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Optical and structural properties of polythiophene-like films deposited by plasma polymerization

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Polymer-like organic thin films obtained by plasma techniques are of wide interest for various applications. Polythiophene-like thin films were deposited by plasma polymerization in a parallel plate radiofrequency reactor starting from thiophene vapors. The optical properties of the films were obtained from spectroscopic ellipsometry, in the 250-1250 nm range. The calculated band gap is in agreement with a polythiophene-like material consisting of cross-linking of oligomers. The presence of functional groups and film stability against oxidation is analyzed by FTIR spectrometry. The monitoring of functional groups incorporation during the film deposition was done by analyzing the integral intensities of specific absorption bands and led to the conclusion that homogeneous films are obtained whatever the process duration.

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1. Introduction

Polythiopene, a relatively large band gap conjugated polymer, is widely studied due to its chemical stability and its high conductivity upon doping [1]. In addition, from applicative point of view, related materials like oligo- and polythiophenes can be used in field effect transistors, rechargeable batteries, photovoltaics, antistatic coatings, light-emitting diodes, sensors, and capacitors. Intrinsic differences in electronic band structure and/or short conjugation lengths caused by limited polymerization, disorder or ring opening, change the properties of such materials. Therefore, based on the relationship of optical properties, charge mobility and conductivity to chain length and film structure, novel polymer films were obtained by various techniques such as organic synthesis [2, 3], electrochemical methods [4, 5], and vapor phase deposition [6].

Plasma polymerization is an attractive technique to obtain organic materials with new properties. The deposition of plasma polymer films is based on the fragmentation of an organic monomer in electrical discharges and the transport of radicals to the substrate where the films grow. The degree of fragmentation can be controlled by various parameters like the injected discharge power, deposition in remote conditions, or by pulsing discharge [7]. Accordingly, the materials obtained by plasma polymerization have different properties in comparison with the classical polymers, which can be tailored via the above parameters, and which can make the material appropriate for new applications. As peculiarity, even organic substances that cannot be polymerized in the classical sense can be used as precursors in a plasma polymerization process.

In this study, an argon radiofrequency discharge in parallel plate electrode geometry configuration, injected with thiophene vapors is used to obtain polymer-like thiophene thin films. The obtained thin films are characterized by Atomic Force Microscopy (AFM), spectroscopic ellipsometry (SE) and FTIR spectrometry.

The effect of different time deposition parameter on the film homogeneity, in-depth functional group distribution and optical properties is evaluated.

2. Experimental details

Materials. Thiophene (99+% purity) was purchased from Aldrich. Electronic grade polished silicon wafers with a native SiO_2 layer of approximately 3 nm on top were used as substrates.

Plasma Polymerization Setup. The films were deposited in a cylindrical stainless steel vacuum chamber (30 cm diameter, 30 cm length) pumped to a base pressure of around 12 Pa by a vacuum system (pump, gauges, and valves). The chamber is provided with a parallel plate electrode configuration. The two electrodes have 8 cm diameter and are separated by 3.9 cm distance. The active RF electrode is built like a shower and it serves also as injector for the thiophene monomer. The substrate was placed on the grounded electrode. A radiofrequency generator (13.56 MHz, maximum power 500 W) capacitively coupled to the electrodes was used to sustain the discharge. The thiophene vapors were transported in the plasma region from an evaporation cell (bubble system) by an argon gas flow. Thin films were obtained at a total pressure of 73 Pa (50% Ar + 50% thiophene) and 20 W RF power, for different deposition times, in the 0-15 minutes range.

AFM Analyses. A NOMAD model from Quesant Instrument Corporation was used for topography and film thickness measurements. The AFM is equipped with a 200X magnification camera microscope, which allows good sample and probe viewing and positioning. The maximum horizontal scan range is about 44X44 μm^2 and the maximum vertical movement is 3.85 µm.

Ellipsometric Analyses. A Woollam Variable Angle Spectroscopic Ellipsometer (VASE) system equipped with a high pressure Xe discharge lamp was used. The lamp is incorporated in an HS-190 monochromator to enable spectral characterization of the interface. Measurements are performed in the visible and near-UV region of the spectrum at energies between 1 and 5 eV, step of 0.01 eV, at a fixed angle of incidence. The polar angle of incidence can be set automatically between 15^o and 90^o; in our case measurements were done at 65, 70 and 75^o. In our present study, making use of WVASE32 software, we used a Cauchy dispersion [8, 9] in the wavelength region where the polymer film is transparent to extract the refractive index and the thickness of the sample. Afterwards, a point by point fit is performed in the entire measured spectrum. The as-obtained optical constants are fitted using different dispersion models as Tauc-Lorentz [10] and Cody-Lorentz [11] in order to extract the true and physically relevant dielectric functions.

FTIR Analyses. Infrared absorption spectra of thin polymeric films were obtained by using a SCIMITAR type FT-IR spectrometer (Digilab model - 2001) in the range of 4000-400 cm^{-1}. Absorptions of silicon substrates mainly corresponding to oxygen and carbon impurities of Si wafer were subtracted using a differential technique. The integral intensity of the absorption bands were calculated in respect to a local baseline.

3. Results and discussion

Surface topography and deposition rate

An AFM image is presented in Figure 1. The deposited films are smooth. The roughness is increasing slightly with the film thickness, with values ranging between 2 and 10 nm.

The thickness of the films as evaluated from ellipsometry is presented in Figure 2 (curve denoted by squares). In addition, the thickness was measured by doing step-AFM. To this purpose a selected region of the substrate was covered with fresh cut scotch tape. The tape was removed after the deposition, leading to a sharp step between the un-deposited and deposited zones, whose height was measured. The results are presented in Figure 2 (curve denoted by circles). The AFM measurements confirms the ellipsometry results, even though the thicknesses supplied by AFM are slightly higher, specially at long deposition times, but within less than 10 percent. This slight discrepancy might be related to the deformation of the film during the mechanical removal of the tape. The deposition rate obtained by averaging the results of the two methods is slightly non-linear, with a decrease from 98 nm/min at low deposition times (1-5 min) to 74 nm/min at long deposition time (10-15 min). The mentioned non-linearity might be explained by the different growth mechanisms on silicon (initial stages) and on already covered substrate; also the plasma heating of the sample may influence the deposition rate.

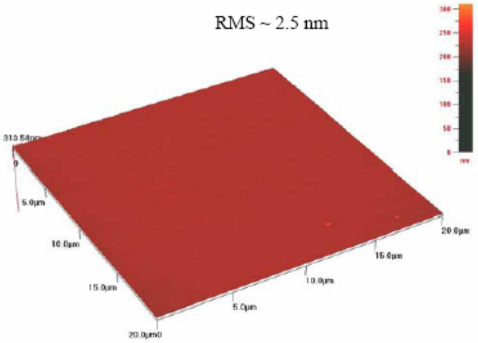


Fig. 1. Typical AFM image of thiophene thin films (1 min deposition).

Optical film properties

Tauc-Lorentz and Cody-Lorentz models, the last one having an Urbach absorption term, were applied in order to extract the optical constants of the film in the entire measured wavelength range. The two models are similar and are designed for amorphous-like materials. Both of them define a band gap energy, E_g, and a Lorentzian absorption peak. The difference is in the absorption-onset region, at energy slightly greater than E_g.

While using the first model the results were very poor, the Cody-Lorentz model gives a good output. In Figure 3 are presented two sets of experimental and fitted spectra for polythiophene-like thin films deposited 1 minute and 15 minutes using the a Cody-Lorentz model with the same parameter values. It is notable the reasonable good fit along the entire spectrum, 1-5eV.

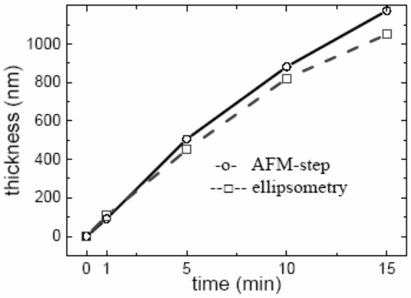


Fig. 2. Dependence of thickness upon the deposition time, as resulted from AFM- step (-o-) and ellipsometry (--□--) measurements.

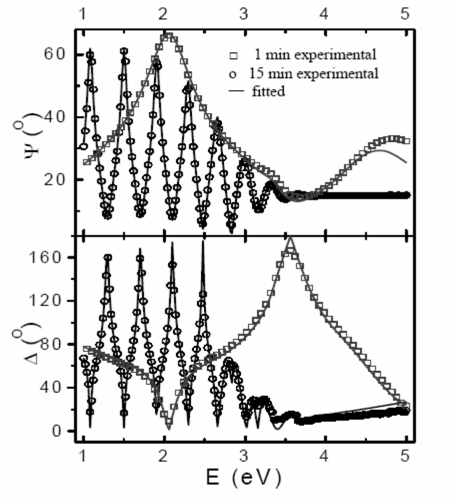


Fig. 3. Experimental (symbols) and fitted (continous lines) spectra for thin films deposited 1 min (squares) and 15 min (dots). The fitting was performed with the Cody-Lorentz model with the same parameter values.

The optical constants of the deposited films are presented in Fig. 4, as function of the photon energy. The E_g parameter is estimated at 2.55 eV, a higher value than the reported band gap for polythiophene of 2 eV, experimentally, and 2.3 eV, theoretically [1]. It is known that the energy gap increases by the decrease of the number of thiophene rings [12] due to the fact that the electron conjugation length of polythiophene decreases with chain length decrease. The higher E_g value obtained indicates that the plasma deposited polymer-like thin films consist of cross-linking of oligomers which is in agreement with expected characteristics of plasma deposited materials, which are built up from fragments of various size. Considering our thin films a mixture of oligomers, the averaged optical properties give an optical band gap of the material as well as the exponential absorption tail (Urbach) that occurs below the E_g value. Another issue is the behaviour in the absorption-onset region of the oligomers mixture, which seems to follow the Cody-Lorentz dependence of dielectric function vs. photon energy.

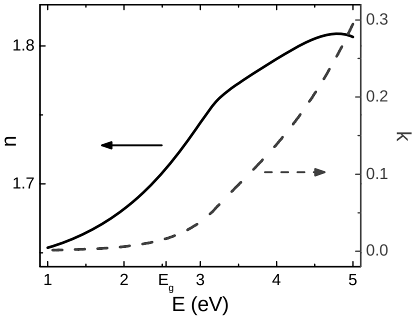


Fig. 4. Dispersions of refractive index, n, and of extinction coefficient, k, of deposited thin films plotted vs. photon energy. The optical band gap is estimated around 2.55 eV.

Film composition and homogeneity

The IR absorption bands corresponding to thiophene chemical structure as C=C-H and those specific to fragments from plasma deposited films as aliphatic CH_2 groups are shown in the Figure 5. The IR active vibrations of C=C-H of thiophene reported at 3034, 3072, 3099 cm^{-1} [13] are not revealed as local maxima, but they are parts of the wide absorption domain extended between 3006-3142 cm^{-1} [13, 14]. This fact is a consequence of light scattering in thin layer samples deposited onto silicon substrate. In the case of the aliphatic CH_2 groups the IR active vibrations are grouped in another domain, extended in the range 2896-3006 cm^{-1}. In this domain two peaks are quite clear at 2920 cm^{-1} and 2975 cm^{-1}.The assignment of these vibrations to the aliphatic CH_2 groups has been done in agreement with other studies, the observed absorptions being close to the normal vibrations at 2810, 2932, 2972 cm^{-1} [13].

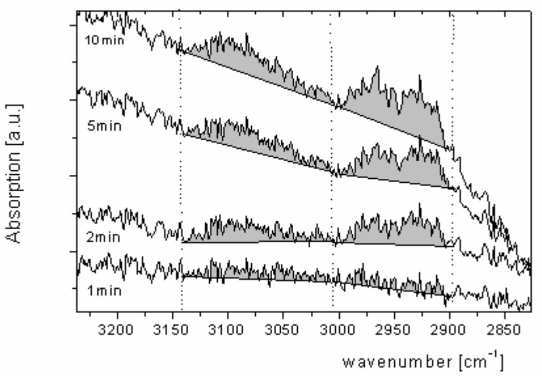
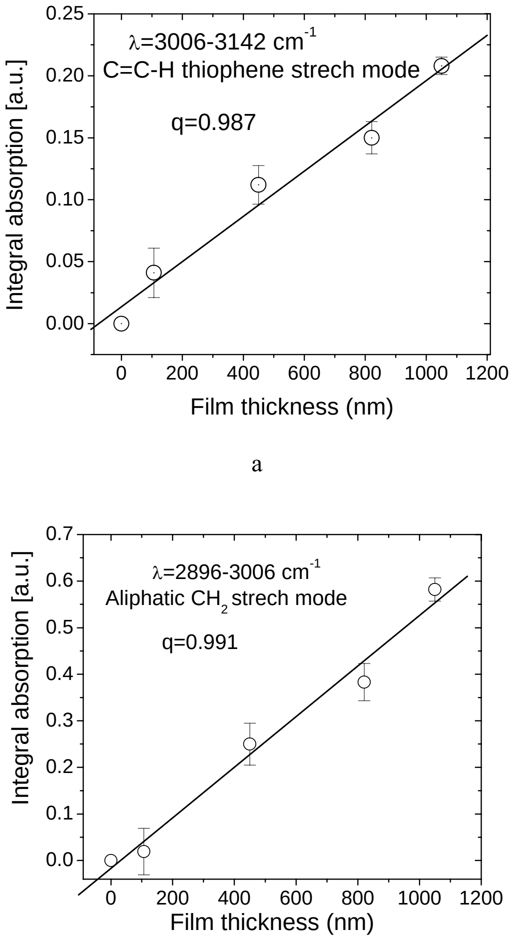


Fig. 5. Details of FTIR absorption spectra of polytiophene-like plasma samples of different thicknesses (on the graph is mentioned the deposition time).

The integral intensities of each IR absorption domain were calculated relative to local baseline as it is shown colored in grey in Figure 5. They were plotted against the corresponding film thickness, as determined by SE (see Figure 2). The results are presented in Figure 6. A good linear dependence (correlation factor of q ~ 0.99) was found in both cases. These results indicate that the C=C-H and CH_2 groups are homogeneously distributed inside of the deposited polymer layer for a thickness greater than 110 nm which is the thinnest sample used in this study. The chain fragmentation of plasma deposited polymer is revealed by aliphatic CH_2 groups. The resulted linear dependency between the CH_2 absorption band intensity versus film thickness indicates that the insertion of respective groups (describing broken chains) is realized at a constant rate during the deposition process and the concentration of the broken chains does not change inside the deposited polymer layer al least above 110 nm from the substrate. The same linear dependency is valid for the C=C-H group which reflects the retention in the film of the thiophene the band around 1700 cm^{-1} structure.



a

b

Fig. 6. Dependencies of the integral absorptions of IR domains specific to thiophene (a) and to aliphatic fragments incorporated in the deposited films (b).

A similar procedure was applied to the band at 1720 cm^{-1} which corresponds to the C=O functional group (Figure 7); a linear dependence of absorption upon the film thickness was obtained as well. The population of this group is due to the incorporation of oxygen impurity in the film during the deposition process and as a result of oxygen attack against chemical structure of the exposed polymer layer into ambient air. The linear dependence in Figure 7 indicates that, in the case of films exposed to air, the degradation of the polymer takes place homogenously in the whole volume of the layer.

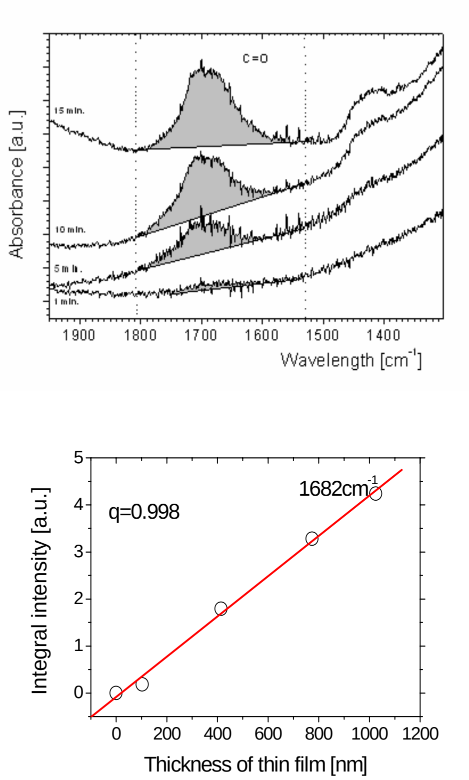


Fig. 7. a) Detail showing the C=O absorption band; b) the dependency of the IR integral absorption bands intensities at 1682 cm^{-1} upon the film thickness.

4. Conclusions

Polytiophene-like thin films were deposited by plasma polymerization in a radiofrequency capacitively coupled plasma reactor starting from thiophene monomer. Smooth thin films were obtained, with a deposition rate of up to 95 nm/min. The optical investigations by ellipsometry showed that the ellipsometric data are fitted well by a Cody Lorentz model. The optical band gap of 2.55 eV corresponds to polymer-like material consisting of cross-linked oligomers. Refractive index values in the range 1.65-1.8, and respectively extinction coefficient values in the range 0.02-0.3 were obtained for the entire measured photon energy range (1-5 eV). The population of functional groups, belonging to the initial monomer and resulted from fragmentation, as analysed by FTIR, indicate that the films are homogeneous, whatever the film thickness, in the investigated range 0.1-1 μm. A uniform distribution of chain fragmentation inside the deposited samples was found. Assuming that at least a part of the C=O functional groups in the samples are related to the polymer degradation due to air exposure, one conclude that the film oxidation takes place homogenously inside the whole volume of the layer.

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