

Deposition of Fluorocarbon Plasma Polymer Nanoparticles and their Basic Properties

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Fluorocarbon plasma polymer nanoparticles have been fabricated using gas aggregation cluster source (GAS) equipped with a planar magnetron with PTFE target. A beam of nanoparticles 20 – 200 nm in diameter was generated. Fluorocarbon nanoparticle films have shown very good water repellent properties. Films immersed in ethanol for two hours exhibited excellent stability that was also good in case of water. Measurements using a deflection system showed the presence of both neutral and charged nanoparticles.

Keywords: poly(tetrafluoroethylene), magnetron sputtering, plasma polymerization, superhydrophobic

1 INTRODUCTION

RF magnetron sputtering of PTFE (poly(tetrafluorocarbonethylene)) has been studied since the seventies of the last century [1]. Detailed history of the field can be found elsewhere [2]. Recently, the processes of the target material degradation were studied in detail as well as the chemical composition of fluorocarbon plasmas, deposition rates and wettability of obtained thin fluorocarbon plasma polymer films [3]. Then Stelmashuk et al [4] investigated an influence of the working gas pressure on the deposition process and showed creation of dust particles at an elevated Ar pressure of 70 Pa. An idea based on formation of super-hydrophobic fluorocarbon thin films with high surface roughness was realized by Drabik and colleagues [5] who used an increase of the working gas pressure and a distance between a magnetron head and a substrate holder. The effect of the creation of nanoparticles at an elevated pressure was used in Haberland type gas aggregation cluster source for fabrication of fluorocarbon plasma polymer nanoparticles [6] and in-depth investigation of the particle formation process and resulting properties of resulting thin fluorocarbon films [7].

This paper is devoted to the study of properties that were not considered previously, such as the charge of the fluorocarbon plasma polymer nanoparticles and stability of coatings based on those nanoparticles in liquid environment.

2 EXPERIMENTAL PART

Detailed description of the experimental arrangement [Fig. 1.] can be found elsewhere [6,7]. A deflection system based on three stainless steel grids was mounted between the exit orifice and the substrate holder. First and last grids were grounded. The central grid was under positive/negative potential or also grounded. This system allowed deflecting the particles with definite charge or depositing all types of particles.

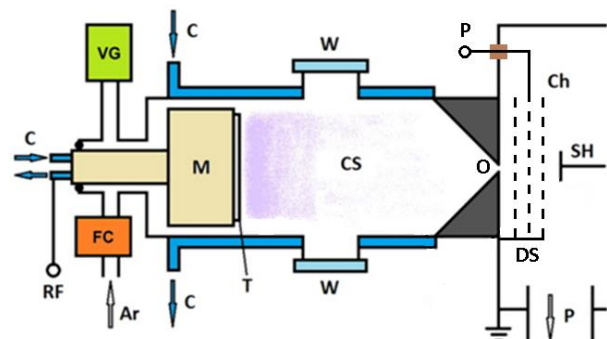


Fig. 1: Experimental arrangement: CS – cluster source, Ch – deposition chamber, VG – vacuum gauge, FC – flow controller, Ar – argon, C – water cooling, RF – radiofrequency power source, M – magnetron, T – PTFE target, W – window, O – orifice, DS – deflection system, P – the central grid under potential, SH – substrate holder, P – pump

At a power 80 W and a flow rate of 3.5 sccm the particle size distribution showed that the most probable size is 200 nm for 135 Pa pressure. As an example, Figure 2 presents the SEM micrographs of the polished silicon wafers

deposited with fluorocarbon plasma polymer nanoparticles.

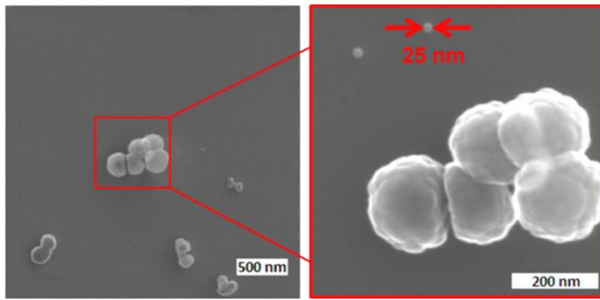


Fig. 2: Fluorocarbon plasma polymer particles obtained at: 80 W discharge power, Ar flow rate 3.5 sccm and pressure in the gas aggregation cluster source 135 Pa

3 RESULTS AND DISCUSSION

Fluorocarbon nanoparticle films have shown very good water repellent properties – they were superhydrophobic and slippery. We therefore investigated the film stability in liquids. A day after deposition nanoparticle coatings on silicon wafers were immersed in water and ethanol for two hours [Fig. 3.]. Water contact angle

of the tested samples was measured directly before immersion, after 5, 10, 15, 30, 60 and 120 minutes of immersion in the liquid. Physical structure [Fig. 4.] and chemical composition [Fig. 5.] were also analyzed using atomic force microscopy and X-Ray photoelectron spectroscopy, respectively, before and after the stability tests.

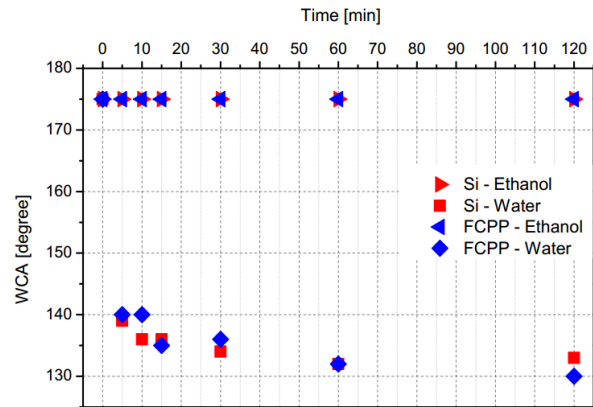


Fig. 3: Coating stability in liquid. Si – polished silicon substrate covered with nanoparticles, FCPP – silicon substrate pre-covered with 150 nm of fluorocarbon plasma polymer film and then covered with nanoparticles

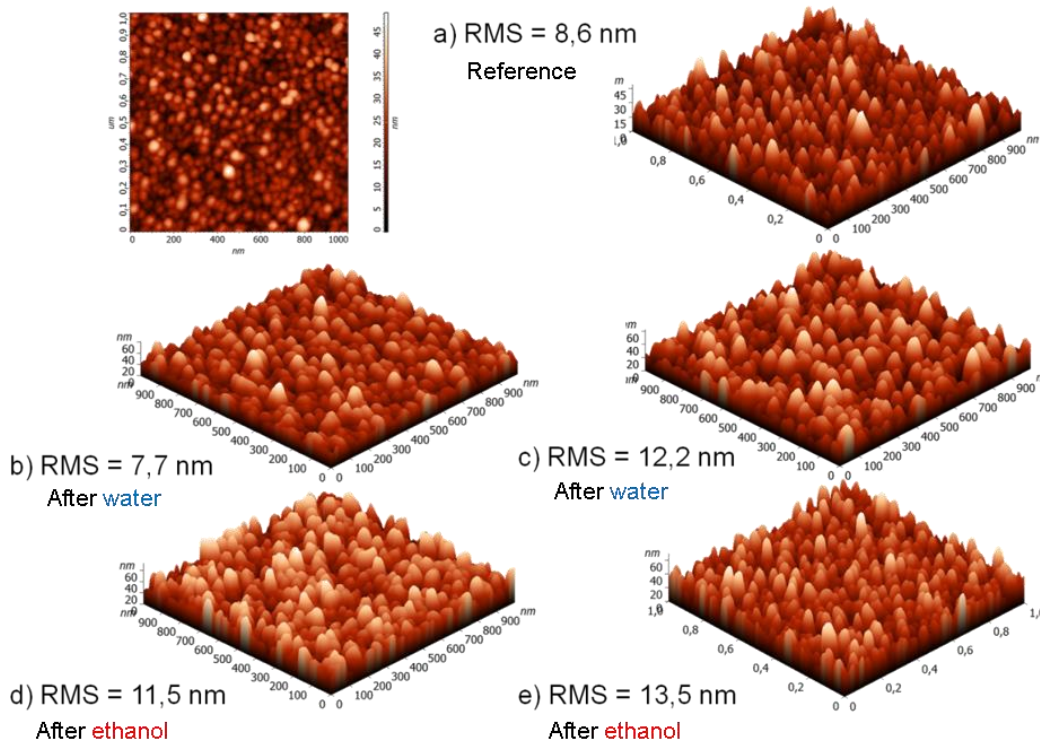


Fig. 4: The influence of the liquid on the morphology of the fluorocarbon plasma polymer nanoparticles: a) reference sample; b) and d) – Si substrates coated with fluorocarbon particles; c) and e) – Si substrates pre-covered with 150 nm of fluorocarbon plasma polymer film and then covered with nanoparticles. RMS – root mean square roughness

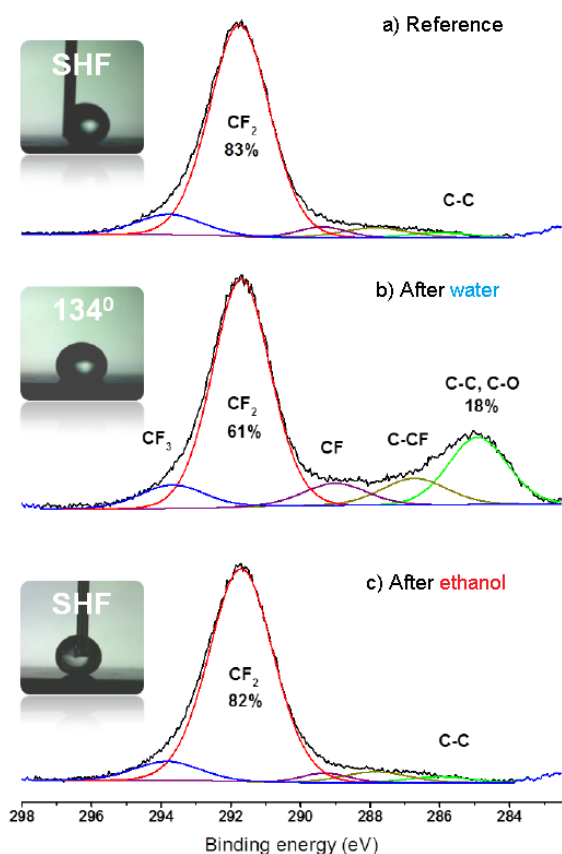


Fig. 5: The influence of the liquid on the chemical composition of the fluorocarbon plasma polymer particles: a) reference sample; b) chemical composition after two hours in the water; c) chemical composition after two hours in ethanol

Films immersed in ethanol for two hours exhibited excellent stability that was also good in case of water. The changes in RMS roughness of the tested samples were negligible in comparison with the reference. However, certain amount of oxygen (about 3%) was detected after a two-hour contact with water. At the same time the sample immersed in ethanol and the reference sample demonstrated the content of CF₂ groups more than 80%. Measurements using a system of deflection

grids showed the presence of both neutral and charged nanoparticles. More than half of the total amount was detected as negatively charged, about one third – positively charged and slightly more than 10 % neutral.

4 CONCLUSIONS

A beam of nanoparticles 20 – 200 nm in diameter was generated using a Haberland type GAS that operates at 40 to 135 Pa working pressure and flow of Ar up to 12 sccm. Deposited nanoparticle films have shown to be superhydrophobic and quite resistive to immersion to ethanol and water. More than half of the obtained particles were negatively charged.

Acknowledgements

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