Characterization of Poly(3-Methylthiophene)-like Films Produced by Plasma Polymerization

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Polymers are widely used in a great number of applications because of their many advantages. For applications requiring optical and conductive properties, the choice of a suitable polymer is limited to polymers with a conjugated chemical structure such as polyacetylene, polypyrrole, and polythiophene. Very thin film of polythiophene can be deposited by electrochemical procedures and plasma polymerization. A plasma consists of a variety of reactive species (electrons, ions, radicals, etc.) and therefore many different reactions can occur. The aim of this study is to produce poly(3-methylthiophene) using the plasma technology in pulsed wave. The influence of RF power on the film properties will be evaluated.

Introduction

Polymers were only considered to be insulating, but all this changed since the discovery of conductive halogen-treated polyacetylene in 1977.[1] Later, in 1990, electroluminescence from poly(*p*-phenylene vinylene) was reported,[2] which generated a strong interest to use these materials for electronic and optoelectronic devices. Polymers can be conductive or semiconductive due to the presence of alternate single and double bonds between the carbon atoms, known as conjugated double bonds, in their backbone. The number of successive bonds in a row in an alternating pattern of single and double bonds is called the "conjugation length". Every double bond contains a strong σ bond and a weak π bond. If a polymer contains only σ bonds, it will be an insulator because of the large bandgap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). HOMO and LUMO are analogous to the valence band edge and conduction band edge, respectively, in inorganic semiconductors. Polymers containing conjugated π bonds have a lower bandgap and can act as semiconductors.[3] Further doping creates ions and cations in the conjugated polymer and improves its conductivity.[1] By bringing together more and more atoms into one molecule, the energy levels will split, but they will stay closer in energy. A chain of more and more atoms will render more levels by splitting further into bonding and anti-bonding levels. Besides more available energy levels, the levels also pack closer together. Supposing that the number of successive atoms in the chain approaches infinity, the energy levels will eventually overlap and a band structure will be created with a forbidden energy gap between the HOMO and LUMO levels. As mentioned before, if the molecule contains only σ bonds, the bandgap will be large, in the range of 5–8 eV. Since the conjugated molecules contain π bonds, their bandgaps are much narrower and encompass the visible light energies.

Conjugated polymers can be synthesized by means of organic synthesis[4] or by electrochemical methods[5] to produce devices as sensors,[6] organic field effect transistor,[7] or solar cells.[8] However, these methods can be limited by the presence of dangerous solvents in the film.[9] Another method to produce conjugated polymers is the plasma polymerization technology,[10] which is a well-established technique in a number of other processes such as plasma cleaning and etching. The main advantages of plasma treatment are the dry nature of the process and the

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possibility of combining different effects. A wide variety of monomers are available as precursors, and the composition and structure of the deposited polymer layer can be tailored (dielectrics or semiconductors polymer) by adjusting the plasma deposition parameters, such as input power, discharge pressure, composition of the gas feeds, and the deposition temperature. A continuous or pulsed wave plasma can be used to produce the polymerization. In continuous wave plasma the monomer undergoes a strong fragmentation even at low powers. In this way, will be generated polymeric films with band gaps greater than 4 eV with excellent insulating properties, as demonstrated by Kim et al.[11] The pulsed plasma allows to minimize the fragmentation of the monomer producing a film with a higher retention of the monomer structure.[12] Few investigations are available in pulsed plasma polymerization to produce conjugated polymers. Martin et al.[13] have demonstrated that the morphological characteristics of films obtained with pulsed plasma are much better than those obtained with continuous plasma, but no information was given on conductivity properties. Groenewoud et al.[14] have demonstrated that the conductivity of plasma polymerized films was higher when the deposition pressure (0.06 vs. 0.3 mbar) was higher. B. Winther-Jensen et al.[15] have studied the preservation of functional groups during pulsed plasma polymerization. The purpose of this project is to produce polymers can be conductive or semiconductive. 3-Methylthiophene has been used as process precursor; this monomer with electrochemical polymerization produces a polymer with low band gap ($E_g = 1.9$ eV).[16]

Experimental Part

The apparatus consists of a parallel-plate, capacitive-coupled plasma enhanced chemical vapor deposition (PECVD) system,[17] made up of a cylindrical stainless steel vacuum chamber of 25 cm inner diameter with an asymmetric electrode configuration and a third floating electrode (Figure 1). The powered electrode is connected to a 13.56 MHz power supply, associated to an automatic impedance matching unit, while the other electrodes are grounded and floating respectively. All the electrodes work as support for the samples. Liquid 3-methylthiophene, contained in a bubbler, was used as organic precursor. Due to high vapor pressure of the precursor itself, no heating was necessary to inject it into the vessel in vapor phase. All the films were deposited on Corning 2947 microslides for spectrophotometry measurements and on Si(100) wafers for all other measurements. The deposition was performed for 60 min at a total plasma process pressure of about 20 Pa, kept constant by a turbomolecular pump backed with a rotary mechanical pump. The total gas pressure was measured by a capacitive vacuum gauge. The plasma polymerized films were produced, varying the RF peak power (30–120 W), in pulsed mode with a 5% of duty cycle, in which the pulse-on time was 5 ms and the pulse-off time was 95 ms. The chemical composition and the bonding nature of the plasma polymerized thin films were studied, respectively by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). Optical properties, such as absorption coefficient and energy gap, were investigated by UV–Vis–NIR spectrophotometry measurements.

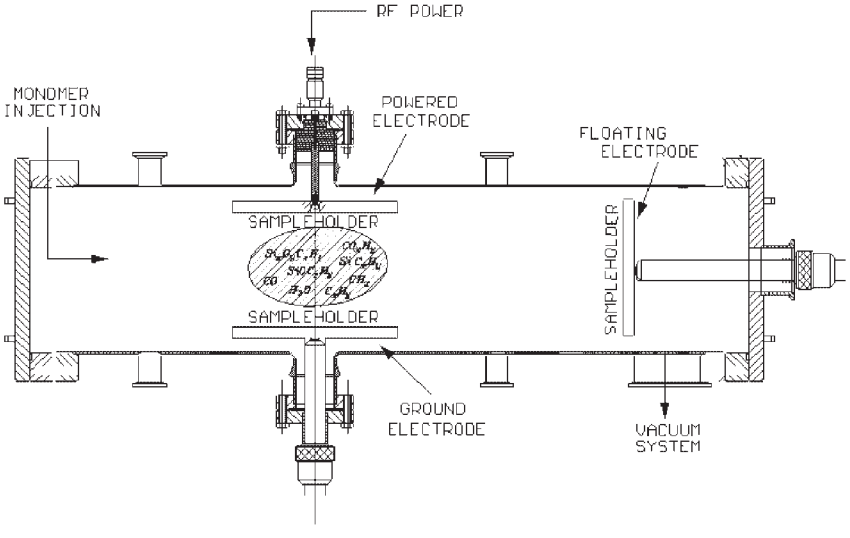

Figure 1. Plasma chamber with three electrodes.

Results and Discussion

FT-IR Analysis

Figure 2 shows the infrared spectra of plasma polymerized films using alkylthiophene as monomer. The analysis has been carried out in transmission mode by a Perkin-Elmer Spectrum One FT-IR spectrometer in the range of 4 000–400 cm^{-1}. The absorption spectra exhibit the following characteristic peaks: C–H stretching mode at around 3 098 cm^{-1} in the (=C–H) on the thiophene ring;[18] asymmetric C–H stretching modes at around 2 955 and 2 920 cm^{-1} in the methyl and the methylene group; symmetric C–H stretching mode at around 2 855 cm^{-1} in the methylene group;[19] symmetric C=C stretching mode at around 1 440 cm^{-1} in the thiophene rings;[20] C–C stretching mode at around 1 375 cm^{-1} in the thiophene rings;[21] C–H out of plane bending at around 835 cm^{-1} in the (=C–H) on the thiophene ring;[18] C–H thiophene ring bending at around 780 and 700 cm^{-1}.[22] The bands at around 3 098, 780, and 700 cm^{-1} indicate the thiophene

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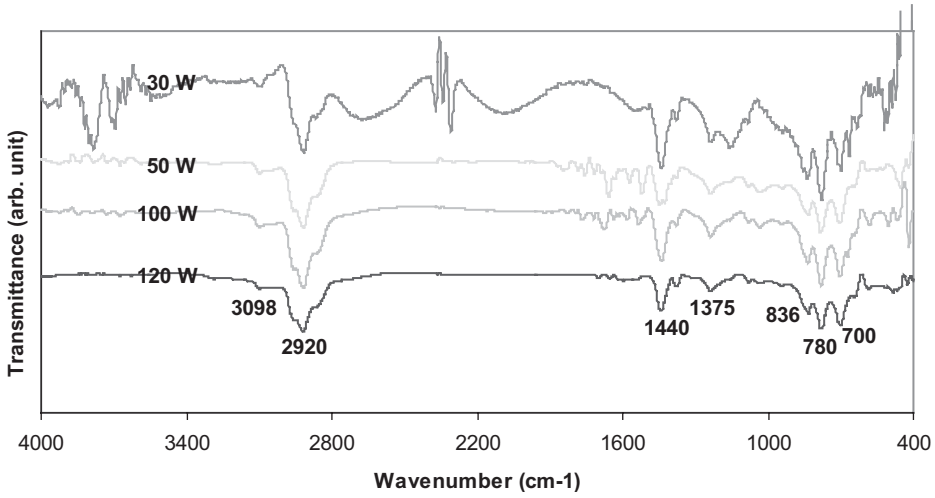

Figure 2. FT-IR spectra of the plasma polymerized films as a function of the RF plasma power.

ring is mostly preserved during plasma polymerization (Figure 3). However, the disappearance of few absorption bands indicates that a partial fragmentation of the monomer occurs, as also confirmed by XPS analysis.

XPS Analysis

The XPS analysis has been performed using a non-monochromatized Al anode X-ray source ($h\nu = 1\,486.6$ eV) VSW model TA10 and a hemispherical analyzer VSW model CLASS 100, equipped with a single channel detector, operating in constant pass energy (22 eV) mode. The overall experimental resolution was previously determined using a polycrystalline Ag sample. The surface of the Ag sample was cleaned by Ar sputtering at 4 keV until only the Ag core lines were detectable. The experimental resolution differs by this one only for the natural width of the core line of the considered element. The survey scans and the core line levels were acquired with an overall experimental resolution of about 2 eV and with a take-off angle of 0°. All spectra were referenced to the same energy scale determined by the calibration of the Ag $3d_{5/2}$ line at 368.3 eV.[23] The pressure inside the analysis chamber was kept at $\sim 8 \times 10^{-8}$ Pa. The samples were analyzed after 10 min of Ar sputtering (primary beam energy 3 keV; beam current ≈ 0.5 μA) in order to remove the surface contaminated layers due to the air exposure. After the XPS analysis the sputtered depth was measured and estimated as ~50 nm. All the samples were affected by charging effects. Calibration of the binding energy (BE) scales was performed by taking the alkyl component of the C1s photoelectron peak (BE = 285 eV).[28]

The core levels fitting was performed through a Voigt profile including a Lorentzian function (accounting for the lifetime broadening) and a Gaussian function (accounting for the finite instrumental resolution). The fitting routine included also a Shirley background, reproducing the secondary electron background. For each element, the relative atomic concentration of the species was estimated from the areas below the prominent spectral lines and after normalization to the atomic sensitivity factors[24] regardless of the specific chemical state. We remark that in the present work the main issues deal with the relative trends and not with the absolute values of the concentrations. This justifies the use of sensitivity factors related to a reference spectrometer rather than ours.

The broad scan XPS spectra of these films reveal the presence of distinct bands at binding energies which correspond to S2p, C1s, and O1s core levels. After sputtering the oxygen species disappear. This indicates that the oxygen is adsorbed only in the surface region of the films. Oxygen contamination may originate from two potential sources. The first may be the desorption of residual oxygen from the reactor walls during the film growth; the second way arise from the reactions of the dangling bonds in the deposit with the atmospheric oxygen

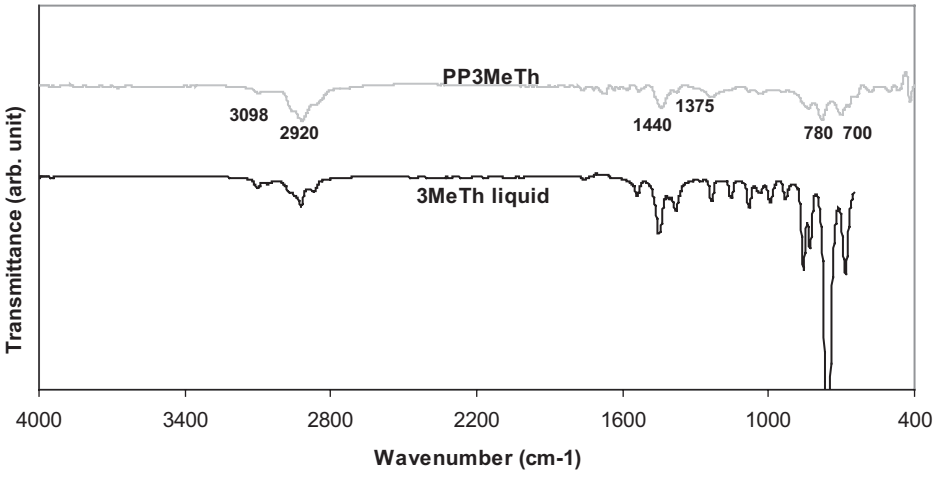

Figure 3. Comparison of FT-IR of plasma polymerized film and the 3-Methylthiophene liquid monomer.

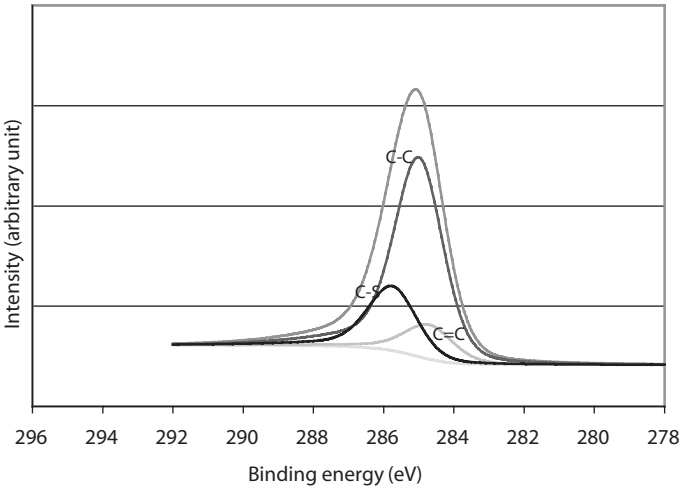

Figure 4. C1s core level spectra of plasma polymerized film at 100 W of power with the deconvolution of C1s into Gaussian–Lorentzian line-shape components.

and moisture after the film exposure to the ambient environment.

Figure 4 shows the C1s core level. As expected the full width at half maximum (FWHM) is large, about 1.7 eV. The C1s peak, at mean binding energy 285 eV, presents the contribute of all C atoms in the polymerized film. In particular, the C1s spectra is a overlapping of C=C, C–C, and C–S components at, respectively, 284.7, 284.9, and 287.5 eV.[25–29]

Figure 5 shows the S2p spectra. The polymerized films show the $S2p_{3/2}$ and $S2p_{1/2}$ spin orbital splitting, and the higher binding energy peak (164.1 eV)[30,31] has about half the intensity of the lower binding energy peak. The S2p spectra is a doublet with 1.2 eV between the peaks,[27] and it is ascribed to S–C bond.[26]

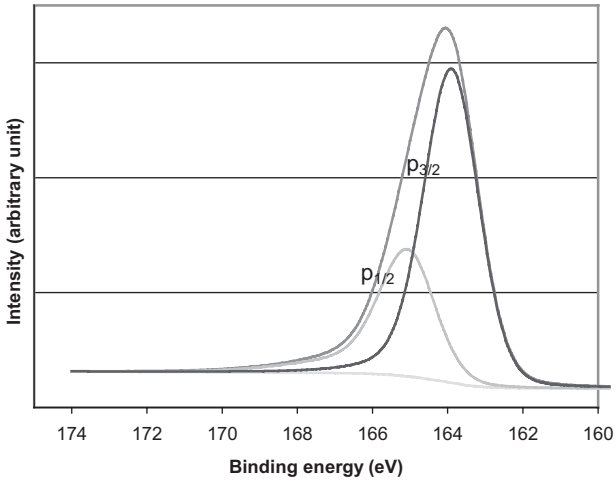

Figure 5. S2p core level spectrum of plasma polymerized film at 100 W of power with the deconvolution of S2p into Gaussian–Lorentzian line-shape components.

Sulfur to carbon ratio for methylthiophene is 0.2. All the plasma polymerized films using methylthiophene showed ratios between 0.11 and 0.12. This indicates similar monomer fragmentation at any power used. However, this monomer fragmentation does not prevent the film to grow with a thiophene-like structure, as shown also by FT-IR measurements.

Optical Properties

Optical absorption spectra near the fundamental absorption edge are a useful tool to study optically induced transitions, energy gap, and band structure of amorphous non-metallic materials.[32] Although amorphous films consist of a continuous random network, some basic features of the electronic properties of a crystalline-like structure, such as allowed bands and energy gap, are preserved due to the presence of a local order.[33,34] The optical absorption coefficient has been deduced from the dispersion of transmittance (T) and reflectance (R), directly measured by a dual beam Perkin-Elmer Lambda 900 UV–Vis–NIR spectrophotometer in the 300–2 500 nm range. The absorption coefficient has been calculated by the theoretical relationship:[35]

$$\alpha = \frac{1}{d}\ln\frac{1-R}{T} \quad (1)$$

where d is the film thickness and R the measured reflectance. In the high absorption region, where absorption is due to interband transitions, the optical absorption coefficient $\alpha(\omega)$ is well fitted by the Tauc dispersion law:[36,37]

$$\alpha(\omega) = B_\alpha(\hbar\omega - E_g)^2 \Big/ \hbar\omega \quad (2)$$

where B_α is a constant and E_g the optical energy gap. According to this relationship, the value of E_g can be obtained by extrapolation of the linear region of the plot of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ to zero. The so-deduced value of energy gap decreases from 2.69 to 1.86 eV with RF plasma power increasing from 30 to 120 W.

Figure 6 shows the UV–Vis absorption spectra of plasma polymerized films based on the 3MeTh. In the polymerized films an absorption band around 320 nm is detected, it shifts at greater wavelengths with the RF power increasing. Furthermore, with the power increasing a broadening of the absorption band is detected. It is well known that the power increasing enhances both the fragmentation in plasma phase and the ion bombardment on the growing film. This can produce more branching and crosslinking reaction inside the film, producing a denser film, and a

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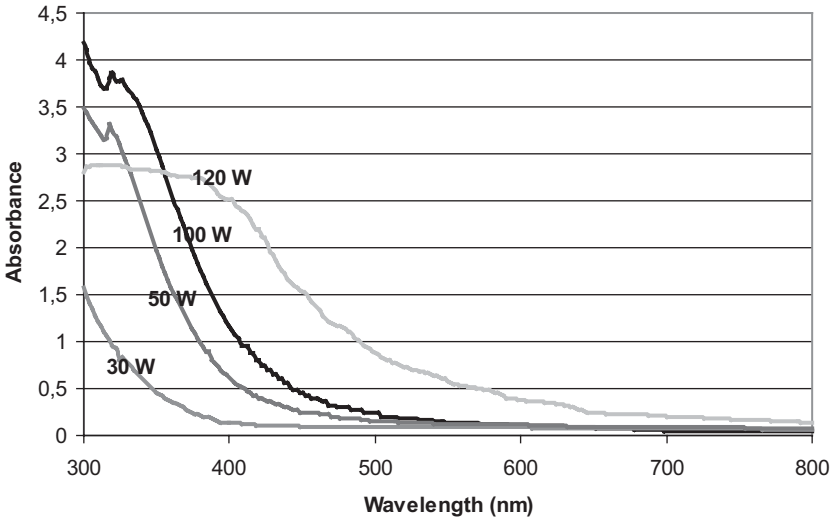

Figure 6. UV–Vis absorbance spectra of plasma polymerized films at various RF powers.

π-electron delocalization in wide band states with a reduction in the band gap.[38,39]

Conclusion

Structural and optical properties of thiophene-like films, deposited by PECVD in pulsed mode using 3-methylthiophene as monomer, were investigated by varying the RF peak powers in the range of 30–120 W. XPS and FT-IR showed thiophene-like structural properties.

The energy gap decreases from 2.69 to 1.86 eV with increase in RF plasma power. These thin films showed semiconductive polymer characteristics. Further analyses will be performed by means of XRD diffractometer to understand whether a partial ordering of the polymeric chains exists.

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