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Conducting polymer films by UV-photo processing

Q. Fang[a,b,*], D.G. Chetwynd[b], J.W. Gardner[b]

[a]*Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, PR China*
[b]*School of Engineering, The Centre for Nanotechnology & Microengineering, University of Warwick, Coventry CV4 7AL, UK*

Abstract

In this paper the synthesis of polypyrrole (PPY) films by a novel photo-induced processing and the characterisation of the thin films by Fourier transform infrared spectroscopy (FT-IR), SEM, surface test instrument (WYKO NT2000) and optical microscopy are reported. As a comparison, the synthesis of PPY films by chemical oxidation was also carried out. The experimental results show that choosing suitable concentration of precursors, spin-rate for forming thin films and synthesis methods can control the thickness and microstructure of the PPY films. The processing selected plays an important role for controlling and designing quality of the PPY films. Ultraviolet (UV)-photo processing of PPY film consists of two stages: photo-polymerisation and surface modification. The latter is benefit for the application of PPY conducting polymers in gas sensors and membranes. A new mechanism of UV-photo processing for polymerisation and surface modification of PPY was discussed.

Keywords: Conducting polymers; Polypyrrole (PPY); UV-photo deposition

1. Introduction

Recent advances in nanotechnology and microengineering using conducting polymers have led to many applications within the field of microelectronics including LED, solar cells, sensors and actuators. Molecular electronic materials, including organic, polymeric or even biological materials, can offer viable alternatives to the traditional inorganic materials in many application because of their extremely small size, ease of production and low cost. Conjugated polymers have been available for many physical measurements and for use as active components in electronic devices as well as gas sensors [1–4]. Polypyrrole (PPY) is one of the most stables conducting polymers and also one of the easiest to synthesise either by chemical or by electrochemical polymerisation [5]. In this work the synthesis of PPY films by ultraviolet (UV) photo-induced processing and the characterisation of the films by Fourier transform infrared spectroscopy (FT-IR), SEM, surface test instrument (WYKO NT2000) and optical microscopy are reported. The films were deposited on silicon substrates by spin coating with thickness between 100 and 2000 nm and then irradiated using an excimer UV reactor with a wavelength of 172 nm for different times between 5 and 20 min at room temperature. The effect of the parameters including exposure time and spin-rate on the polymerisation has been investigated. The chemical changes of the films and degree of the polymerisation were monitored by FT-IR whilst SEM, WYKO were used to observe the microstructure and the morphology of the conducting polymer thin films.

2. Photo-synthesis using excimer ultraviolet (UV) source

Applications of photo-induced processes using UV-radiation have over the years become essential technologies in several industrial sectors involving electronics, chemical reactions, multilayer techniques, and medical treatments. Polymer coatings are applied to metal mainly to provide protection against corrosion or for decorative purposes. Recently, a new generation of excimer UV lamps capable of producing high power radiation over large areas and extended availability of wavelengths from the near UV (354 nm) to the deep UV (126 nm) has been developed [6,7]. The development of these novel lamps offers enormous potential for materials processing. Several possibilities of applications of the UV sources have already been shown and include material deposition, polymer etching and surface modification [8–10]. The experimental results have shown that excimer VUV and UV sources are ideal for initiating the photo-polymerisation processes because for very rapid polymerisation at ambient temperature. The photochemical processing potential of electronic devices has been recognised and various groups are investigating

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[*] Corresponding author. Tel.: +44-2076-793196;
fax: +44-2073-889325.
E-mail address: q.fang@ee.ucl.ac.uk (Q. Fang).

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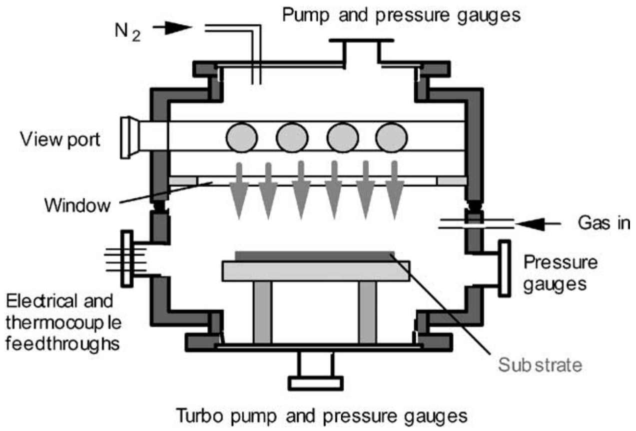


Fig. 1. Schematic of ultraviolet (172 nm) equipment used in the experiment of PPY deposition.

their use in a variety of environmental and industrial situations [11,12]. Fig. 1 shows the schematic of ultraviolet (172 nm) equipment used in the experiment of PPY deposition. The further equipment can be found elsewhere [6,7,13].

3. Experimental details

Si (1 1 1) wafer was used as the substrate. Pyrrole (AR) and chemical oxidants anhydrous $FeCl_3$ (AR) were obtained from Aldrich UK. The Si (1 1 1) substrates were cleaned by ultrasonic washing in a propanol solution, and then dipped in dilute HF (1%), finally being rinsed in de-ionised water and blown dry using high purity nitrogen. The pyrrole monomer was filtered using ultra fine Al_2O_3 (size <1.0 μm) and preparation of precursor solution use in chemical oxidation and photo-induced processing was under nitrogen flow. For chemical oxidation, 0.2 M pyrrole in purified water was stirred constantly under nitrogen flow, then $FeCl_3$ solution was added dropwise to it with a pyrrole: $FeCl_3$ mole ratio of 1:1.5. A spin coating technique was used to form polymer thin films. The spin-rate was from 500 to 2000 rpm. After spin coating, the specimens dry under a nitrogen flow. For UV-photo processing, a precursor was prepared by using 0.2 M pyrrole and 0.2 M sodium dodecyl sulphate. After spin coating, the formed film exposed under UV (wavelength of 172 nm) lamp for 1–20 min. The distance between the sample and lamp was 1.5 cm, with the power density on the sample being about 50 mW/cm^2. At the highest power densities applied, the sample surface temperature did not rise above 85 °C.

4. Results and discussion

4.1. WYKO measurement for thickness and morphology of the deposited films

Both of chemical oxidation and photo-induced processing can prepare uniform and black PPY thin films. The thickness of the PPY film depends on the concentration of the precursor solution and spin-rate. The WYKO technique confirmed that the thickness of the PPY films using above experimental condition is between 100 and 2000 nm, and the thickness of PPY films decreases with increased spin-rate. In our case, the thickness of the PPY films is about 1–2 μm at spin-rate of 500 rpm and 100–200 nm at 3000 rpm.

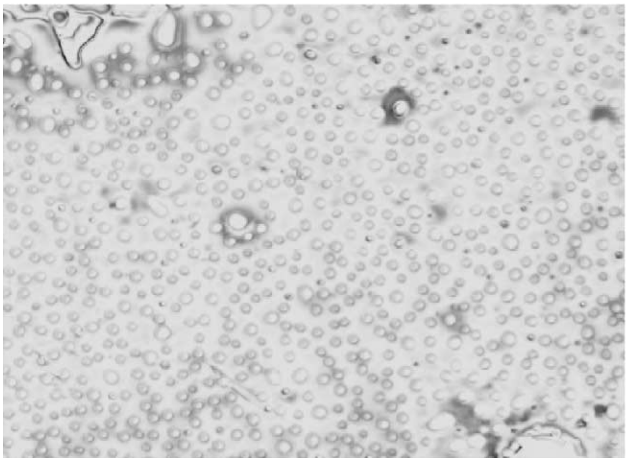


Fig. 2. Morphological structures of the deposited films measured by WYKO. Surface of PPY film by UV-processing at a spin-rate of 2000 rpm, 20 min UV-radiation. ($R_a = 61.82$ nm).

The morphological structures and the thickness of the deposited films were measured by WYKO. The average roughness R_a of the PPY/$FeCl_3$ film by chemical oxidation at a spin-rate of 3000 rpm is 38.40 nm on a measured size of 300 × 230 μm, while that of the PPY/$FeCl_3$ film at a spin-rate of 1000 rpm is 63.85 nm. The results above demonstrate clearly that morphology of a PPY film can be improved by choosing a suitable spin-rate to form the film. Using a 172 nm wavelength of UV photosynthesis shows the morphological structure of PPY/SDS film with a spin-rate of 2000 rpm by using a 172 nm wavelength of UV photosynthesis in Fig. 2. The UV-radiation time was 20 min. The average roughness R_a of the PPY/SDS film by UV-radiation at a spin-rate of 2000 rpm is 61.82 nm. It is noted that round holes are distributed uniformly on the surface of PPY film. The diameter of the round hole is about 300 nm. The exist of the round holes on the surface PPY film led to increase of the average roughness R_a of the PPY/SDS film by UV-radiation. Mechanism of formation of round holes on the surface of PPY film by UV-photo processing will discuss in Section 4.4, combining with the results of SEM and FT-IR.

4.2. FT-IR of the deposited thin films

The PPY films were characterised by FT-IR. The FT-IR spectrum of pyrrole on Si substrate (1 1 1) is shown in Fig. 3a. The FT-IR spectrum of PPY/$FeCl_3$ film (Fig. 3b) by chemical oxidation with spin-rate of 1000 rpm shows a monotonic increase in transmittance at wavenumbers between 3000 and 1700 cm^{-1}, while the spectrum monomer

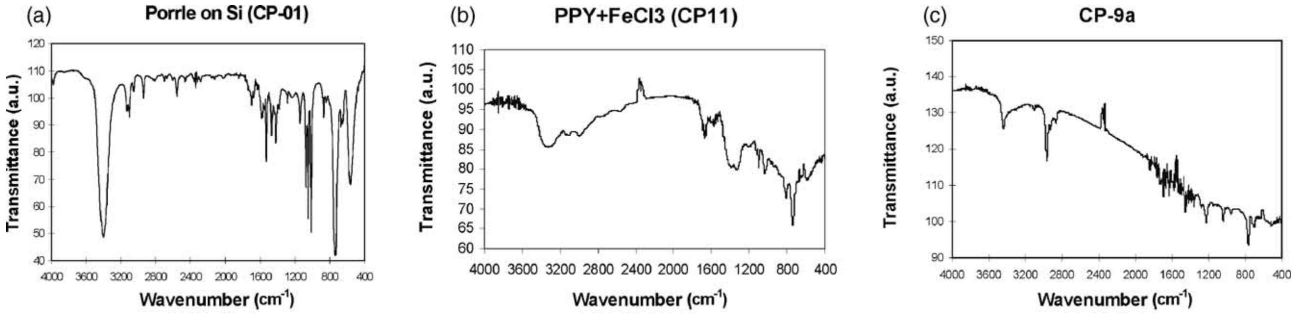


Fig. 3. FT-IR spectrum of monomer pyrrole and PPY films by chemical oxidation and UV-processing.

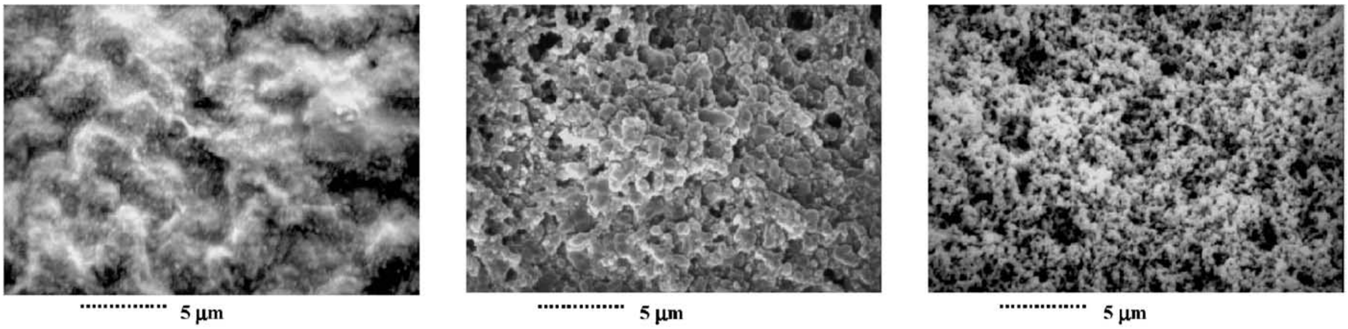
pyrrole keeps flat in transmittance comparison with the spectrum of Fig. 3a. The reason is due to free-carrier absorption, which is characteristic of the conductive state (metallic system) [14]. The broader band between 3400 and 3000 cm^{-1} corresponds to NH stretching (ν_{NH}), aromatic CH stretching (ν_{CH}) and free-carrier absorbance in the doped film. The region below 1700 cm^{-1} shows characteristic PPY band. The so-called doping vibration bands can be seen at about 960 and 750 cm^{-1}. Fig. 3c shows the FT-IR spectrum of PPY/SDS film with spin-rate of 2000 rpm by using a 172 nm wavelength of UV photosynthesis. The UV-radiation time was 20 min. The monotonic decrease in transmittance from 4000 to 1700 cm, as a characteristic of the conductive state, was also observed. The bands due to NH stretching (ν_{NH}) (3400 cm^{-1}), aromatic (3100 cm^{-1}) and aliphatic (3000–2800 cm^{-1}) CH stretching (ν_{CH}) were visible. As in doped PPY a very broad band at 1700–400 cm^{-1} was observed. Vibration bands due to PPY (1550, 1230 and 1030 cm^{-1}) were clearly visible. It is noted that there are weaker peaks in the case of UV-radiation. Higher spin-rate and microstructural changes by UV-photo processing are main reason.

4.3. SEM of PPY films

Fig. 4 show SEM of PPY films prepared by chemical oxidation and UV-processing. The surface of PPY/$\mathrm{FeCl_3}$ film (Fig. 4a) looks denser than that from UV treated PPY film (see Fig. 4b and c). The microstructure of UV photo prepared PPY films look more porous and the porosity and the polymer particle size is different with various UV exposure time. The measurement of WYKO shows that the thickness of PPY film decreases with increased UV exposure time at spin-rate of 2000 rpm (0.85 μm under UV 10 min and 0.65 μm under UV 20 min). The SEM from Fig. 4c demonstrates that PPY film by UV-radiation for 20 min consists of microholes (about 200 nm in diameter) and forms a microporous structure. It is well evidenced that UV-photo processing of PPY film consists of two stages: first; photo-polymerisation; then PPY film surface etching and modification under an UV-radiation.

4.4. Mechanisms of PPY film by UV-photo processing

The novel UV-photo processing can deposit PPY films. However, the detailed mechanism of the UV-deposition of PPY is still uncertain. In this section we will describe the UV-photo deposition of PPY thin film on Si substrate and discuss the mechanisms of the processing. As well known, polymerisation occurs when a radical cation or an active radical reacts with more than one monomer before picking up an electron. The first step in a polymerisation process is the formation of a radical cation or an active radical. In our case, The initial step may come from two routes: firstly, UV irradiation can cause excitation or charge separation in the Si semiconductor. After excitation, the conduction-band electron, SC (e^-), and the valence-band electron hole, SC (h^+) may undergo either electron transfer reaction with pyrrole



(a) SEM of PPY/$\mathrm{FeCl_3}$ film (b) PPY/SDS film under UV- radiation of 10 min (c) PPY/SDS film under UV-radiation of 20 min

Fig. 4. SEM of PPY films by chemical oxidation and UV-processing.

monomer to form a radical cation or recombine. Secondly, monomer itself may form an active radical by abstraction of hydrogen from the α-carbon under UV irradiation. This radical or radical cation is a reactive species and has a number of possible pathways: (a) It can recombine with an electron to monomer again; (b) it can react with other species, which present in the solution, to give side products; (c) it could react with another pyrrole monomer to give a dimer. The next step towards the polymerisation is to produce a dimer radical cation or a dimer radical. The dimer is more readily excited than the monomer because of its more extensive π-orbital system. Finally, such process continues building up longer PPY chain.

Undoping PPY as a semiconducting polymer, is rather stable towards UV irradiation, which can ever increase its conductivity [15]. However, the stability of PPYs against UV irradiation depends on the type of dopant present in the polymer and power density of UV irradiation [16]. The UV (wavelength of 172 nm) lamp used in this investigation has the power density of about 50 mW/cm^2. At such highest power densities applied, it is not surprise that the sample surface microstructure and morphology have been changed by UV-photo processing, which has been showed in Fig. 2 and Fig. 4c. UV etching and surface modification mechanisms may take this responsibility for thinner film and rougher surface of PPY after 20 min irradiation.

5. Conclusions

Chemical oxidation and excimer UV-synthesis processing have been used to deposit PPY conducting polymer thin films. Choosing suitable concentration of precursors, spin-rate, and synthesis methods can control the thickness and microstructure of the PPY film, and meantime, processing selection plays an important role for controlling and designing quality of the PPY films. UV-photo processing of PPY film consists of two stages: photo-polymerisation and surface modification. The latter is benefit for the application of PPY conducting polymers in gas sensors, membranes.

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