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## Plasma polymers: From thin films to nanocolumnar coatings

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### ABSTRACT

Plasma polymers are employed in impressive range of applications due to their unique properties. Although films of plasma polymers are traditionally described as smooth and pinhole free, the possibility to produce nanorough and nanostructured plasma polymerized coatings receives increasing attention. In this study, we tested a fully vacuum-based strategy for production of nanostructured plasma polymers. In the first step of this method, the smooth substrate is seeded by plasma polymer nanoparticles produced by means of a gas aggregation source with a semi-hollow magnetron equipped with a Nylon target. In the second step, the nanoparticles are subjected to fluxes of organic fragments produced by magnetron sputtering of Nylon and such depositions are performed at various angles of incidence. As observed, this enables at higher incidence angles to prepare coatings with well-separated individual plasma polymer nanocolumns.

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### 1. Introduction

Plasma polymers are macromolecular solids created as a result of the passage of organic vapor through plasma. In contrast to conventional polymers with long chains of regularly repeating monomer units, plasma polymers are characterized by short chains, randomly branched structure as well as by high degree of cross-linking. However, the properties of plasma polymers may be deliberately tailored in a wide range by deposition parameters (precursor, working gas mixture, applied power, pressure etc.) that enabled to produce materials with bio-repellent [1–4] or bio-adhesive character [5–7], adjustable wettability [8] or excellent barrier properties [9].

Plasma polymers are traditionally described as smooth, compact and pinhole free. However, there is growing interest in the possibility to produce nanorough and nanostructured plasma polymer coatings that can expand the range of their possible applications. From this point of view, probably the most investigated plasma polymers are fluorocarbons. It has been documented that depending on the deposition conditions fluorocarbon plasma polymers may form diverse surface topographies that range from ribbons, petals to bumps [10–15]. It has been postulated that the key factor that governs nanostructuring of C:F plasma polymers is the combination of ion bombardment of the growing films and flux of incoming radicals, primarily  $CF_2$ . Reduction of both ion and radical fluxes, which was achieved either by pulsed plasma polymerization with low duty cycle or by placing substrates in the afterglow region, enabled unperturbed migration of chain-forming radicals over the surface

and diffusion-mediated film growth. Both pulsing and deposition in the afterglow, however, results not only in the nanostructuring of the surface, but also in the substantial decrease of the deposition rates. Because of this, an alternative strategy for production of nanostructured plasma polymer surfaces was proposed. This is based on deposition of plasma polymer nanoparticles (NPs). In this case, the NPs are formed in the plasma volume as a result of radical recombination with subsequent nucleation, radical-induced surface growth and coagulation [16].

The first experimental evidence of formation of particles during plasma polymerization dates back to the 60's of the last century when Kobayashi et al. [17] reported occurrence of sub-micron size particles in the deposited coatings at elevated pressures (~100 Pa). Since then the investigation of plasma polymer NPs was attempted in numerous studies mainly with respect to the process of their growth, charging, heating and investigation of their effect on plasma parameters. However, less attention was dedicated to utilization of these NPs for fabrication of nanostructured coatings. Further development was achieved when so-called gas aggregation sources (GAS) were introduced that had been initially employed for production of metallic NPs [18]. Plasma polymerization of volatile organic precursors or magnetron sputtering of solid polymer targets were employed in the configuration of GAS to produce plasma polymer NPs as it was shown for C:F [19,20], C:H [21,22], C:H:N:O [23] and (C:H):SiO<sub>x</sub> nanoparticles [24]. In contrast to conventional methods, the NPs are formed in high pressure aggregation chamber and are dragged by a carrier gas through an exit orifice to a low pressure deposition chamber. The produced NPs in this case reach the surface in the form of nanoparticle beam and are deposited initially as separated NPs and later on as rather porous films consisting of individual NPs. Furthermore, as demonstrated in our previous works, the size and chemical

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composition of produced NPs may be altered by operational conditions such as length of aggregation chamber, flow rate and applied power. The possibility to vary NPs sizes was recently reported to enable production of mesoporous coatings with multi-modal size distribution of NPs mimicking hierarchical structures observed in nature [24].

In this study, we introduce the strategy that utilizes plasma polymerized NPs for production of nanocolumnar structures of plasma polymers. This method, which was previously applied for production of metallic nanocolumnar films [25] consists of two steps. In the first one, the substrate is coated with NPs prepared by gas aggregation source. In the second step, the film of plasma polymer is deposited by means of low-pressure RF magnetron over the NPs that act as seeds for columnar growth of plasma polymer. C:H:N:O plasma polymer prepared by sputtering of Nylon was chosen for both of the steps with the perspective of its use in biomedical applications.

## 2. Experimental

### 2.1. Fabrication of C:H:N:O nanoparticles

C:H:N:O NPs were produced by means of gas aggregation source with semi-hollow magnetron (see Fig. 1). The cylindrical extension (internal diameter 60 mm, hollow depth 70 mm) was protruding beyond a circular plane. This configuration enabled to increase the area of the target and hence increase the amount of the sputtered species. The magnetron was equipped with a Nylon 6,6 target (Goodfellow, 5 mm thickness in the bottom and 1 mm thickness in the hollow cross-section) [26]. The gas (Ar) was introduced through a small hole in the center of the magnetron. The semi-hollow magnetron was placed into water cooled aggregation chamber, which was ended with a conical orifice (3 mm in diameter). The pressure in the aggregation chamber was 50 Pa. The particle source assembly was attached to a high vacuum chamber pumped by rotary and diffusion pumps. The pressure in the main deposition chamber during NPs deposition was 3.5 Pa. The magnetron plasma was excited by RF generator (Dressler Cesar) connected to the magnetron electrode through a matching box. Applied RF power was 60 W and was operated in pulsed mode with frequency 1 Hz and 90% duty-cycle.

### 2.2. Deposition of C:H:N:O films

C:H:N:O films were deposited by means of a planar RF magnetron equipped with Nylon 6,6 target (81 mm, Goodfellow). The magnetic field was designed especially for low-pressure operation with the enhanced intensity of 0.2 T above the erosion track [27]. Nitrogen was used as the working gas with the flow rate of 5 sccm and the pressure of 0.2 Pa. The applied RF power was 40 W. The depositions were done under different deposition angles, i.e. angles between the substrate and magnetron normals (see Fig. 2). The distance between electrode and center of the substrate was 8 cm.

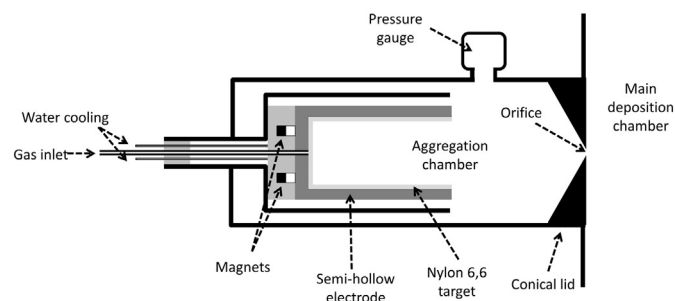


Fig. 1. Schematic illustration of the gas aggregation particle source.

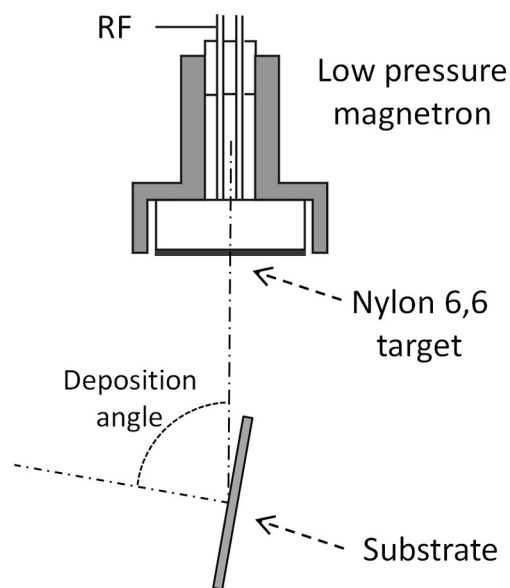


Fig. 2. Schematic illustration of the glancing angle deposition.

### 2.3. Samples characterization

Surface morphology of fabricated samples was determined by means of atomic force microscopy (AFM) and by scanning electron microscopy (SEM). The AFM measurements were performed using an AFM Quesant Q-scope 350 in the semi-contact mode (scan rate 4 Hz, resolution  $512 \times 512$  points) using Q-Wave-ACLA cantilevers (Schaefer Technologie, GmbH). Analysis of AFM  $10 \mu\text{m} \times 10 \mu\text{m}$  scans was performed using program Gwyddion. At least three measurements on randomly selected positions were performed for each sample. Mira3 (Tescan) scanning electron microscope (SEM) was used for SEM analysis. The top view and the cross-sectional SEM images were acquired with accelerating voltage 15 kV in the secondary electron mode.

Chemical composition of produced samples was determined by means of X-ray photoelectron spectroscopy (XPS) that was carried out using an XPS spectrometer equipped with a hemispherical analyzer (Phoibos 100, Specs). The XPS scans were acquired using Al K $\alpha$  X-ray source (1486.6 eV, 200 W, Specs) at constant take-off angle of 90°. Survey spectra used for the evaluation of elemental composition were measured for binding energies in the range of 0–1100 eV at a pass energy of 40 eV (dwell time 100 ms, step 0.5 eV). C1 s region spectra were recorded at a pass energy of 10 eV with 10 scans (dwell time 100 ms, step 0.05 eV) to obtain a higher spectral resolution and to lower the noise level. All the XPS spectra were referenced to the binding energy of aliphatic C—C bonds at 285.0 eV. The fitting of high resolution XPS spectra of C1 s was performed after Shirley background subtraction with mixed Gauss-Lorentzian lines (70% Gaussian and 30% Lorentzian) using the CasaXPS software.

## 3. Results

In order to highlight the effect of NPs used as seeds for columnar growth of plasma polymers, the first step in this study was evaluation of properties of films of sputtered Nylon deposited on smooth Si wafers, i.e. surfaces without any pre-seeded NPs. As can be seen in Fig. 3A, sputtered Nylon coatings deposited at 0° angle are smooth and compact with no visible nanostructuring, i.e. situation common for plasma polymer films deposited at low pressure. When the deposition angle was increased to higher values slight texturing with indication of formation of nanocolumnar structure started to be visible. However, even for the highest deposition angle used in this study (80°) formed nanocolumns

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