Materials Chemistry and Physics 169 (2016) 120–127

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Polythiophene films obtained by polymerization under atmospheric pressure plasma conditions

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HIGHLIGHTS

- We obtained polythiophene films (pPTh) by atmospheric pressure plasma technique.
- The pPTh films showed a hydrophobic character and conducting properties.
- The pPTh films were used as sensor for iodine vapors in biological environment.

ARTICLE INFO

Article history:
Received 23 October 2014
Received in revised form
13 July 2015
Accepted 21 November 2015
Available online 30 November 2015

Keywords:
Plasma deposition
Polymers
Thin films
Adsorption

ABSTRACT

The present work describes the experimental arrangement used to initiate polymerization reactions of thiophene monomer based on a dielectric barrier discharge with plane – parallel geometry, working at atmospheric pressure in argon, in turn to obtain conductive polymeric films for different applications.

The resulting plasma polymerized polythiophene (pPTh) film was characterized by FT-IR, UV–Vis, XPS spectroscopy, AFM and contact angle measurements. Characterization of pPTh films showed a higher hydrophobic character and roughness, as compared with films obtained by chemical methods, and the thickness is depending on polymerization duration. Also it can conclude that our samples represent oxidised state of pPTh. As a possible application, it analysed *in situ* the iodine absorption phenomenon in the pPTh matrix and its time evolution by UV–Vis spectroscopy. The presence of iodine $3d_{5/2}$ and $3d_{3/2}$ peaks in the pPTh sample after absorption was identified by XPS spectroscopy. The hydrophobic pPTh film is transformed in a super hydrophilic film after absorption of iodine vapors.

1. Introduction

Conducting polymers such as polythiophene (PTh), polypyrrole (PPy), polyaniline (PANI) and their derivatives have been widely studied due to their potential applications. Among conductive polymers, PTh is a heterocyclic polymer that has particular interest due to its properties that can be used in various applications, such as solar and photovoltaic cells [1–3], chemical sensors [4,5], also in medicine, as biosensors, tissue engineering [6].

The chemical and physical properties of PTh films are strongly influenced by the experimental conditions of preparation. Therefore, PTh was synthesized by several methods, including chemical and electrochemical polymerization [6–9] and, also by the use of dry methods, such as physical vapor deposition and plasma polymerization [10–18]. Under the plasma conditions it is possible to obtain plasma polymerized thiophene (pPTh) films with specific properties by changing the working parameters, respectively composition of gases, flow rates, geometrical and electrical parameters of discharge. pPTh films were obtained in low and atmospheric pressure plasma condition. Different types of plasma sources, such as RF discharges [11,15,16,19,20], microwave discharge [21] and dielectric barrier discharges (DBD) [10] were used for deposition of pPTh films.

Plasma polymerization is found to be an excellent technique for the preparation of high quality polymer films from different monomers precursors without requiring the use of solvents and additives. In addition plasma polymerization processes are faster compared to the traditional techniques that demand multi-step processes and can take from one to several hours. Compared with vacuum plasma polymerization technique, the atmospheric pressure plasma has some advantages such as flexibility of geometrical arrangement, easy access in order to use various types of substrates and low operation costs.

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http://dx.doi.org/10.1016/j.matchemphys.2015.11.038
0254-0584/

Most of studies on pPTh films focused on enhancement of conductivity properties by simultaneously incorporation of doping agents into the polymer film, during polymerization reactions [5,21], also by *ex situ* exposure to different species, such as iodine, chlorine [18,22,23]. Thus, higher conductivity values (i.e. from 1.4×10^{-5} to 1×10^{-4} S/cm) were obtained for pPTh films doped with iodine, by comparing with undoped films (i.e. 5.4×10^{-7} to 1.9×10^{-6} S/cm) [21].

Biosensors have been extensively developed and applied for biomedical and environmental studies [24,25]. Generally, the performance of a biosensor depends on the physico-chemical properties of the bioreceptor – transducer system and also on the target analite [26].

The polythiophene and its derivatives provide new opportunities as biosensors, due to their special behavior based on the conductivity and optical properties, and the sensibility and selectivity at certain molecules recognition [4,27,28].

In our experiments we developed a method of pPTh film preparation based on a dielectric barrier discharge with plane – parallel geometry, working at atmospheric pressure in a mixture of argon and thiophene (Th) vapors. The scope of this research is to obtain pPTh films with reproducible and stable properties for iodine sensing in biological environment.

Plasma polymerization at atmospheric pressure is a convenient technique for synthesis of thin polymer films, in particular PTh films. Characterization of the plasma polymer was performed by FT-IR, UV–Vis, XPS spectroscopy, AFM and Contact Angle Measurements. Chemical composition of pPTh films before and after absorption of iodine vapors was determined. Also optical properties of pPTh films before and after absorption of iodine vapors were determined.

The Ar and Ar/thiophene plasma generated in a dielectric barrier discharge at atmospheric pressure was characterized using voltage – current measurements and optical emission spectroscopy.

2. Experimental

2.1. Materials

Thiophene (C_4H_4S, 99.00% purity, M = 84.14 g/mol) was purchased from Merck, Germany. Argon (98.999%, Messer Gas Romania) was used as working gas for the plasma phase. Different substrates were used to mechanically support the polymer film, depending of analysis type, respectively quartz slides for UV–Vis spectroscopy, NaCl discs for FTIR spectroscopy and glass slide for contact angle measurements. Substrates were cleaned with ethanol and bidistiled water.

2.2. Plasma reactor for polymerization

Plasma polymerization reactions of thiophene (Th) monomer were performed in a dielectric barrier discharge (DBD) reactor. The reactor consists of stainless steel chamber containing two plane – parallel glass dielectrics coated with copper electrodes having 30 mm diameter (Fig. 1). The gap between electrodes was fixed to 5 mm. The gas flow rates were kept in the same conditions during plasma polymerization reactions using two flowmeters (MKS type 1179B) and flow controller (MKS type 247). Argon was introduced in the reactor by flowmeter 1 and film deposition was ensured by introducing the Th vapors, transported by argon gas, after bubbling a reservoir of monomer at room temperature (flowmeter 2). The argon and the precursor flow rates were fixed to 3 l/min and 50 µl/min (corresponding to 0.1 l/min flow rate of bubbling gas).

High voltage pulses are applied on the power electrode using a digital waveform generator (Tabor Electronics, WW5064) and high voltage amplifier (Trek Model PD07016). The wave shape of applied signal was a square type, the frequency was 2 kHz, 6 kV amplitude and duty cycle 50%. The deposition duration was 2 min. The voltage pulses applied on the discharge gap, together with discharge current were recorded using a digital oscilloscope (Tektronix TDS5034B).

Optical diagnosis of plasma was performed by Optical Emission Spectroscopy (OES). The light emitted by the discharge was collected using an optical fiber, through a quartz window, and then analyzed with a monochromator (Triax 550 type) with CCD detector. The detection range for the emission spectra was 200–1000 nm.

2.3. Polymer films characterization

The chemical structure of pPTh film has been investigated by FTIR and XPS techniques. FTIR analysis were achieved using a Bomem MB–10^4 spectrometer in the range of 4000–400 cm^{-1} and XPS analyses were performed using a PHI 5000 VersaProbe spectrometer (Physical Electronics) equipped with a monochromatic Al K_α X-ray source ($h\nu = 1486{,}7$ eV). The photoelectron take-off angle of 45° and the vacuum was kept at 2×10^{-6} Pa during measurements. The energy scale was calibrated by reference to carbon peak C1s at 284.6 eV and resolution of the XPS analyzer is 0.85 eV for organic materials.

The polymer films topography was analyzed by the use of a NT-MDT Solver Pro-M type AFM. The analysis was performed in tapping mode with 0.1 nm resolution in z direction, with a typical tip radius of 10 nm.

Contact Angle Measurements (CAM) were performed using an optical system, with a photo camera and a telescope with 20x magnification. A 1 µl drop of bidistilled water was placed on the surface of a dry sample at room temperature and an image was captured using an Optika Microscopy Digital USB camera. The contact angles were analyzed using ImageJ (version 1.40g) software.

The film thickness was determined by the use of a profilometer (Alfa Step IQ).

UV–Vis absorption spectroscopy (Thermo Evolution spectrometer, Model EVO 300 PC) was used to analyze the response of pPTh films properties to certain stimuli such as specific elements in the biological environment. pPTh films were placed in a quartz cuvette containing iodine crystals. The absorption spectra were acquired in the range of 300–800 cm^{-1} until absorption of iodine vapors reaches the saturation.

The dielectric properties of the pPTh samples before and after absorption of iodine vapors have been determined by Impedance Spectroscopy in the frequency range of 1–10^6 Hz at room temperature. The measurements were performed with a Solatron 1260A Impedance/Gain Phase Analyser using an electrode kit with two plates with adjustable thickness. The measurements were performed at an applied voltage of 0.1 V.

For XPS and Impedance Spectroscopy pPTh films were placed in Petri Dish containing iodine crystals for one hour.

3. Results and discussion

In order to ensure the reproducibility and stability of our polymeric film we analyzed the plasma by the methods mentioned above. Plasma parameters monitored in our experiments are changing after introduction of Th vapors in the argon discharge, as it was observed also in previous experiments [29]. In present experimental conditions, the discharge current shows a multiple peak behavior, with maximum amplitude during so called primary discharge around 17 mA (Fig. 2). Introduction of Th vapors induces