PLASMOCHEMICAL METHOD OF POLYANILINE FILM OBTAINED

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Abstract. The results of the polymer film investigation are considered in that paper. These films are obtained in atmospheric pressure barrier discharge from aniline with simultaneous generation of carbon particles in the films. It is demonstrated that the structure of these films corresponds to one of the amorphous polymers. Carbon particles produce agglomerates with a concentration that slightly depends on the discharge energy density. The authors show that the conductivity of aniline films with carbon particles mainly depends on water saturation.

1. Introduction
A variety of properties that conductive polyaniline (PANI) films demonstrate, from electric conductivity and magnetization to photoelectricity and gas permeability, define a wide range of their practical application [1, 2]. PANI films synthesis technique based on electrochemical polymerization of aniline with doping is the most widespread one, as it is the method that ensures the minimum impurities in the final material [1 - 3]. At the same time, there are two issues related to the reproducibility of PANI properties and treatment of powder being synthesized as a result of oxidative polymerization of aniline. In particular, functionalization of the initial monomer solves these two problems [2, 4]. There are other ways to obtain conductive PANI film for practical application that are based either on the galvanic deposition of aniline monomer directly on electrodes, or vacuum deposition methods using a Knudsen effusion cell [4]. Plasma enhanced chemical vapor deposition (PECVD) at pressures up to 100 mTorr significantly simplifies conductive PANI film synthesis [2]. The transition to atmospheric-pressure plasma, using a barrier discharge, makes it possible to obtain a polymer film, generating carbon particles simultaneously [5]. It increases the power conversion efficiency of photovoltaic cells and conductivity [1, 6]. The application of conductive PANI demonstrates how the environment affects the durability of properties associated with a change in conductivity [3, 4]. Taking into account studies [7], it is possible to assume that the change in conductivity is associated with the doping of PANI molecules with hydroxyl groups from the environment.

This paper presents the results of the study on how the conditions of PANI film synthesis in atmospheric-pressure plasma of a barrier corona discharge affect its morphology.
2. Methods

PANI film was synthesized from aniline vapor over argon with simultaneous carbon particles generation in AC barrier corona discharge using a method described in [3,5,8] on a slide (SP-7102 glass, 1mm thick). It was then polymerized in a vacuum (the pressure up to $10^{-1}$ Torr) at 20-25°C after preliminary 4-hour exposure at 95±5°C. There was no nitrogen, oxygen, or moisture contained in the atmosphere, so there were no redox reactions during PANI film polymerization. Four types of PANI film samples were obtained in the course of experiments at the following densities of the energy released in the streamer: sample no. 1 – 10±2 mJ/m; sample no. 2 – 20±2 mJ/m; sample no. 3 – 30±2 mJ/m; sample no. 4 – 40±2 mJ/m.

The surface morphology of the film samples after polymerization was studied by scanning electron microscopy using a Zeiss Libra 120 electron microscope with a built-in OMEGA filter. Carbon particles generated in PANI film were identified by transmission electron microscopy using the same Zeiss Libra 120 electron microscope with a built-in OMEGA filter at the following conditions: accelerating voltage of 120 kV, LaB6 electron source. For that purpose, a polymer film was dissolved in acetone (99,9%) to obtain a suspension. After that, the solution was exposed to an ultrasonic disperser for up to 10 minutes at the frequency of 44 kHz and ultrasonic power of ~10 W. Then, 2µl of the solution was applied onto the 3mm copper mesh with Formvar/Carbon coating (Ted Pella, Inc.).

The color of the films helps to distinguish PANI molecules structures (leukoemeraldine, emeraldine, pernigraniline) that ensure different conductivity [3]. That is why conductivity absorption spectra were identified using a StellarNet EPP2000 spectrometer with a resolution of 0.5nm when studying the dynamics of PANI film.

3. Results and discussion

The surface morphology of PANI film corresponds to one of the amorphous polymers (Fig. 1). Carbon agglomerates of ~1µm are evenly distributed along the film area. It should be noted that carbon agglomerates concentration slightly increases with an increase in the energy input of the discharge and is estimated at $(4÷7)\cdot10^4$ 1/cm$^2$. The growth rate is $~2\cdot10^3$ particles/cm$^2$·mJ.

![Figure 1. PANI film surface morphology – sample no. 3.](image)

The type of the particles is identified by transmission electron microscopy based on the analysis of diffraction patterns (Fig. 2 [5,9,10].)
The halo (Fig. 2) indicate that agglomerates contain carbon particles with an amorphous structure. Moreover, the agglomerates contain the carbon particles with crystalline fractions, that indicated by the reflections correspond to the hexagonal structure: \( \frac{d_{100}}{d_{110}} \approx 1.73 \) [11]. It should be noted that the percentage of crystalline particles increases with an increase in the energy input into the discharge at a rate close to the rate of growth in the number of agglomerates themselves. The increase in the percentage of crystalline carbon particles is due to the temperature increase in corona hood and streamers [5, 12].

The absorption spectrum of the PANI film after polymerization corresponds to the leukoemeraldine form of polyaniline (Fig. 3): sample no. 1 – (1), sample no. 2 – (2), sample no. 3 – (3), sample no. 4 – (4) [8].

This is characterized by the absence of an absorption band in the long-wavelength part of the spectrum, which is determined by the oxidized block in the polyaniline unit [13]. Atmospheric impact on PANI film leads to an increase of absorption at the wavelength of 500 nm and up, which indicates
the oxidation of a part of the reduced blocks and the transition of leukoemeraldine into emeraldine [7]. The reason is the interaction of PANI molecules with hydroxyl groups and the water saturation of the film with atmospheric moisture. Oxidation of leukoemeraldine into emeraldine is apparently carried out according to the scheme illustrated in Fig. 4 [7]: leukoemeraldine-conductive emeraldine oxidation scheme in the form of two polarons – conductive emeraldine in the form of a polaron – non-conductive emeraldine in the form of a base.

![Figure 4. Leukoemeraldine-conductive emeraldine oxidation scheme.](image)

It should be noted that right after PANI film is obtained $y=1$ (PANI molecules have the form of leukoemeraldine) because the film was polymerized at the pressure of up to $10^{-1}$ Torr. Oxidation is initiated after the film has been withdrawn from the vacuum chamber and saturated with atmospheric hydroxyl groups [14]. During oxidation, first, the $y$ decreases, and the $x$ increases [7]. The absolute value of the conductivity is determined, on our opinion, by the number of doped blocks of PANI polymer molecules, which depends on the humidity of the atmosphere, as well as the permeability of the film itself. It should also be noted that a separate absorption band in the region of 980 nm (Fig. 3) can be associated with an increase in the number of OH-groups absorbed from the atmosphere [14].
4. Conclusion

Thus, plasma-enhanced chemical deposition from aniline vapor provides a possibility to obtain homogenous films without granular fractions. A percentage of allotropic crystalline carbon particles increases with an increase in the density of discharge energy which is associated with temperature increase in the corona streamers and hood. It is established that the surface structure of the films corresponds to the one specific to amorphous polymers. Moreover, the coating continuity is achieved at energy densities above ~35 J/m, and the average film growth rate changes from ~1.2 ± 0.2 μm/min (at ~25 mJ/m) to ~3 ± 0.5 μm/min (at ~45 J/m).

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Acknowledgments

The research is carried out under the financial support of the Ministry of Science and Higher Education of Russia Reg. No.AAAA-A20-120102190039-6. The authors thank the Applied Nanotechnology Multiple Access Center at KNRTU-KAI for the images of PANI films surfaces and electron diffraction on agglomerates of carbon particles (the work is carried out under the Priorities-2030 program) and M.S. Pudovkina personally for the measurement of absorption spectra of PANI films.