solvent. The corresponding

Table 1
Parameters of the MAPLE films as a function of the deposition temperature

Temperature (°C)	Time (min)	Thickness (nm)	λ_{max} (nm)	OD_{max}	Roughness (nm)
Spin-coated	–	350	554	0.27	10[a]
−30	90	300	528	0.24	0.6
20	3	Na	500	0.05	22
	360	200	513	0.36	70
80	240	Na	516	0.15	1.7

[a] For the spin-coated film, the roughness compares to that of the substrate (quartz-plate).

small amount of matter resulted in a substantial degradation of the signal on noise ratio, as shown in Fig. 3(b). However, the spectrum clearly shows regularly spaced peaks that can be attributed to polymer fractions. One may point out that the spread of the distribution in the low *m/z* region represents a higher fraction of that in the high *m/z* region than in the spectrum of the solution.

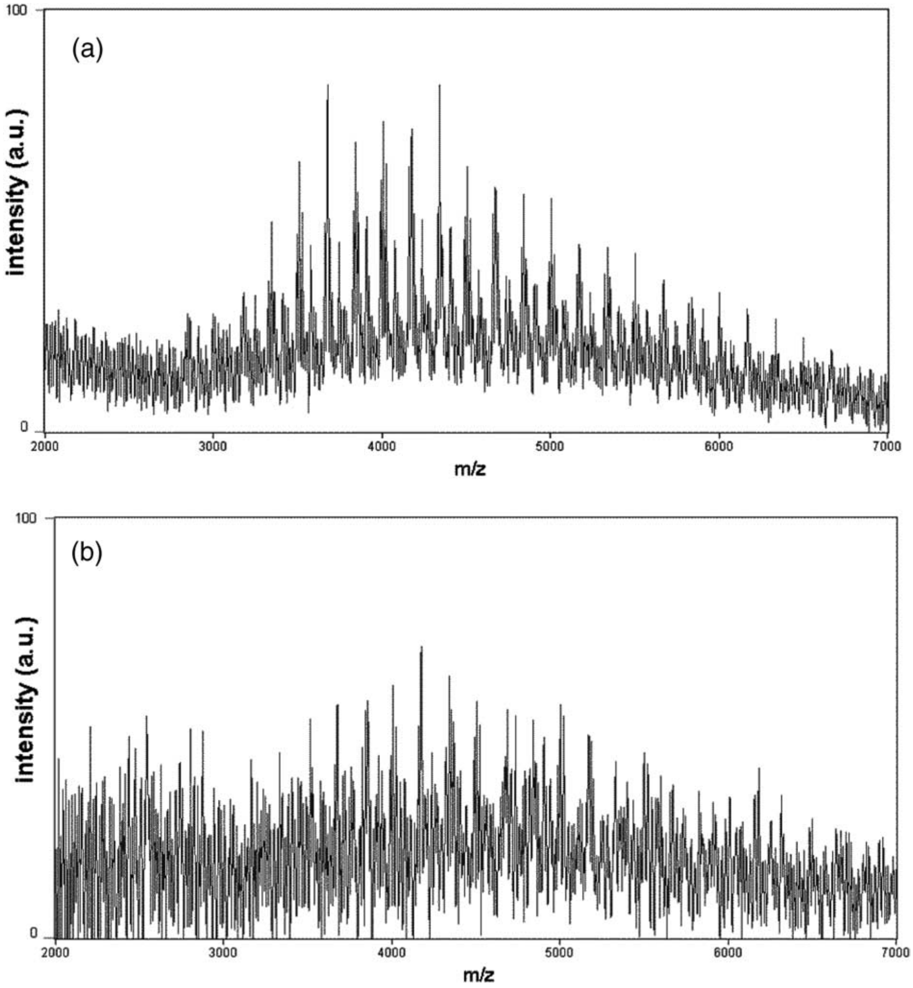

Fig. 3. MALDI-MS spectrum of RR-P3HT in solution (a) and MAPLE film (b).

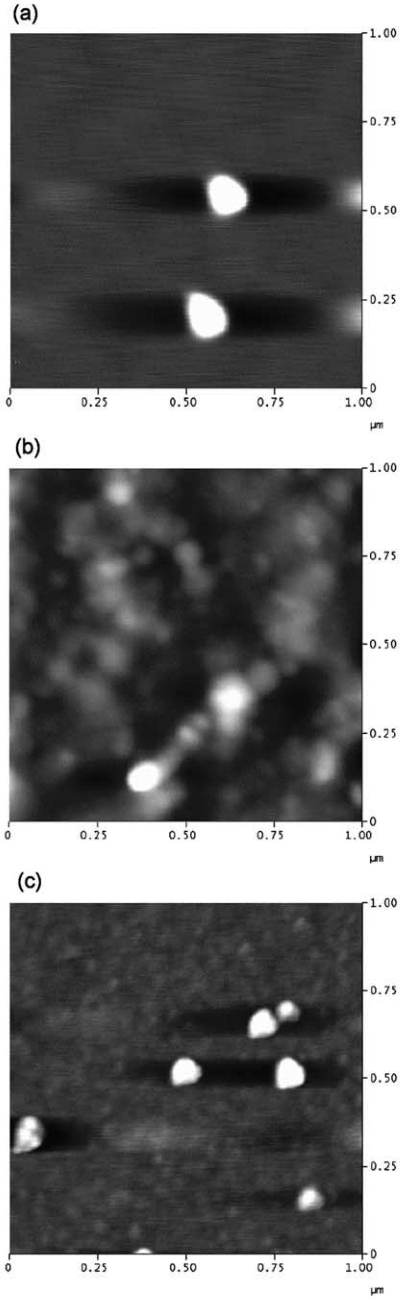

Fig. 4. AFM images of RR-P3HT MAPLE films deposited on substrates held at various temperatures: (a) −30 °C; (b) 20 °C; (c) 80 °C. In all cases, the image area is 1×1 µm^2.

However, peaks in this region are not regularly spaced, and are therefore not likely to originate from degradation of the polymer. We conclude that the deposition process does not cause any thermal breaking of the starting polymer.

3.3. AFM

The AFM images of RR-P3HT films grown at various substrate temperatures are shown in Fig. 4. Two features are worth mentioning. The first one is the presence of isolated peaks in the films grown at −30 and 80 °C. The height of these peaks ranges between 15 and 20 nm. Their origin is not yet elucidated. They could be due to aggregates already present in the solution, or that form during the deposition process.

The second feature is the strong dependence of the film roughness as a function of the substrate temperature. The estimated roughness is given in Table 1. On a film grown at −30 °C, we find a roughness of 0.6 nm, which compares with that of the substrate (silicon wafer). The roughness increases considerably on a film deposited at room temperature; it is 22 nm for a film with a deposition time of 3 min, and 70 nm for a deposition time of 180 min. Note that in this last case, the isolated peaks are almost completely obscured. Finally, raising the substrate temperature up to 80 °C results in lowering the roughness down to 1.7 nm.

For comparison, the roughness of the spin-coated film was estimated from the profile image recorded with the profilometer. As indicated in Table 1, we found a roughness of around 10 nm, which nicely compares to that of the substrate (quartz plate in that case).

4. Summary

Regio-random and regio-regular poly(3-hexylthiophene) was successfully deposited as thin solid films by matrix assisted pulsed laser deposition. In this technique, the target consists of a frozen solution of the polymer in orthoxylene. MALDI mass spectroscopy indicates that no degradation of the polymer occurs during the deposition process. With regio-random P3HT, the UV–visible absorption spectrum of the film is similar to that of the solution, while we observe a substantial red shift of the absorption maximum with regio-regular P3HT. This is interpreted as evidence for structural ordering in the last case. Best results in term of organization are obtained on films deposited on substrates held at low temperature. A similar trend is observed by atomic force microscopy, which shows a roughness of around 0.6 nm for films deposited at −30 °C and 70 nm for films deposited at 20 °C.

Works are currently in progress to realize organic electronic devices based on MAPLE films.

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