

# Fabrication of plasma polymerized polythiophene and polypyrrole thin films as chloroform vapor sensors\*

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Polythiophene (PTH) and polypyrrole (PPY) thin films were fabricated via a plasma polymerization technique, using a plasma based electron beam generator. Glass and quartz crystal substrates were used for the deposition of thin layers, at a pressure of 1 mbar. The electron beam generator had a fast filamentary discharge formed from the superposition of an ordinary low-pressure dc glow discharge and high-current pulsed one. As conjugated polymers, PTH and PPY have been used as the active layers of gas sensors, due to their high sensitivities and short response times. A novel plasma polymerization method was employed to synthesize the PTH and PPY films. The characterisation of these films by UV-visible spectroscopy, and the sensing properties against chloroform vapor using different concentration ratios, were studied by the Quartz Crystal Microbalance (QCM) method. Our results show that these plasma polymerized thin films were found to be highly sensitive to chloroform, with a fast, large and reversible response that depends on the concentration.

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## 1. Introduction

Polymeric thin films have received a great deal of interest, with a range of applications in physics, chemistry, materials and the sensing industry, because of their mechanical, chemical and physical properties [1]. Among the conjugated polymers, polythiophene (PTH), polypyrrole (PPY), polyaniline, and their derivatives and composites, are widely studied in gas sensing applications [2]. These polymers have the characteristics of high sensitivities, short response times and optimum performance at low to ambient temperatures. Moreover, PTH and PPY are environmentally and thermally stable materials, and they have high potentials for applications in many areas; in light emitting diodes (LED) [3, 4], thin film transistors (TFT) [5, 6], and solar cells [7, 8, 9].

There are two main methods for synthesizing polymer thin films; wet processing (conventional) methods, such as chemical, electrochemical and spreading, and dry processing methods, such as physical vapor deposition and plasma polymerization. The drawbacks of wet processing methods are the low reproducibility, poor spatially controlled deposition and inhomogeneous films with thicknesses  $> 1 \mu\text{m}$  [10]. Plasma polymerization is gaining recognition as a plasma assisted deposition process that is a solvent-free, room temperature process and can be used to deposit onto almost any substrate, with thickness ranges from tens of angstroms to micrometers [11, 12]. In

contrast to conventional methods, it is difficult to predict the exact chemical structure of a deposited surface from the plasma technique, because of the reactive species (e.g. radicals, ions, and electrons) present. The molecular structure and properties of the plasma polymer depend on the monomer, gas phase composition, monomer flow rate, reactor pressure, plasma power and the geometry of the reactor [13].

Chloroform is a common solvent, because it is relatively unreactive, miscible with most organic liquids and conveniently volatile. The major uses of chloroform today are in the air conditioning industry, in the study of malaria, and in the film and television industry. It is also used as a solvent in the pharmaceutical industry and for producing dyes and pesticides. Breathing chloroform (above 900 ppm) for a short time can cause dizziness, fatigue, and headache. Breathing air, eating food or drinking water containing high levels of chloroform for long periods of time can damage the liver and kidneys. Large amounts of it may cause sores when chloroform touches the skin. These effects and the toxicity of chloroform attract most researchers to study reliable, selective and sensitive chloroform sensors, and there have been increasing efforts towards the design and synthesis of new molecules to detect and identify chloroform vapor at low concentrations.

In this work, plasma polymerized PTH and PPY thin films were prepared by a double discharge technique, as a

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sensing layer to chloroform vapor where thiophene ( $C_4H_4S$ ) and pyrrole ( $C_4H_5N$ ) monomer were used as plasma precursors. UV-vis spectroscopy was employed to monitor the fabrication process of these films, and a

Quartz Crystal Microbalance (QCM) system was used to investigate the chloroform sensing properties.

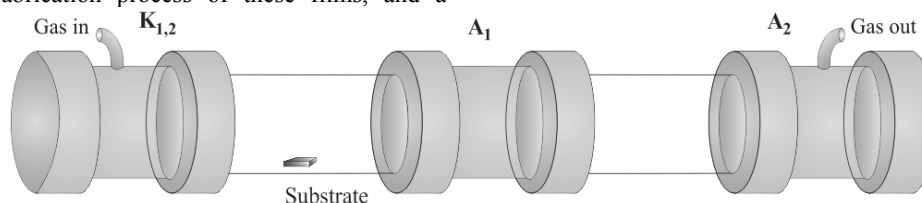


Fig 1. The locations of the substrate within the experimental set-up.

## 2. Experimental details

The details of the experimental setup of the plasma system are given in the literature [14, 15]. A part of the system, shown in Fig.1, consists of three cylindrical hollow electrodes  $K_{1,2}$ ,  $A_1$ ,  $A_2$  and two quartz tubes with 100 mm length and 30 mm internal diameter in between them. A high pulsed voltage with a 5 Hz repetition rate was applied to  $K_{1,2}$  and  $A_2$ , while an ordinary low-pressure glow discharge was operating between the hollow cathode,  $K_{1,2}$  and  $A_1$ . A filamentary pulsed discharge with 2 mm diameter forms along the symmetrical axis of the tube at specific values of the current and pressure [14].

The thin films were produced at fixed 1.5 kV dc and 19 kV pulsed voltages, with a 5 Hz repetition rate, for a 10 min deposition time. The base pressure was 0.2 mbar, and the operating one was 1 mbar. The thiophene and pyrrole monomer (Alfa Aesar, A Johnson Matthey Company) were evaporated at constant temperatures of 80 °C and 100 °C, respectively. They were fed to the reactor at the “Gas in” part. A solution, heated for an hour at 350 °C, made from  $H_2SO_4$  (100 mL) and  $K_2Cr_2O_7$  (5 gr.) was prepared for the cleaning of the glassware and quartz glass substrates. The substrates were submerged in the solution for 30 min., and then rinsed with water and acetone. After that, the samples were dried at room temperature.

The absorption behavior of the liquid monomer and the plasma polymerized thin films was investigated by UV-vis spectroscopy. This has long been used as a structural diagnostic method to detect the presence, the nature and the extent of conjugation [16]. While the extent of the conjugation increases, the absorption band due to the  $\pi$ - $\pi^*$  transition moves to a longer wavelength. The UV-vis spectra of the samples were recorded by an Analytikjena Specord S600 spectrometer.

A thinly cut wafer of raw quartz, sandwiched between two electrodes in an overlapping keyhole design, was used for a fully computer controlled QCM measurement system. Values of the frequency change for this system, which indicates the degree of response, were measured with an accuracy of 1 % Hz. QCM measurements were performed at room temperature, using an in-house designed oscillating circuit and a standard quartz crystal with a nominal resonance frequency of 10 MHz. The QCM technique can be easily applied to monitor the kinetic response of these films against chloroform vapor, using a special gas cell. The variation of the frequency

changes was monitored as a function of time, when the sample was periodically exposed to the chloroform for at least 5 minutes and then allowed to recover after the injection of dry air. The vapor concentration response of these films has also been measured using the QCM system.

## 3. Result and discussion

The UV-vis spectra of the liquid monomer and the plasma polymerized thin films are given in Fig. 2. As mentioned previously, the length of conjugation directly affects the observed energy of the  $\pi$ - $\pi^*$  transition, which appears as the maximum absorption [17]. The maximum absorption wavelengths ( $\lambda_{max}$ ), attributed to the  $\pi$ - $\pi^*$  transition, were observed at around 233 [18] and 315 nm for the thiophene and pyrrole monomer, respectively (Fig. 2 a). The  $\lambda_{max}$  values of the plasma polymerized thin films of PTH and PPY were at around 345 and 376 nm, respectively (Fig. 2 b). The  $\lambda_{max}$  of the monomer was significantly lower than that of the PTH and PPY thin films. The UV-vis spectra revealed that the conjugation length increases after the polymerization process, and the conjugation length of PPY is higher than the PTH one.

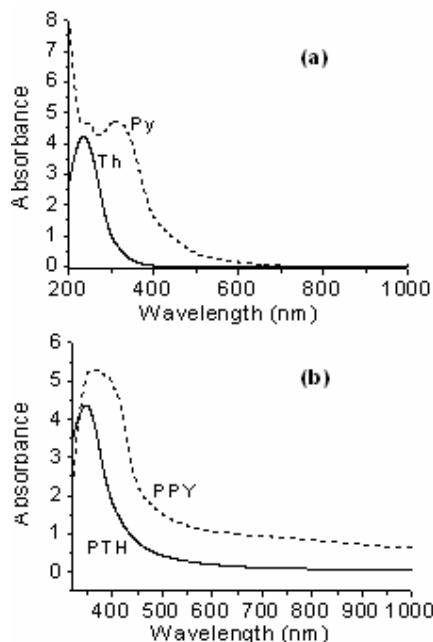


Fig. 2. UV-vis absorption spectra of: (a) Th, thiophene and Py, pyrrole monomer (b) the plasma polymerized PTH and PPY thin films on quartz glass.

An indirect band gap from the UV-vis spectra was calculated using the equation [19]:

$$E_g = 1242/\lambda_{\text{onset}} \quad (1)$$

The  $\lambda_{\text{onset}}$  is the wavelength number of the spectra at which the absorption goes to zero. The calculated  $E_g$  values for the thiophene and pyrrole monomer were  $3.70 \pm 0.18$  and  $2.92 \pm 0.15$  eV, respectively, so they can be considered as non-conductive materials. However, the obtained  $E_g$  values for the thin films of PTH and PPY were  $2.75 \pm 0.14$ , and  $2.67 \pm 0.13$  eV, respectively. These values indicate that the plasma polymerized thin films showed semiconducting behaviour.

Fig. 3 shows the kinetic response as a function of time, for PTH and PPY thin films, to chloroform vapor at room temperature. The responses of these samples are almost fully reversible, with fast response and recovery times. They are large, and depend on the concentration of chloroform after flushing the gas cell with fresh air. The frequency increased when the concentration of chloroform increased. These films also yielded a relatively stable repeatability, a good reproducibility and almost uniform changes in frequency.

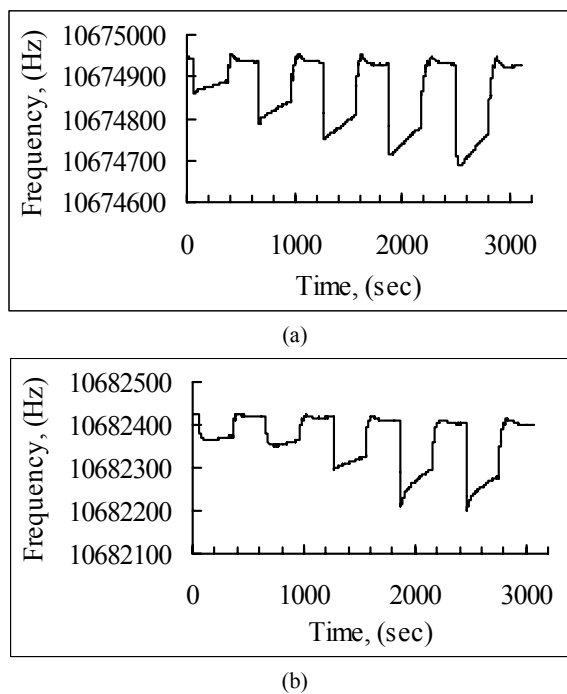


Fig. 3. Kinetic response of (a) PTH, (b) PPY thin films to chloroform vapour.

#### 4. Conclusions

Plasma polymerized PTH and PPY thin films were synthesized by a double discharge technique, and these films were employed as sensing layers for chloroform vapor. The UV-vis spectra revealed the formation of PTH and PPY films on the substrates, and the semiconducting nature of the thin films was inferred from the calculated energy band gap, without any doping process.

Both thin films were found to be significantly sensitive to chloroform vapor, with a fast, large and reversible response, and both responses depended on the concentration of chloroform. As a result of this work, these thin films can be used sensing membrane materials on a quartz resonator, with an excellent sensitivity for chloroform. They may thus find potential applications in the development of room temperature organic vapor sensing devices.

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