GROWTH AND PROPERTIES OF CONDUCTING POLYANILINE THIN FILMS OBTAINED BY MEANS OF IONIC SPUTTERING IN CROSSED ELECTRICAL AND MAGNETIC FIELDS

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Abstract. Thin films of polyaniline in a conductive form were formed by means of ionic sputtering within the argon discharge in crossed DC electrical and magnetic fields. The structure properties of deposited polyaniline films according to the FTIR and UV-VIS spectra were similar to those observed for the emeraldine form of polyaniline.

1. INTRODUCTION

Polymers having intrinsic electron conductivity appear to be one of the most interesting organic semiconductor materials [1]. These polymers posses semiconductor properties [2] that are attributed to the availability of conjugate π- electron bonds. One of the most beneficially used conjugated polymers is polyaniline which is characterized by simplicity of synthesis, non-toxicity, high sensitivity to external factors and reproducibility of optical properties [3]. In particular, polyaniline is widely utilized as a basic material for solar cells, sensors of various type of radiation as well as light emitting devices [4]. Polyaniline films are usually produced by electrochemical techniques on current-conductive surfaces of ITO electrodes, while either polymer solution spreading or oxygen polymerization are utilized for dielectric surfaces, which results in a certain nonuniformity of the obtained polymer films.

Alternative techniques of obtaining polyaniline films on the surface of conductors and insulators are vacuum deposition of a polymer [5-9], infrared pulsed laser deposition (RIR-PLD) [10] and RF plasma-polymerization of thin films [11]. The latter methods allow the layer thickness to be controlled in a rather accurate way, but result in the formation of non-conducting polymeric forms which limits their application.

In this paper, a dry physical vapor deposition technique for preparation of conductive polyaniline films by means of ionic sputtering within the argon discharge in crossed DC electrical and magnetic fields is reported. The films are characterized by X-ray diffraction (XRD), infrared and UV-Vis spectroscopy, and ellipsometric measurements.

2. EXPERIMENTAL PROCEDURE

H_2SO_4 – doped polyaniline powder was prepared using a procedure described in [10] and then pressed in between two nickel screens.

The device used for the deposition of conductive films in the discharge within the crossed electrical

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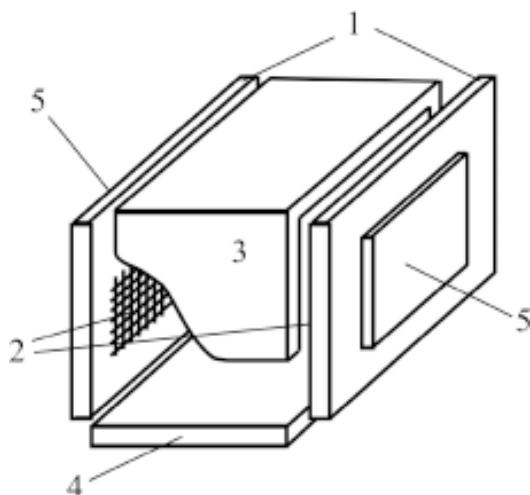Corresponding author: P. Stakhira, e-mail: stakhira@polynet.lviv.ua

Fig. 1. Cell: 1 – cathodes, 2 – nickel screens with a polyaniline layer pressed in between, 3 – anode, 4 – substrate, 5 – magnets.

Fig. 2. Infrared spectra of polyaniline films after the Fourier-transformation.

and magnetic fields had a cell form (Fig. 1) including two rectangular steel cathodes on the inner side which had nickel screens fixed with a pressed polyaniline layer on them and a Π shaped copper anode with a substrate underneath. In contrast to a conventional cathode sputtering technique, the presence of a magnetic field in the proposed structure caused movement of electrons via cycloidal pathways, thus increasing the plasma ionization and, hence, giving a possibility of reducing the argon pressure during synthesis. A magnetic field was created by two permanent samarium-cobalt magnets, thus being $B = 0.26$ T on the cathode surface. The process of sputtering was carried out at the argon pressure of 0.13 Pa and at a constant voltage of 500-800 V. The argon plasma was localized on the device cathodes.

The film deposition time was 50 minutes. Polyaniline films were deposited on a glass plate with an ITO layer on its surfaces, on the KBr substrates as well as on the single crystalline silicon surface.

The molecular structure of the deposited polyaniline films was studied using the FTIR absorption spectroscopy on a Nicolet Impact 410 FTIR spectrometer. The spectral characteristics of the films were checked in the wavelength range of 330-700 nm at room temperature using a "Specord M-40" spectrophotometer. The thickness of the films was determined using the ellipsometry method at a zero-ellipsometrer LEF-3M-1 ($\lambda = 632.8$ nm) based on the 4-zone method. The ellipsometric measure-
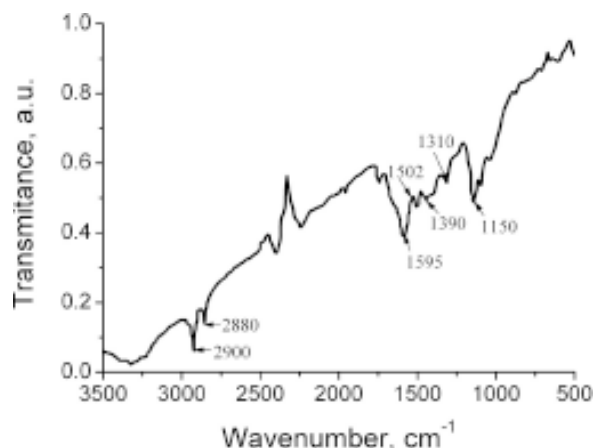
ments were performed on different regions of polyaniline films taking into consideration the dependences of refraction indices of the films of the torsion angle a of the films relatively to the plane of the incidence angle of the beam incidence φ, $n = f(\alpha)$ and $n = f(\varphi)$ in accordance with the approach described in [5] in detail.

An X-ray diffraction (XRD) analysis on the samples (polyaniline films were deposited onto ITO) was performed using a Rigaku Rapid diffractometer. The X-ray beam was incident on the sample at the angle of 3°. The diffracted pattern of Cu K_a radiation ($\lambda = 0.154$ nm) was registered using a cylindrical detector.
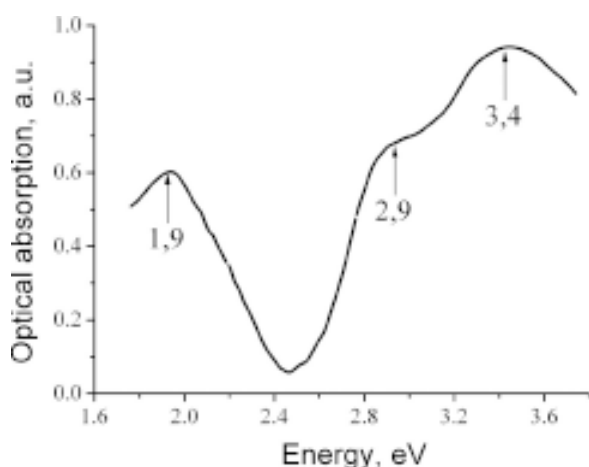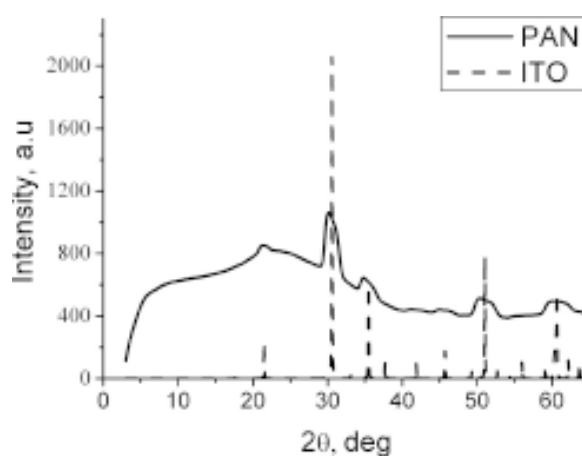
3. RESULTS AND DISCUSSION

Fig. 2. shows infrared absorption spectra using the Fourier-transformation of polyaniline films formed by means of ionic sputtering in the crossed electric and magnetic fields.

As is seen in Fig. 2. the peak amplitude characteristic of the absorption upon a quinoid ring (1595 cm^{-1}) is found quite close to that corresponding to the absorption of a benzene ring (1502 cm^{-1}) which is a characteristic feature of the conductive form of polyaminoarenes [12,13]. The observed peak around 1390 cm^{-1} can be attributed to torsion C-N oscillations in the alkyl chain, the peak at 1310 cm^{-1} – to torsion oscillations C-N in the benzene ring, the peak at 1150 cm^{-1} – to the plane valence oscillations C-H. The peak close to 2880-2900 cm^{-1} can be probably related to the valence oscillations of the C-H and N-H bonds within the benzene ring [13].

Table 1. The main optical parameters of polyaniline thin films.

Incidence angle of beam φ	Refraction index of polyaniline films n	Extinction coefficient of polyaniline films k	Thickness of polyaniline films d, nm	Complex refraction index of the substrate N_{Si}
45°00'	1.5750	0.0126	88.3±0.05	3.88-i×0.02
47°30'	1.5752			
50°00'	1.5750			
52°30'	1.5752			
55°00'	1.5744			
57°30'	1.5738			
60°00'	1.5741			

Fig. 3. Absorption spectrum of polyaniline films obtained in the argon discharge within the electrical and magnetic fields.

Fig. 4. X-ray diffraction pattern of polyaniline thin films on an ITO covered glass substrate.

The optical spectrum of the polyaniline films obtained by means of magnetron techniques is shown in Fig. 3 and it is characterized by the presence of three main absorption bands at ca. 1.9, 2.9, and 3.4 eV.

Similar behavior occurred in the spectrum of electrochemically-prepared protonated emeraldine, where two well defined peaks around 1.5 and 3 eV were observed [14]. These peaks are indicative of the formation of a polaron band and a little higher energy of the transition (1.8 eV) can be attributed to the transition from the valance band to the hole polaron trapped near a quinoid [15], bearing in mind the shorter conjugation length in emeraldine [16,17]. The effect observed around 2.9 eV may be related to the transition from the polaron band to the conduction band [15], whilst the peak near 3.4 eV is characteristic of the π - π^* band gap transition in polyaniline [18].

The X-ray diffraction pattern of the deposited films (Fig. 4) does not reveal any traces of crystalline polyaniline films [19]. A broad hump in the region $2\theta = 20 - 30$ degrees is caused by an amorphous glass substrate [20], whereas other observed peaks can be assigned to a polycrystalline ITO.

As can be seen from Fig. 3 the polyaniline films show a quite strong absorption band in the wavelength region $\lambda = 632.8$ nm (~1.94 eV) which corresponds to the working wavelength of a laser zero-ellipsometer LEF-3M-1. In order to correlate the UV-Vis spectra and the ellipsometric studies, the relation between the coefficient of extinction of the film k and its thickness d was determined applying the value of the optical transmission of polyaniline films on glass at $\lambda = 632.8$ nm.

Ellipsometric measurements were performed using a multiangular technique. The obtained results were analyzed on the basis of an "isotropic environ-

ment-isotropic (absorption or non-absorbing) films-isotropic absorbing substrate" [21, 22] and optical parameters of polyaniline films were derived, which after averaging over the different ranges of the film yielded the following values: $N_{PAN} = n\text{-}ik = (1.5790 \pm 0.0005) - i0.0126$, $d_{PAN} = (88.0 \pm 0.05)$ nm, $N_{Si} = 3.88 - i0.02$.

It should be noted that having once determined the magnitude of the complex refraction index of the substrate N_{Si}, we did not change it in our further calculation. The value of the film extinction coefficient at the above mentioned magnitude had a very little effect on the ultimate results. That is why having corrected it in accordance within results of the spectrometric studies, we also fixed the value of k. Thus, the main parameters of the fitting were n and d listed in Table 1 and it can be seen that the obtained polyaniline films are quite uniform both in thickness and in its complex composition, which is indirectly evidenced by a slight spread in values of the film refraction index. No essential changes of n as well as no traces of its dependence either on a or j angles have been noticed. Optical constants of the polyaniline films determined from ellipsometric measurements at different incident angles j are listed in Table 1 for selected regions of the film surface. These results show that the obtained polyaniline films are optically isotropic which confirms the correctness of applying an "isotropic" model to the analysis of the present ellipsomertic measurements.

It is worth noting that the magnitude of the refraction index of polyaniline films is obtained by means of crossed magnetic and the electric fields are in a proper relation to the magnitude of the refraction index of nanosize polyaniline films obtained by means of electrochemical cycling grows techniques (~1.6) [23].

4. CONCLUSION

The results of this study show that the technique of ionic sputtering of polyaniline in permanent crossed electrical and magnetic fields within the argon discharge make it possible to create thin films of a polyaniline emeraldine form. These films are amorphous and isotropic which is confirmed by the results of an X-ray analysis and by ellipsometry.

The application of this technique of deposition enables us to form chemically pure conductive polymer films which may be used in organic microelectronics.

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