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# Nanotexturing of plasma-polymer thin films using argon plasma treatment

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## ARTICLE INFO

## ABSTRACT

Plasma-polyaniline films are treated by argon plasma in order to obtain nanostructured surfaces. The polymer deposition and its subsequent treatment are realized in a low pressure microwave reactor. The effects of several operating conditions, *i.e.*, discharge power, argon pressure, processing time and substrate bias on the chemical and morphological structure of the obtained layers are examined. The chemical structure of the polymer is characterized using Fourier Transform Infra-Red spectroscopy whereas the film morphology is determined by Atomic Force Microscopy. The results show that the density and the dimensions of the nanostructures can be finely tuned by the plasma parameters. Low argon flow rate or microwave power, short treatment time and the use of substrate polarization yield high structured surfaces. We show that the formation of the nanodots is mainly ion-dependent according to the ion energy and the ion flux. Concerning the chemical structure of treated films, a moderate destruction of aromatic character and a partial loss of amine groups are observed.

## 1. Introduction

Conductive polymer nanostructures (nanofibres, nanotubes) have great importance in different fields of application. This type of material exhibits some unique electrical properties that makes possible new developments for different devices such as field emission displays [1] and for heat dissipation [2]. Another property of polymer nanostructures is the high shape factor, allowing enhancement of surface interactions. One example of such applications is gas sensing (ammonia [3–4], nitrogen dioxide [5,6], methanol [7,8] etc).

One of the most widely used conductive polymers is polyaniline (PANI). Chemical synthesis of its nanostructures has been deeply discussed by Stejskal et al. [9,10], Konyushenko et al. [11] as well as Chiou et al. [12–14] Despite its simplicity, such chemical synthesis exhibits numerous drawbacks, such as the use of chemical products and post-synthesis steps (filtering, purification and deposition onto the substrate). Furthermore, reported nanofibers are not aligned normally to the surface, thus limiting their application. However, the work reported by Chiou [15] demonstrates the synthesis of vertically aligned polyaniline nanofibres by chemical oxidation of aniline in diluted solution (8 mM against 0.4 M usually used) at low temperature (below 5 °C) and low proportion of oxidant (2:1 against 4:1). Such a preparation presents a further drawback concerning the poor homogeneity of diameter and height.

A promising way for the elaboration of polymer nanofiber arrays is plasma degradation. This process is considered environmentally friendly and yields well-defined fibers oriented normally to the surface directly on the substrate. Numerous works [16–24] describe such a technique for a variety of polymers such as polystyrene [16], poly (ethylene terephtalate) (PET) [17–20], poly(N-isopropyl acrylamide) [21], poly(methyl methacrylate) (PMMA) [22,23]. No commonly accepted theory is described on the mechanism of nanofiber formation. The only general statement claims that the selectivity in degradation is due to the difference in density through the material. According to the authors [16–18,21–23], this difference is intrinsic for a given material or is formed during exposure to plasma. The most common theory for semi-crystalline polymer is that crystalline domains have higher density and thus are degraded with lower rate than amorphous ones. For amorphous polymers, the selectivity is achieved by formation of crystallites on the surface upon exposure to plasma [16–18]. Differential scanning calorimetry (DSC) measurements of pristine and plasma treated samples has confirmed the aforementioned predictions, through the presence of crystallinity in amorphous polymers exposed to plasma.

Another possibility of selectivity, as described by Fang et al. [24] and Ko et al. [19,20], arises from metal deposition on the surface. Fang et al. [24] used a thin film of metal deposited on any type of polymer. This thin film, exposed to plasma, aggregates into metal nanoparticles that act as a mask for a post-treatment step. The drawback of such a

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method is that metal deposition and degradation steps are performed in separate reactors. However, Ko et al. [19,20] showed that metal nanoparticles can be sputtered from the electrodes during the treatment. These particles, randomly deposited on the polymer surface, play the same role as that previously described. It must be pointed out that with such a process, no control of the particle deposition is achieved. Furthermore, the sputtering of electrodes leads to their degradation with time.

All the methods described above concern plasma degradation of industrial bulk polymers, while no application to plasma-deposited film was found. The issue with plasma polymers is the absence of linear chains which makes them difficult to form crystalline domains. Thus, no selectivity of degradation is possible by crystallization. Furthermore, the deposition of metallic nanoparticles coming from the sputtering of electrodes is not a desired phenomenon in a normal plasma process. Herein, we report the synthesis of polyaniline nanostructures directly formed on the substrate. The polyaniline synthesis and its post plasma-treatment occur in the same plasma reactor in which plasma polymerization is followed by argon plasma treatment of the deposited polymer film. This process allows a quick and environmentally-friendly synthesis of polymer nanostructures. Moreover, these nanostructures are directly formed on the substrate which is important for potential applications. For the best of our knowledge, this is one of the first reports on the structuring of plasma-deposited polymer films.

## 2. Experimental

### 2.1. Substrate preparation

Polyaniline films were deposited onto clean (100) silicon wafers. In order to remove the surface contamination, wafers were cleaned with acetone and ethanol in ultrasonic bath (10 min) and rinsed with deionized water. Finally, the wafers were immersed into boiling piranha solution ($H_2SO_4$:$H_2O_2$ = 3:1), then rinsed with deionized water and dried with compressed air. The wafers were exposed to UV light for 10 min prior to use.

### 2.2. Polyaniline synthesis

The experimental set-up and synthesis of polyaniline films were described in a previous publication [25]. The plasma device (Boreal Plasmas-7050) is based on the distribution of microwave applicators fed with microwave at 2.45 GHz. The plasma is produced at electron cyclotron resonance (ECR) by twelve dipolar elementary plasma sources evenly distributed on one ring on the wall of the plasma chamber (Fig. 1). Such a design allows to operate at low precursor pressure (down to 0.1 mTorr) leading to high plasma homogeneity and scalability.

The system was pumped to a base pressure of $5 \times 10^{-2}$ Pa using a turbomolecular pump (Adixen ATH300Ci) backed up by a dry pump (Adixen ACP28G). The gas pressure was measured using a Pirani-cold cathode combined gauge (Pfeiffer PKR251). Liquid aniline (Sigma-Aldrich, *ReagentPlus*®, 99%) was in a glass tube which was connected to the vacuum through the upper flange of the plasma chamber. This tube was maintained at 40 °C by hot water. The working pressure of aniline vapor was fixed at 0.2 Pa and was measured by a capacitive gauge (Pfeiffer CCR364). The calculated mass flow rate (as measured by weighing the tube containing the aniline before and after deposition) was 1.6 g/h. The sample was placed on the substrate holder situated in the post-discharge zone, at the bottom center of the chamber. The plasma was generated using a microwave generator (Sairem GMP20KED 2.45 GHz) and the reflected power was minimized separately for every applicator.

For current research, the deposition time for the plasma polymerization of aniline was fixed at 30 min and the discharge power at 60 W.
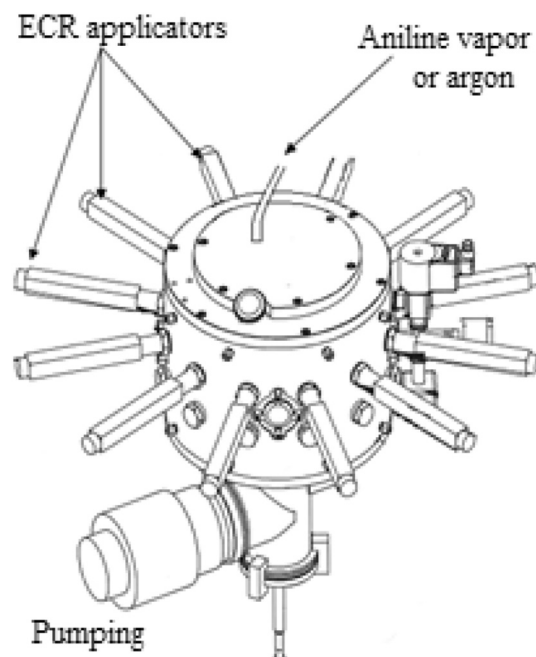


**Fig. 1.** Scheme of the microwave plasma reactor used for the plasma-polymerization.

### 2.3. Argon plasma treatment of plasma-polyaniline

Deposited plasma polyaniline films were treated by argon plasma. Argon (Air Liquide) is selected because of its chemical inertia that does not directly induce the appearance of new chemical groups (especially oxygen-containing ones, such as alcohols, aldehydes *etc.*), as opposed to oxygen. Argon was introduced into the reactor through the upper flange (like the deposition gas) and its flow was varied between 5 sccm and 50 sccm as measured by mass flow meter (Brooks Delta Smart II). Thus, the pressure range was from 0.1 Pa to 1 Pa. Different input powers (420 W to 1200 W) and process times (5–30 min) were used. Furthermore, the effect of the substrate polarization on the PANI structure was studied by applying a DC bias voltage of −100 V or −200 V. Throughout the polymer deposition and its argon treatment, the substrate was kept at room temperature by water cooling.

### 2.4. Atomic force microscopy measurements

The surface roughness of the films was investigated with a Veeco AFM (Dimension Nanoscope V) in tapping mode. The cantilever (antimony-doped silicon, Bruker) has a typical stiffness coefficient of 40 N/m and a resonant frequency near 330 kHz. Scan region was fixed at $5 \times 5$ μm, scan frequency at 0.5 Hz with 512 samples and 512 lines. Raw data were treated with Gwyddion software. Different parameters were used to describe the surface structuring: RMS roughness ($R_q$), mean height and mean diameter of the grains and their density on the surface.

### 2.5. FT-IR measurements

The FT-IR spectroscopy was performed on Bruker IFS66 spectrometer (Globar source, 32 scans, DTGS detector, resolution 2 cm$^{-1}$) in transmission mode on PANI films deposited directly onto potassium bromide (KBr, Sigma-Aldrich, FT-IR grade 99.99%) pellets. In order to prepare KBr pellets, 100 mg of KBr were introduced into stainless steel form (diameter 10 mm, Eurolabo) and then pressed under 12 tons for 3 min. A pure KBr pellet was used as reference.

Transmittance spectra were treated with Opus software for baseline correction (polynomial) and $CO_2$/$H_2O$ compensation and also