IN-SITU IODINE DOPED POLYTHIOPHONE-LIKE THIN FILMS OBTAINED BY POST-DISCHARGE RF PLASMA

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This work reports on the synthesis of polythiophene-like thin films by using a post-discharge RF plasma configuration in which thiophene vapors are introduced in the substrate proximity. The deposition process is assisted by a controlled iodine flow for in-situ doping leading to a material with improved conductivity. The influence of iodine mass flow rate on the deposition rate, optical parameters, composition, chemical structure and electrical properties of the material obtained in various discharge conditions is reported.

Key words: post-discharge, plasma polymerization, polythiophene, in-situ iodine doping.

1. INTRODUCTION

Organic polymers with conjugated structure have attracted considerable attention in electronics field due to the opportunity to control their conductivity via doping similar to the case of inorganic materials [1, 2, 3]. Conjugated polymers become conductive when charge carriers, generated by dopants, are present in their structure [4]. One of the widely studied conjugated polymers is polythiophene, which becomes highly conductive upon doping [5], while iodine is often used as dopant agent due to its electronegativity, high vapor pressure [6] and the easiness of the doping procedure.

Besides the classical methods for obtaining conductive polymers, like chemical [7], electrochemical [8] or photoinduced [9] polymerization, plasma polymerization is among the most used techniques [10, 11, 12]. In this case, the process is sustained by plasma species, such as electrons, ions, radicals and photons, which interact with the precursor and lead to its fragmentation. Upon different reactions in gas phase or on the substrate level [13], a thin film is deposited on the substrate. However, the obtained polymer differ significantly in respect to that obtained by classical polymerization, due to the lack of a single repetitive unit, the branched chains and the highly cross-linking character of the deposits; therefore they are often called polymer-like materials.

Several plasma configurations have been used for the synthesis of the polythiophene-like thin films [14, 15], while various methods for iodine doping have been reported in order to improve the electrical conductivity of the conjugated plasma-polymers [5, 10, 16].

The most studied doping method is the ex-situ iodine doping, which implies the post-deposition exposure of the polymeric layers to iodine vapors. The main drawback of this method is the decreasing of the conductivity over time, due to dopant desorption [5]. In addition, a good homogeneity of the doping element in the polymeric matrix is very difficult to reach [15]. For a better distribution of the doping atoms in the structure of the plasma polymerized thin films, it is necessary to incorporate them during the deposition process. This is possible when the doping agent is covalently bound to the monomer, and thus it is inherently incorporated in film during plasma polymerization process. One precursor of this type is 2-iodothiophene, which consists in an iodine atom weakly bounded to the thiophene monomer. Studies of Kruse et al. [15] and Ryan et al. [16] on plasma polymerization of 2-iodothiophene using microwaves, and respectively RF plasma discharge pointed out that the iodine bond was preferentially broken from the monomer in the plasma [15, 16].

In a more recent paper, Paosawatanyong et al. [5] reported on a procedure of in situ iodine doping of polythiophene, based on the iodine crystals placement in the deposition chamber. They used a microwave plasma source configuration for the synthesis of polythiophene-like thin films in the presence of iodine vapors and reported data regarding gas composition and material properties, while chemical polymerized polythiophene layers were also prepared for comparison purposes. Nevertheless, no method for controlling the iodine flow rate in the deposition chamber was provided.

In the present work, we propose a novel method to obtain polythiophene-like thin films, by using a remote RF plasma source. In this case the precursors are injected into the post-discharge, which is characterized by lower energies of particles, smaller numbers of ions and a significant number of long life-time metastables [17]. Thus, the energy utilized for dissociation of molecules is decreased, the probability for obtaining thin films with composition closed to the initial monomer is higher, favoring the maintaining of conjugated bonds in plasma-polymers. In addition, we describe a procedure for in-situ controlling the flow rate of iodine during one-step plasma polymerization and doping process and present the influence of the iodine flow rate on the surface morphology, optical properties, chemical composition, structure and the electrical resistivity of the in situ doped polythiophene-like thin films.
2. EXPERIMENTAL SET-UP

The plasma polymerization process was conducted in a tubular glass reactor of 50 cm length and 6.5 cm internal diameter, which is pumped down by a rotary mechanical pump that allows a base pressure of $2.4 \times 10^{-2}$ mbar, as measured by a Pfeiffer Vacuum gauge. The chamber was provided at both ends with metallic flanges that contain access ports to the vacuum system, precursor admission and pressure measurement, as sketched in Figure 1.

The plasma is generated between two parallel plate electrodes separated by 0.5 cm distance, the RF active electrode having 2 cm diameter, while the grounded one is provisioned with a small orifice diameter (2 mm) through which the plasma is expanding like a jet in the deposition chamber [18]. A radiofrequency generator (13.56 MHz, maximum power 550 W, ADTEC) capacitively coupled to the plasma source through an automatic impedance matching unit was used for discharge ignition at 80 W RF power in nitrogen flow at 70 sccm.

![Fig. 1 – Experimental configuration for deposition of in-situ iodine doped polythiophene-like thin films.](image)

Thiophene ($C_4H_4S$, Aldrich Chemicals purity, 99%) was used as organic precursor, without further purification. The thiophene vapors were injected at various distances from the plasma generation zone (5–11 cm) through a CEM (Control, Evaporator and Mixing) controlling unit. The CEM unit insured the monomer evaporation at a constant flow rate of 0.5 g/h (equivalent to 2.22 sccm), and vapor homogeneous mixing with a small argon carrier flow (5 sccm).

The depositing species generated upon monomer dissociation in plasma were collected onto various kinds of substrates, placed 1 cm downstream the precursor injection point. Polished silicon wafers (100) with a native SiO$_2$ layer (3 nm thickness) on top were used for Spectroscopic Ellipsometry (SE), X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) analysis. Glass slides with four gold electrodes of 100 nm thickness each, deposited by magnetron sputtering, were used for the electrical measurements. Prior to plasma deposition, all substrates were ultrasonically cleaned in ethanol for 15 minutes and dried with compressed air.
In order to provide the iodine vapors for in-situ doping of the polythiophene-like thin films, a recipient containing iodine crystals was placed in the reaction chamber at 4 cm from the nozzle. The iodine flow was controlled via the number and diameter of several orifices performed in the recipient’s cap, insuring a controlled area (in the range 0–50.24 mm²) for the vapors transfer into the reactor.

During the plasma deposition of polythiophene-like thin films the total working pressure, which is established by the introduction of nitrogen, argon, thiophene, and iodine in the deposition chamber, was in the range 2.4–2.9 mbar. This range is actually given by the various iodine flows introduced in the discharge, as all the other parameters were kept constant.

The deposition time for all the samples was 15 minutes.

The surface topography of the obtained plasma-polythiophene (PPTh) thin films was investigated using an atomic force microscope, XE-100 Park Systems apparatus, in non-contact mode. A variable incidence angle spectroscopic ellipsometer (WVASE32, J.A. Woollam Company, Inc., spectral range between 250 nm and 1800 nm) was used to determine the thickness and the optical constants of the plasma-polymerized thin films. The experimental data (Ψ and Δ) were obtained at 60° incidence angle.

XPS spectra were recorded using a Vacuum Generator ESCA 3 MKII Spectrometer with a monochromatic Al Kα X-ray source for photoelectron production. Survey spectra (0–1200 eV) were recorded at pass energy of 100 eV over 5 passes in order to provide the elemental concentration on the surface. The FTIR spectra of the monomer and of the plasma deposited polythiophene were taken in transmission mode with a JASCO 6300 spectrometer, in the range 7800–400 cm⁻¹, with a resolution of 4 cm⁻¹ and using an average number of 128 scans.

The thin films electrical characteristics were measured with a Keithley K6517A electrometer by four points probe method. During plasma processing, the gold electrodes were partially covered with an aluminum mask in order to produce a total deposited area of 1×1 cm², and to allow electrical contacting of the samples.

3. RESULTS AND DISCUSSIONS

3.1. ESTIMATION OF IODINE FLOW IN THE DISCHARGE

The evaluation of the iodine flow rate introduced in the discharge has been done considering several assumptions. Under the hypothesis of a free movement of the iodine molecules inside the box, their velocity distribution is Maxwellian. Thus, the current of iodine particles Γ (particles/cm²·sec) which exits the box through the openings and is introduced in the plasma is given by the relation:

\[ \Gamma = \frac{1}{4} n v_p, \]  

(1)
where \( n \) is the particles concentration and \( v_p \) is the average velocity for the considered Maxwellian distribution. In the approximation that the sublimated iodine vapors behave like an ideal gas, these quantities are given by:

\[
\begin{align*}
  n &= \frac{p}{kT}, \\
  v_p &= \sqrt{\frac{2kT}{m}},
\end{align*}
\]

where \( k \) is the Boltzmann constant, \( T \) is the room temperature, \( p \) is the vapor pressure of iodine at the considered temperature, and \( m \) is the iodine mass. Upon appropriate calculations, we obtain that the iodine flow rate introduced in the discharge during plasma polymerization of thiophene was in the range 0.7 sccm (obtained for one hole of 1 mm diameter) up to 45 sccm (obtained for a surface of 4 holes of 4 mm diameter each).

3.2. MORPHOLOGICAL AND OPTICAL PROPERTIES (AFM AND SE)

The Atomic Force Microscopy performed on undoped polythiophene-like thin films over areas of \( 10 \times 10 \mu m^2 \), presented in Fig. 2a, showed that by post-discharge plasma polymerization one obtains quite featureless polythiophene-like surfaces without cracks or pores. Only a few particulates of several tens of nm are present on the surface and the roughness value RMS is below 1 nm. Upon introduction of iodine in the discharge, the surface of the \textit{in-situ} doped samples presents a different topography (aspect of an undulated surface) as observed in Fig. 2b. The average roughness increases correspondingly, up to a value of 8.6 nm in the case of an iodine flow of 22.7 sccm.

![AFM images](image)

**Fig. 2** – AFM images of a) undoped and b) \textit{in-situ} iodine doped (22.7 sccm) polythiophene samples.

The spectroscopic ellipsometry data obtained experimentally (\( \Psi \) and \( \Delta \)) were fitted using the software VASE 32 in order to determine the thickness, refractive index and extinction coefficient of the \textit{in-situ} iodine doped polythiophene-like thin films. Four materials layers were considered for simulating the ellipsometric data: the silicon substrate, the native silicon oxide (3 nm thickness), the plasma polymerized layer and a layer counting for the sample roughness. For the silicon

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and native oxide, the optical constants were taken from literature [19]. The Cauchy-Urbach model was applied for calculating the optical constants in the wavelength range 400–1700 nm. The roughness was calculated using Bruggeman effective medium approximation considering this layer as a mixture of the plasma polymer and air in proportion 50:50 [20].

The described optical model fits very accurate the undoped samples over the entire spectral range (400–1700 nm). However, for the in-situ iodine doped polythiophene samples, the 400–450 nm region cannot be perfectly fitted, even in case of low doping, due to the Cauchy limitations in handling absorbing layers. To exemplify, the experimental and modeled data for a sample deposited under iodine flow of 2.8 sccm are presented in Figure 3. Nevertheless, one can notice that for such samples the MSE value is still acceptable (~24). The obtained value for the roughness, around 6 nm, is in accordance with AFM results.

The optical constants of the undoped and in situ iodine doped polythiophene-like thin films are comparatively presented in Fig. 4, for an iodine flow of 2.8 sccm.

The higher values of the refractive index and of the absorption coefficient obtained for the in situ iodine doped samples indicate that the obtained material is more compact and more absorbing in comparison to the undoped polythiophene obtained by plasma polymerization.

At iodine flows above ~12 sccm, the obtained material becomes extremely absorptive and the light amplitude upon reflection is almost zero, therefore the experimental data are affected by large errors or even impossible to record.

![Graphs showing ellipsometric angles and absorption coefficient](image)

**Fig. 3** – a) Experimental and modeled ellipsometric angles Ψ and Δ of in-situ iodine doped polythiophene thin film (2.8 sccm iodine flow); MSE (mean square error) ~ 24; b) Comparison of the absorption coefficient (and refractive index in the inset) of the undoped and in-situ iodine doped polythiophene thin films.
3.3. INVESTIGATION OF THE CHEMICAL COMPOSITION (FTIR AND XPS)

Typical XPS survey spectrum for the in-situ iodine doped polythiophene shows the presence of carbon and sulfur associated to the thiophene polymerization, while iodine signal evidences successful incorporation of dopant in the polymer. The presence of nitrogen signal is related to the discharge nature during plasma polymerization process, while the oxygen signal is associated to the residual atmosphere in the deposition chamber and/or to the post-oxidation of the samples. The results regarding the elemental composition for samples obtained under various iodine flow rates are presented in Table 1.

The sulfur concentration is almost equal to that in the monomer (~20%), and the nitrogen content is maintained at low levels, in all cases. At the same time, the oxygen seems to incorporate preferentially in the undoped samples in comparison to the doped ones. This is because the unsaturated bonds available upon thiophene dissociation in plasma are saturated by oxygen in the case of undoped samples, and respectively by iodine for the in-situ doped polymers. Moreover, a limitation of iodine incorporation is observed at higher iodine flows, suggesting a saturation of the doping process.

<table>
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<th>Iodine flow (sccm)</th>
<th>C (at.%</th>
<th>O (at.%</th>
<th>I (at.%</th>
<th>N (at.%</th>
<th>S (at.%</th>
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<td>8.2</td>
<td>–</td>
<td>5.5</td>
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<td>4.6</td>
<td>4.2</td>
<td>4.6</td>
<td>17.8</td>
</tr>
<tr>
<td>11.3</td>
<td>67.5</td>
<td>4.1</td>
<td>5.8</td>
<td>6.2</td>
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The chemical composition of the polythiophene-like thin films was investigated by FTIR. A typical absorption spectrum of polythiophene film obtained by plasma polymerization in a plane-parallel electrode discharge configuration was presented in [21]. The material obtained by plasma polymerization by using the post-discharge configuration presents similar characteristics. The main IR absorption bands are associated to the pentacyclic ring vibrations [22], namely: in the region around 700 cm$^{-1}$ due to the C–H out of plane ring deformation; three bands related to the C=C in plane vibrations in the region 1380–1580 cm$^{-1}$, and a double peak in the wave number region above 3000 cm$^{-1}$ corresponding to =C–H stretching [23].

We will focus here mostly on the IR regions that provide information regarding the specific chemistry driven by the post-discharge nitrogen plasma in presence of thiophene vapors and iodine doping agent. Therefore, in Fig. 5 are compared the FTIR spectrum of the initial precursor, with those of the un-doped polythiophene obtained in post-discharge plasma configuration, and in-situ iodine doped polythiophene samples obtained under various iodine flows.
In-situ iodine doped polythiophene-like thin films obtained by post-discharge RF plasma

Fig. 4 – FTIR spectra of a) thiophene monomer; b) polythiophene thin film (undoped); c–d) in-situ iodine doped polythiophene layers with various iodine content.

One might notice the much broader bands obtained in the undoped polythiophene material (Fig. 4b) in comparison to those in the initial precursor (Fig. 4a), as well as the presence of additional IR absorption peaks. Namely, a large band with a maximum around 2919 cm⁻¹ is covering the region associated to the aliphatic stretching bonds of CH₃ symmetric, CH₂ asymmetric and CH₃ asymmetric [24] as well as the band around 3235 cm⁻¹ corresponding to the –C≡C–H bond [10] points out toward the ring destruction during the plasma processing, even under soft post-discharge conditions. Additionally, two bands positioned at 2082 cm⁻¹ and 2215 cm⁻¹ are appearing in the undoped polythiophene films; they are associated to H–C≡N and C≡N triple bonds [25] which are formed upon the dissociation of thiophene and the reaction with atomic nitrogen provided from the discharge. The C=C ring vibration appearing at 1406 cm⁻¹ in thiophene monomer is shifted toward higher wavenumbers (1420 cm⁻¹) in the undoped polythiophene due to the increased disorder in the polymeric matrix. Upon in-situ iodine doping process (Fig. 4c–d), the H–C≡N peak is disappearing, while an extremely wide band covers all the peaks previously identified separately in the region 2800–3300 cm⁻¹.

The most important feature of the doped samples is related to the modifications encountered in the peak around 1400 cm⁻¹, which becomes very sharp and narrow as the amount of iodine in the discharge increases. This peak is associated [26] to the iodine doped polythiophene C=C stretching vibration localized in the transition region between the heteroquinoid and the heteroaromatic structures. The iodine presence in the polymeric matrix is inducing characteristic vibrations of polaron-type defects in segmented conjugated polymer [26] obtained by plasma polymerization. According to theoretical calculations, the iodine doping should actually give rise to an absorption positioned at 1443 cm⁻¹, similar to that
associated to –CH\textsubscript{2}I or –Cl=CH\textsubscript{2} bonds reported for ex-situ doping procedure [7]. Actually, the peak shifts its position toward lower wavenumbers when the iodine flow rate is increasing, down to 1392 cm\textsuperscript{-1}. Such a behavior was previously observed by other authors [27] in correspondence with an increasing level of doping. This relates to the introduction of additional levels between lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) levels.

3.4. ELECTRICAL MEASUREMENTS

The electrical properties of the polythiophene-like thin films were determined by van der Pauw method. The undoped material shows a resistivity of 4 × 10\textsuperscript{9}Ωcm. Figure 5 presents the variation of the electrical resistivity as a function of the iodine flow introduced in the discharge. The doping has large effects on conductivity: even for iodine flow rates as low as 1 sccm the conductivity is improved already with one order of magnitude, and continues to improve with the iodine flow.

![Fig. 5 – Dependence of resistivity upon the iodine flow introduced in the discharge during the polymerization process.](image)

By iodine incorporation in the in-situ doped polythiophene materials, polarons are generated and they facilitate the conduction. At higher doping levels, bipolarons are formed [28], which are energetically favored upon two polarons excitation, and the material is passing from a partially oxidized state to a fully oxidized state [29]. In this state, corresponding to a maximum level of iodine doping, a minimum resistivity is achieved.

Thus, the results regarding the electrical conductivity of the in-situ iodine doped polythiophene material corroborate to XPS measurements, which
evidenced a saturation of the iodine incorporation, and reinforce the conduction mechanism proposed for doped polymers based on the generation of polaron and bipolarons.

4. CONCLUSIONS

A post-discharge RF plasma configuration generated in nitrogen has been used for the synthesis of polythiophene-like thin films starting from thiophene monomer. In-situ iodine doping of the material was obtained under controlled introduction of iodine vapors in the discharge: the atomic percentage of iodine in the plasma polymer film increases with the iodine flow rate, as the XPS measurements indicate. The doped polymers are rougher and show stronger absorption of light in respect to the undoped ones. They present specific IR absorption bands associated to the iodine doped polythiophene material, which shifts toward lower wavenumbers, as the amount of dopant increases. The improvement of conductivity upon doping is explained by the generation of polarons and bipolarons in the obtained structure.

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