



Poly(tetrafluoroethylene) sputtering in a gas aggregation source for fabrication of nano-structured deposits



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ABSTRACT

R. f. magnetron sputtering of poly(tetrafluoroethylene) in configuration of a gas aggregation source is shown to produce super-hydrophobic nano-structured coatings in which cross-linked nano-particles of fluorocarbon plasma polymer are embedded in an uncross-linked continuous $\{-CF_2\}_x$ matrix. The 20–30 nm nano-particles appear in proximity of the magnetron and have cross-linked structure as a result of fast random radical recombination in the plasma. The continuous phase is formed at remote distances from the magnetron as a result of slower step-growth gas phase polymerization of CF_2 bi-radicals. The matrix has highly crystalline structure in which the CF_2 groups tend to adopt a 15/7 helical configuration. At least part of the macromolecules constituting the polymeric phase are oligomers with the molar mass below 1400 g/mol.

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1. Introduction

Fluoropolymers, and poly(tetrafluoroethylene) (PTFE) in particular, feature extremely low surface energy, low coefficient of friction, high thermal stability and chemical inertness. Since its discovery in 1938, PTFE has become widely used in a great variety of applications and its worldwide demand is estimated to be 160,000 metric tons in 2016 [1].

Development of new technologies requires fabrication of nanoscale fluorocarbon coatings with enhanced characteristics. Such coatings may be useful, for example, in microelectronics as high-performance electrical insulation with low dielectric losses, high flexibility and chemical inertness, or as non-wettable surfaces for biomedical applications. Traditional technology of fluorocarbon polymer coatings involves their deposition from solutions in perfluorinated solvents [1]. Reduction or complete removal of toxic initiator/surfactant residues is a technological challenge in this case. An advanced method utilizes supercritical carbon dioxide used as a solvent which replaces environmentally hazardous chlorofluorocarbons [2,3]. Significant efforts have also been applied to fabricate thin fluorocarbon coatings by solvent-free, plasma-based processes. Among these, r. f. magnetron sputtering of polymers [4–6] can be distinguished as a method that uses all-solid-state precursors, producing small amounts of waste and, hence, being much more environmentally benign. R. f. magnetron sputtering of PTFE has been studied since 1969 [7] and various thin films of fluorocarbon plasma polymers have been produced with a wide variety of properties [8–21].

Recently, search for unique physical properties has led to research on fluorocarbon polymers with advanced nanostructure. Novel fluorinated nano-particles (NPs) of compact [2,3], core-shell [22] or hyper-branched star-shaped architecture [23] have been fabricated by advanced chemical pathways in solutions. Plasma-based methods also offer the possibility to fabricate nano-structured fluorocarbon surfaces with all the advantages inherent to vacuum technology. Both plasma-enhanced chemical vapor deposition of volatile precursors [24] and r. f. magnetron sputtering of PTFE [21,25,26] were reported to produce thin films with tunable nano-architecture. The films grow via recombination of fluorocarbon radicals created in result of fragmentation of precursors in the glow discharge. Since typical pressures used are in the units of Pa range, such recombination occurs predominantly on the surfaces adjacent to plasma. Evolution of the film structure is given by the interplay between fluxes of the film-forming species and their surface diffusion as well as by intensity of ion bombardment.

In contrast to low pressure depositions, plasma polymerization at increased pressure may lead to the formation of submicron-sized particles in the discharge volume [24,27–30] as probability of gas phase radical recombination is higher in this case – the effect known as “dusty plasma”. Even smaller fluorocarbon NPs can also be produced and transported to substrates if a gas aggregation source (GAS) is used with an r. f. magnetron equipped with a PTFE target. This is a variation of the GAS first designed for fabrication of metallic NPs [31]. R. f. magnetron sputtering is operated in the aggregation chamber under increased Ar pressure. The aggregation chamber is ended with an orifice which separates it from the low pressure deposition chamber. Gas flow caused by the pressure difference drags particles formed in the GAS through the

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orifice into the deposition chamber in the form of a beam. Deposition of hydrocarbon [32] and nitrogen-rich [33] plasma polymer particles was demonstrated. Our recent research showed that the configuration of GAS can also be utilized for fabrication of fluorocarbon plasma polymer nano-particles by r. f. magnetron sputtering of PTFE [34]. The particles of 30 nm average size with chemical composition close to that of original PTFE were successfully produced. This paper aims at getting deeper insight into the general trends of the particle formation and investigates the influence of operational parameters on resultant fluorocarbon nano-particles.

2. Experimental

The experimental arrangement used for deposition of the fluorocarbon plasma polymer NPs is shown in Fig. 1. The gas aggregation source (GAS) consisted of a cylindrical stainless steel chamber ($\varnothing = 10$ cm) with the walls cooled by water. An r. f. magnetron with the 3-inch diameter was installed at the outer side of the GAS where an inlet of argon was introduced as well. The magnetron was equipped with a PTFE target (Goodfellow) of 5 mm thickness. R. f. power of 13.56 MHz was delivered to the magnetron from a generator (Cesar 300) via a matching unit. The opposite side of the GAS was attached to the main deposition chamber, the entire assembly being separated by an inner cap with an orifice. The cap was replaceable with the orifice size ranging from 1 to 3 mm. The GAS was pumped through the orifice and the main deposition chamber by rotary and diffusion pumps. The experiments were started when the base pressure in the main deposition chamber reached 10^{-3} Pa. The pressure and the flow rate of Ar in the GAS were adjusted by a flow-controller and by changing the diameter of the orifice separating the GAS and the main deposition chamber. The pressure in the main deposition chamber during the experiments was below 0.1 Pa.

The residence time t , i.e. the time NPs spend in the GAS on their way to the orifice, was calculated from the pressure P and the flow rate Q of Ar taking into account that the volume of the GAS was $V = 1200$ cm³: $t = PV/P_0Q$, where $P_0 = 10^5$ Pa is the standard pressure.

Polished silicon and gold-covered glass were used as substrates. Thickness of the deposits was measured by spectroscopic ellipsometry (Woollam 2000). Morphology of the deposits was studied by Scanning Electron Microscopy (SEM, Tescan Mira III) working at 30 kV acceleration voltage. Chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS) and by Fourier transform infrared spectroscopy (FTIR). XPS was measured using an unmonochromated 1486.6 eV Al K α X-ray source (Phobios 100, Specs). Pass energy of 40 eV and 10 eV was chosen for acquiring wide and high-resolution spectra, respectively. The high-resolution spectra were charge referenced to the CF₂ photoelectron peak at 292.0 eV. The FTIR spectra in the reflection-absorption arrangement (Bruker Equinox 55) were obtained for the samples

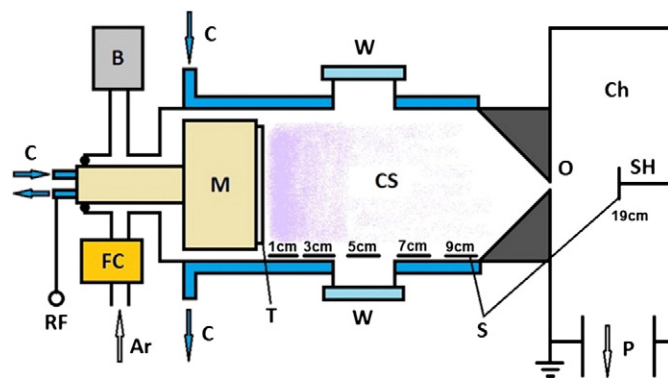


Fig. 1. The experimental scheme: C—cooling water, B—pressure gauge, FC—flow controller, M—magnetron, T—PTFE target, W—window, CS—gas aggregation source, S—substrates, SH—substrate-holder, O—orifice, Ch—main deposition chamber, P—pumping.

deposited on gold-covered glass. The spectra were acquired with 400 scans at 2 cm⁻¹ resolution.

Water contact angles were measured by a sessile droplet method or, in case of super-hydrophobic samples, by dynamic measurements in which a droplet of water was gently brought in contact with the surface in an advancing/receding manner, staying in contact with a releasing syringe as well.

3. Results and discussion

3.1. Evolution of nano-particle growth

In order to study the spatial dependence of how fluorocarbon plasma polymer NPs are formed and grow on their way from the magnetron target to the deposition chamber, the following arrangement was used. The substrates were placed inside the GAS at different distances from the target as shown in Fig. 1. One substrate was also placed in the deposition chamber 3 cm away from the orifice (19 cm from the target). Thus, it was possible to prepare a set of the samples during the same experimental run. The influence of the Ar flow rate and the discharge power was investigated.

Fig. 2 shows the SEM images of the NPs deposited for 30 min at 140 W power under 40 Pa/0.8 sccm of Ar. Only three representative images are given: the samples located in the GAS close to the magnetron (3 cm distance), in the GAS close to the orifice (9 cm distance) and in the deposition chamber (19 cm), others not shown for simplicity. No changes in particle size along the distance from the magnetron can be observed. The same trend was found for other flow rates and powers used. In the case of the 0.8, 3.2 and 8.2 sccm Ar flows at a constant pressure of 40 Pa, the average size of the NPs remained at 23 ± 5 nm (Fig. 3). Slightly bigger particles with the average size of 28 ± 7 nm were produced at 200 W discharge power, their size did not vary with the distance from the target either. It is worth noting that all the particles produced in this work are significantly smaller than those reported for solution-based processes and for plasma polymerization of volatile precursors [29,30,35–37], except for the paper by Feng et al. [28] who reported on fabrication of 17 nm NPs by pulsed plasma polymerization of heptadecafluorodecyl acrylate. Remarkably, the authors showed that the size of their particles decreased with r. f. power delivered to the discharge. It was argued that higher power produced more reactive species (radicals) which gave rise to more nucleation sites. Under constant monomer concentration (at given pressure and flow rate) more nucleation sites lead to bigger amount of smaller particles. The mechanism is different in our work: here, higher power leads to enhanced sputtering and faster supply of the fluorocarbon fragments (that serve as precursors for subsequent plasma polymerization) into the gas phase. Higher concentration of nucleation sites gets counterbalanced by more intensive supply of polymerizable species which results in a small change in particle size, at least for the cases of 140 and 200 W studied.

Fig. 4 shows the change of the thickness of the deposits produced at varying flow rates of Ar and constant pressure (40 Pa) and power (140 W) along the distance from the magnetron. The highest deposition rate is observed in immediate proximity of the target while it decreases drastically at longer distances. It suggests that the efficiency of NP formation is highest close to the target where the magnetron discharge is most intensive. A magnetic trap confines the discharge in a ring-shaped zone spreading for about 1 cm away from the target surface and this position corresponds to the first datapoints in Fig. 4. Obviously, the partial pressure of condensable species sputtered from the target is highest here, they readily nucleate with the formation of NPs and the gas flow drags them away from the discharge zone. Taking into account that the residence time of the NPs in the GAS is relatively long ($t = 3.5$ s for $Q = 8.2$ sccm and $t = 36$ s for $Q = 0.8$ sccm), one would expect that their size should increase with the distance from the magnetron, provided that attachment of new species to existing NPs is still effective.

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