

Polymer-like thin films obtained by RF plasma polymerization of pentacyclic monomers

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Plasma polymerization has been carried out in a parallel plate RF discharge reactor in mixtures of argon with pentacyclic precursors, namely thiophene, furan and pyrrole. The plasma characterization showed the presence of emission bands peculiar to each monomer. The deposition of highly transparent films with partial conservation of the pentacyclic structure, inclusion of various oligomers, roughness and surface energy depending on the precursor nature was demonstrated by material investigations results. The material conductivity is significantly improved upon iodine doping in the case of polythiophene and polypyrrole-like films, while an opposite behavior was observed for the polyfuran-like films.

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1. Introduction

Important effort has been devoted in the last years to the research in the field of conductive polymers due to their promising applications, mostly in the field of organic electronics [1]. The materials include intrinsically conductive polymers and doped conjugated polymers like polythiophene, polypyrrole, polyfuran and their derivatives which become conductive when doped with a suitable oxidizing reagent as I_2 and $FeCl_3$. Polythiophene, polypyrrole and polyfuran are interesting as regard their electronic and optoelectronic properties, for organic – based devices as transistors, light emitting diodes and sensors [2].

Plasma polymerization is a solvent-free, room-temperature process which showed its capability to rapidly deposit thin polymer film onto a wide variety of substrates [3,4]. The monomer introduced in the discharge is fragmented into reactive species, which subsequently recombine, forming a polymer. Besides the clear advantages of the process, which include the deposition of highly adherent, pinhole-free films and the simplicity of the reactor chamber (Bell-Jar configuration) [5-6], the main disadvantage comes from the unpredictable structure of the resulting material, which is also cross-linked. The dependencies of the molecular structure and properties of the plasma polymer upon the monomer type and plasma process conditions (gas phase composition, monomer flow rate, pressure, and input power) are insufficiently known, although some effort was devoted to clarify this issue [7,8].

This paper presents results on the RF plasma polymerization of pentacyclic monomers, namely thiophene, pyrrole and furan, in a discharge with parallel-plate electrode configuration. The precursor fragmentation was monitored by Optical Emission Spectroscopy. The deposition rate, wettability properties, surface morphology and molecular structure of the obtained materials are presented, for various experimental conditions. The

influence of the iodine doping time on the conductivity properties is discussed, as well.

2. Experimental

2.1 Materials

Thiophene (C_4H_4S), furan (C_4H_4O) and pyrrole (C_4H_5N), used as monomers were purchased from Aldrich Chemicals. Silicon wafers (125 mm diameter, 510-540 μm thick and (100) orientation), optical glass and 4 electrodes covered glass were used as substrates after ultrasonic cleaning and rinsing in ethanol.

2.2 Film deposition (Plasma polymerization)

Plasma polymerization was carried out in a classical set-up shown in Fig. 1.

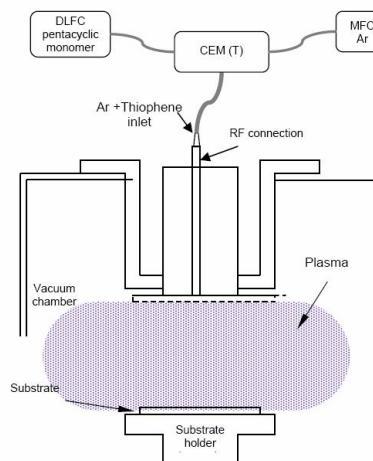


Fig. 1. Schematic of the experimental set-up for plasma polymerization.

The capacitively coupled RF plasma (13.56 MHz, power in the range 10-25 W) was generated between two parallel electrodes. The upper electrode is RF powered, and was designed as a shower allowing the homogeneous introduction of the argon/pentacyclic monomers vapors in the reactor [9]. The bottom one, placed 4 cm below, is grounded and is accommodating the substrate. Before deposition the reactor (stainless steel chamber) was evacuated with rotary pumps to a base pressure down to 2 Pa. Monomers were introduced into the reactor through a control, evaporator and mixing system (CEM, Bronkhorst) that combines a small and constant argon carrier flow of 10 sccm with the vaporized pentacyclic monomers flow under constant temperature of 40 °C. The precursor flow was varied from 0.5 to 2.5 g/h, leading to a maximum pressure of 15 Pa during deposition. The deposition time was in the range 15 – 30 min.

The plasma polymerized thiophene; furan and pyrrole films were subsequently iodine doped by placing them in a Petri dish containing iodine crystals for 2 to 60 minutes. The color of the film changed from light brown color noticed already for 2 minutes iodine doping to dark brown for 60 minutes iodine exposure indicating the successful introduction of the iodine [10]. By this procedure, it is supposed to introduce charge carriers into the material which render it more conductive [11]. All the measurements on doped films took place after storage for about the same time period.

2.3 Plasma and material investigation techniques

Plasma emission has been investigated by Optical Emission Spectroscopy (OES) in the region 200 – 1000 nm using a Bruker spectrograph (focal length 0.5 m, grating 1200 mm⁻¹, entrance slit 25 μm) equipped with an Andor CCD camera, which allowed a good signal to noise ratio in the recorded spectra.

The surface characteristics were investigated by Atomic Force Microscopy (AFM), using a Park Systems apparatus, model: XE-100, in non-contact mode, and by contact angle measurements using water sessile drop method, performed 14 days after deposition, when is assumed that the surface bonding environment is stabilized.

A Woollam Variable Angle Spectroscopic Ellipsometer (WVASE 32, J.A. Woollam Company, Inc) was used to measure the thickness and the optical constants of the plasma-polymerized thin films.

Fourier Transform Infrared spectroscopy (FTIR) was used to analyze the chemical structure of the plasma-

polymerized thin films of thiophene, furan and pyrrole. The spectra were recorded with a JASCO 6300 spectrometer in the 400-7800 cm⁻¹ range, with a resolution of 4 cm⁻¹ and an average number of 128 scanning.

The thin films resistances were measured using an assembly of four electrical circular gold contacts sputtered on the corners of 1cm² square of the glass substrate. During plasma deposition, the contact areas were partially covered with aluminum mask to prevent local deposition. The samples were doped immediately after deposition by placing them in iodine saturated vapor at atmospheric pressure at room temperature.

3. Results and discussion

3.1 Plasma characterization

Optical emission spectroscopy of the discharge generated in the parallel plate configuration shows the quenching of Ar lines when the pentacyclic monomer is introduced and the appearance of the H_α line at 656.2 nm, as can be seen in Fig. 2 (a). Nevertheless, the lack of emission related to CH, and C₂ bands is suggesting only a soft decomposition of the monomer by plasma, in contrast to what was observed by other authors at high power levels [7]. Besides, specific emission bands related to decomposition of each monomer can be detected. Namely, in the case of Ar/C₄H₄S mixtures (Fig. 2 (b)) the presence of the CS radical A¹Π – X¹Σ with the band head (0,0) at 257.6 nm is obvious [12], while no emission related to S₂ or SH could be determined, in contrast to the results previously reported by Kim et al. [7] for the case of Ar/Thiophene/H₂ plasma. This points out toward the specificity of the plasma chemistry for each configuration and used admixture during polymerization process. The Ar/C₄H₄O plasma reveals the emission of CO radical bands, corresponding to the transitions B¹Σ – A¹Π, with the (0,0) band head at 450 nm (Fig. 2 (c)) as well as of the OH radical (A²Σ – X²Π) with the band head (1,1) at 312,6 nm), and the CHO Vaidya's hydrocarbon flame bands around 329.9 nm (not shown) [13]. The discharge generated in Ar/C₄H₅N is dominated by the emission of CN Violet System B²Σ⁺ – X²Σ⁺ with the band head (0,0) at 388.3 nm (Fig. 2 (d)), but also the formation of N₂ molecule is obvious as its SPS bands (C³Π_u – B³Π_g, Δv = -1,0,1) are present in the spectra [14].

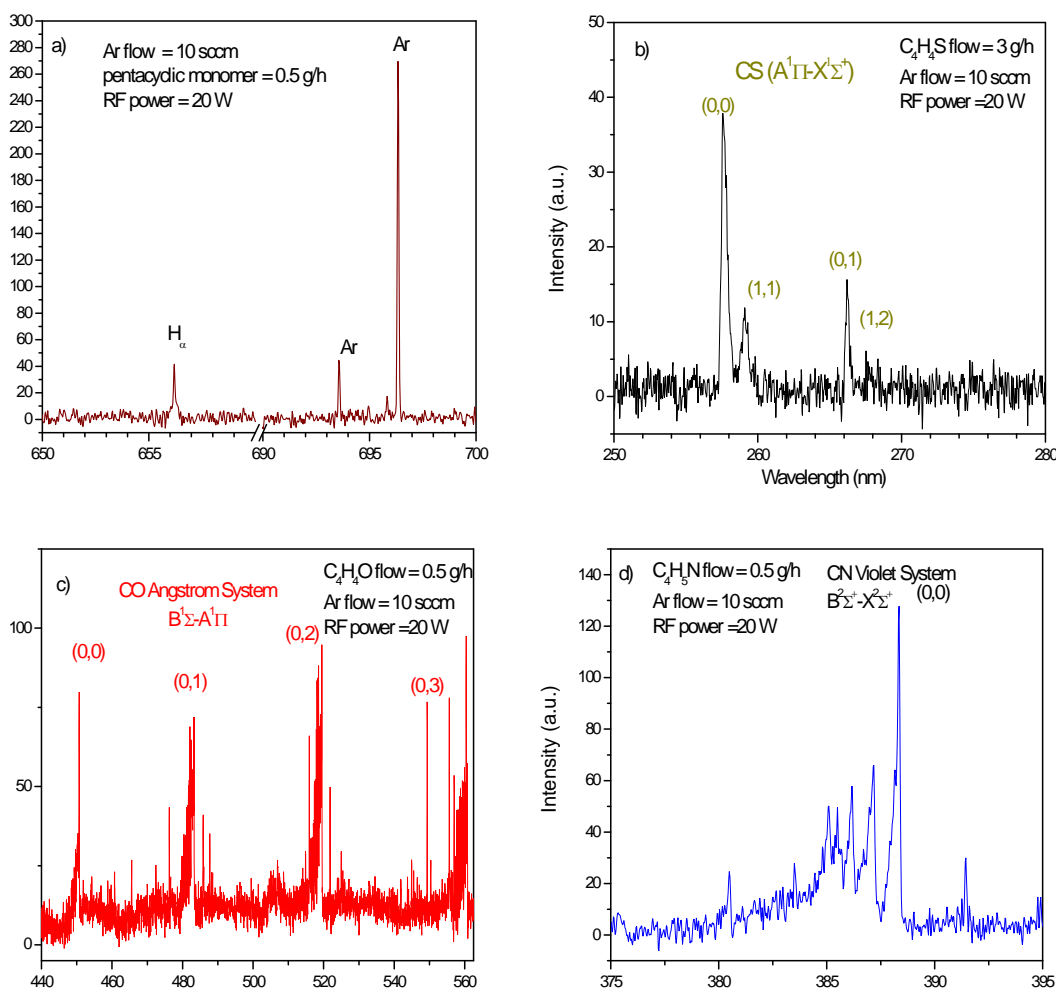


Fig. 2. Optical emission spectra of the pentacyclic monomers: (a) Common region corresponding to H α and Ar lines; (b) CS bands in thiophene; (c) CO bands in furan; (d) CN bands in pyrrole.

3.2 Material characterization

3.2.1 Surface characteristics (AFM, contact angle) and optical properties (SE)

The deposition rates, surface roughness and the water contact angle of the polymeric films obtained by plasma polymerization of thiophene, pyrrole and furan at constant mass flow of 0.5 g/h and RF power of 20 W are presented in Table 1. The highest value of the deposition rate is obtained for polymerization of thiophene, while the polyfuran-like films present the lowest deposition rate values, most probably due to an additional etching mechanism sustained by the oxygen resulted from the monomer decomposition [15].

The deposition rate increases by increasing the monomer flow for all the pentacyclic monomers, while the RF power increase lead to its increase only in the case of polythiophene and polypyrrole-like films. However, a non-

monotonic behavior of the deposition rate is obtained during plasma polymerization of C₄H₄O when increasing the applied RF power. It correlates with the competition between the growth and the etch processes.

Table 1. Deposition rate and surface characteristics of plasma polymerized films.

Precursor type	Deposition rate (nm/min)	Roughness RMS (nm)	Contact angle (degrees)
Thiophene	23.73	0.9	83
Pyrrole	14.73	5.3	75
Furan	10.66	19.9	82

The surface topographies of the polythiophene, polyfuran and polypyrrole thin films are presented in

Fig. 3. The smoothest film is obtained in the case of thiophene (RMS = 0.9 nm), which has the highest hydrophobic tendency (Table 1). The largest roughness observed for the polyfuran material (RMS = 19.9 nm) is sustaining the hypothesis of the etching mechanism during

plasma polymerization. The contact angle for all the polymerized pentacyclic monomers presents only slight variation upon the injected monomer flow and the applied RF power.

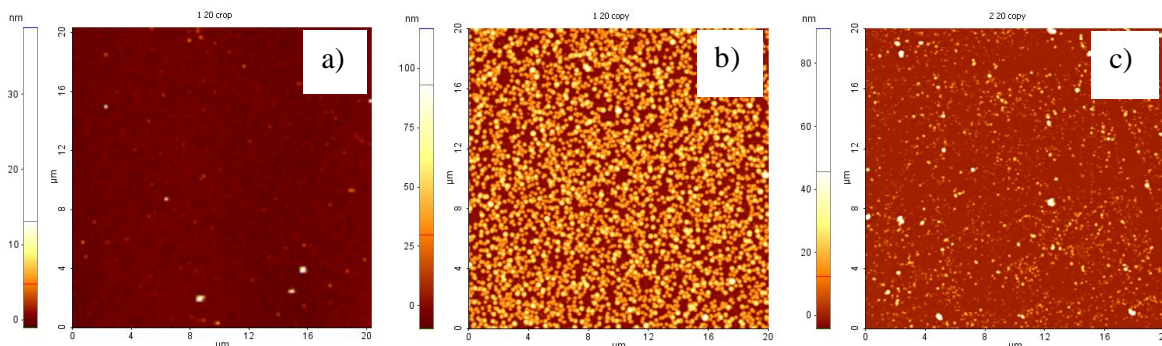


Fig. 3. AFM images of the films deposited at 10 sccm Ar, 0.5 g/h monomer flow and RF power 20 W: (a) polythiophene; (b) polyfuran; (c) polypyrrole.

All the plasma polymerized films proved to be transparent in the region 600 – 1300 nm, allowing the interpretation of the spectroscopic ellipsometry data by using a Cauchy model [16]. The results regarding the refractive index dependency upon the wavelength are presented in Fig. 4. They show higher values for the polythiophene-like films (around 1.72) in comparison to the polypyrrole-like and polyfuran-like films, suggesting more dense deposited material in the first case.

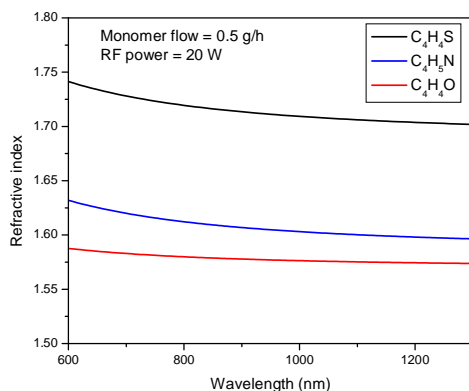


Fig. 4. Dependency of the refractive index upon the wavelength for the poly-pentacyclic films deposited by plasma polymerization.

3.2.2 Chemical composition

The FT-IR spectra of plasma polymerized pentacyclic compounds are presented in Fig. 5. They show several common absorption bands, summarized in Table 2. The most important ones are related to the C–H out of plane deformation vibration in ring, in the region 700 – 730 cm^{-1} , a sequence of 3 bands in the region 1380 – 1580 cm^{-1} related to the C=C in plane vibrations and two small peaks in the wave number region above 3000 cm^{-1} related to the =C–H stretching bond in aromatic compounds [17]. Therefore, it can be concluded that the monomers structure is partially preserved during plasma polymerization under the soft conditions used in the present work. Still, the peaks at around 2872 cm^{-1} , 2926 cm^{-1} , and 2962 cm^{-1} related to the aliphatic stretching bonds of CH_3 symmetric, CH_2 asymmetric and CH_3 asymmetric, respectively, are pointing out towards the ring breaking [18]. Moreover, the well defined peak at 3290 – 3300 cm^{-1} attributed to $-\text{C}\equiv\text{C}-\text{H}$ prove the existence of different oligomers in the deposited film [9], which is highly cross-linked as usually observed in plasma polymer materials.

Table 2. FTIR common bands of the films deposited by plasma polymerization of pentacyclic monomers.

Bond	Aromatic bonds (cm ⁻¹)			Aliphatic bonds (cm ⁻¹)			
	C-H out of plane deformation	=C-H stretching	C=C in plane ring vibrations	CH ₃ asymmetric stretching	CH ₂ asymmetric stretching	CH ₃ symmetric stretching	-C≡C-H stretching
Thiophene	700	3064, 3098	1373, 1436, 1513	2960	2919	2867	3289
Furan	720	3126, 3148	1378, 1498, 1561	2961	2928	2872	3303
Pyrrrole	728	3104, 3127	1430, 1449, 1529	2964	2932	2871	Imposed to NH

Besides the common peaks, specific band vibrations are uniquely identifying the materials according to the used monomers. Namely, in the case of polythiophene-like films (Fig. 5 (a)), the band at 644 cm⁻¹ is associated to C-S bond, the small band around 2559 cm⁻¹ relates to S-H bond while the C=S bond is present at around 1677 cm⁻¹ [19]. For the polyfuran-like films (Fig. 5 (b)), specific bands, with high intensity, are related to the presence of the conjugated bonds C=C-C=O at 1689 cm⁻¹, and C=O bond at 1721 cm⁻¹ [20]. The polypyrrole-like films are presenting FTIR bands corresponding to the NH and NH₂ bending vibrations with the peaks at 1620 cm⁻¹ and 1680 cm⁻¹, respectively, correlated to a broad and intense band in the region 3200 – 3500 cm⁻¹ associated to NH and NH₂ stretching vibrations (Fig. 5 (c)). Also, triple bonds of type -C≡N and -N≡C stretching are observed in the range 2150 – 2250 cm⁻¹ [21].

3.2.3 Electrical properties

The resistivities of the polymer-like films deposited on glass substrate with gold contacts were determined by van der Pauw method for iodine doped and undoped samples. The results are comparatively presented in Fig. 6. The lowest resistivity of the undoped sample is obtained for the polyfuran-like films, but upon doping, an unexpected increase of the resistivity was observed in this case. In spite of the fact that furan is presenting the π bonds which are responsible for the conduction mechanism in polymers [22], it seems that iodine doping is not a right procedure to decrease resistivity for plasma-polymerized films. To our knowledge no data on conductivity of undoped or doped polyfuran-like films were reported. This behavior might explain the lack of data concerning the electrical properties of plasma polyfuran-like films.

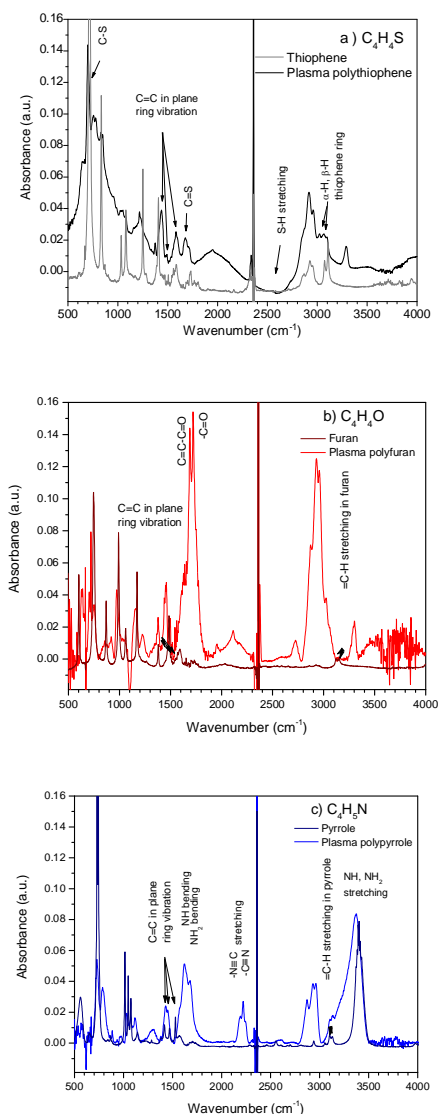


Fig. 5. FTIR spectra of initial monomers and plasma polymers of pentacyclic precursors: (a) thiophene; (b) furan and (c) pyrrole.

As concerning the other materials, resistivity decreases with up to 3 orders of magnitude for the polythiophene layers, while a decrease of 2 orders of magnitude was encountered for the polypyrrole samples, results which are in agreement with those published by other authors [11, 23].

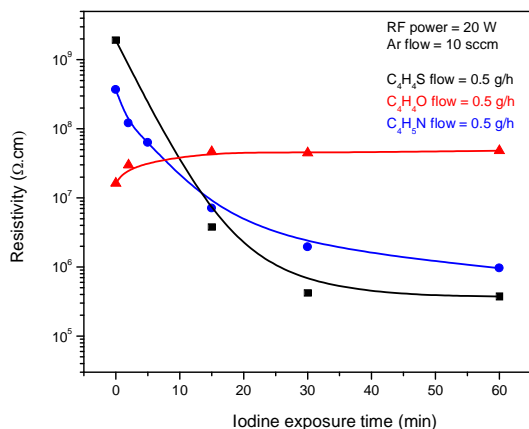


Fig. 6. Resistivity variation upon the iodine doping time for the thin films of plasma polymerized pentacyclic monomers.

4. Conclusions

Transparent polymer-like thin films have been obtained by RF plasma polymerization of pentacyclic monomers. The plasma investigation showed the emission of specific radicals for each precursor, namely CS for thiophene, CO for furan and CN for pyrrole.

The FTIR spectra present general bands related to the pentacyclic structure, as well as particular bands related to characteristic bonds of each monomer. They point out toward partial conservation of the ring structure during plasma polymerization and the formation of oligomers which conducted to highly cross-linked polymer like thin films.

The polyfuran like thin films present particularities possible related to the oxygen presence in its monomer structure, which led to etching, film roughening and an increase of the resistivity upon doping. Comparatively, the polythiophene-like and polypyrrole-like films seem to be denser, present lower roughness and possess significant improved conductivity upon iodine incorporation, indicating the possibility of use as transparent and conductive polymers. Further experiments for increasing the material conductivity are envisaged by introducing the iodine vapors in the reactor during plasma polymerization of pentacyclic monomers.

Acknowledgements

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