

Biocompatible Nanolayered Polymerization of MEMS Devices

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Abstract—Deposition of polymeric and biocompatible nanolayers on the solid-state substrates is done using a simple vacuum chamber. The chemical characteristics of the deposited nanolayer are analyzed using Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The surface morphology of the nanolayers is analyzed using contact angle goniometer and scanning electron microscopy. The coated nanolayers show excellent stability in different chemical surroundings including the physiological pH therefore making it applicable in coating 3D MEMS devices and body implants which need medicated coating. A micropore is coated with this approach and results depict uniform coating of the structure.

I. INTRODUCTION

NANOTEXTURED fluorinated polymer surfaces play important roles in barrier property of materials, membranes, sensors and medical implants. These help in obtaining low critical surface tensions causing hydrophilic and hydrophobic layers to bead up on exposure [1, 2]. Methods commonly used to deposit fluorinated polymers onto a surface include plasma polymerization, biomimetic mineralization, spin coating, chemical absorption, chemical vapor deposition (CVD) and self assembled monolayer (SAM) formation [3-5]. These methods provide good surface deposition but little control of the polymer surface properties and conformality on uneven surfaces [6, 7]. Film conformality can be achieved by growing the fluorinated films using plasma polymerization and CVD but, these require specialized equipment, trained users and are cost prohibitive at mass scales [8-10].

This paper presents a facile coating process using a simple vacuum chamber to deposit fluorinated organic nanolayers. The chemicals used for the layer formation were 3-Aminopropyltrimethoxysilane (APTMS) and 1H,1H,2H,2H-Perfluorooctyl-trichlorosilane (PFTS). The organic nanolayers obtained by the reaction of the two non-toxic chemicals were characterized for chemical and physical stability [11-13]. It was seen that the film was capable of surviving various chemical surroundings. These nanolayers

were also used to coat a 3D MEMS structure to study coverage performance in coating such devices. A micropore was coated which showed the presence of the coating in the inner periphery of the pore and angled walls of the cavity.

II. METHODS AND MATERIALS

A. Materials Used

Two polymers were used in the experiments; APTMS and PFTS. APTMS is known to be hydrophilic while PFTS is hydrophobic. These chemicals were used as received (Sigma-Aldrich, St. Louis, MO, USA). Silicon wafers, with (100) orientation and ~550 μm thickness, were used as the substrates to deposit the polymer nanolayers for characterization. The micropores were made in the silicon wafers with same orientation but these wafers were ~375 μm thick. The process of micropore fabrication was adapted from the nanopore fabrication as reported before [14].

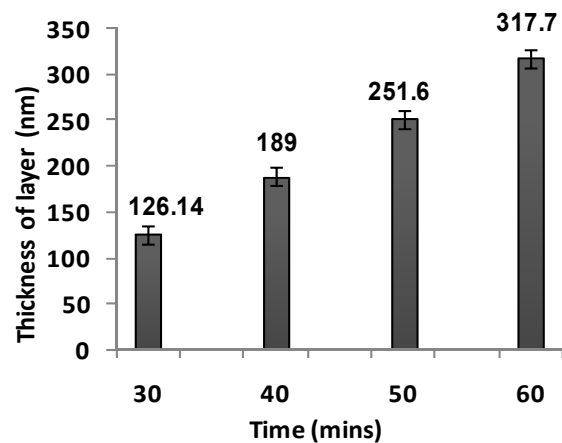


Fig.1. Thicknesses of nanolayers deposited on five samples at reaction times of 20, 30, 40, 50 and 60 mins. The thicknesses are measured using surface profilometer. Data is average of readings for each sample measured at 5 different locations.

B. Nanolayer Deposition

The nanolayer deposition was performed using a simple vacuum chamber where the two monomers, APTMS and PFTS, were placed inside the vacuum chamber. These monomers were allowed to react in vapor phase under controlled vacuum of 22-25 mmHg. A silicon wafer chip of size 0.5 cmx0.5 cm was placed in the chamber along with the monomers which acted as a solid substrate for the nanolayer deposition. When the two monomers reacted, they formed a thin film coating on the surface of the silicon wafer chip. Fig 1 illustrates the thickness graph based on the

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time of deposition of the film. Fig 2 shows the SEM micrographs of the coating. During the SEM imaging, the samples did not require conductive coating.

The surface morphology and the thickness of the film could be controlled by three main parameters: ratio of concentration of the monomers, reaction time and vacuum inside the chamber. The volumetric ratios between APTMS and PFTS ranging between 2:1–3:1 and vacuum in the range of 22 – 25 mmHg, the deposited nanolayers depicted porous texture with pore sizes ranging between 100-500 nm [1].

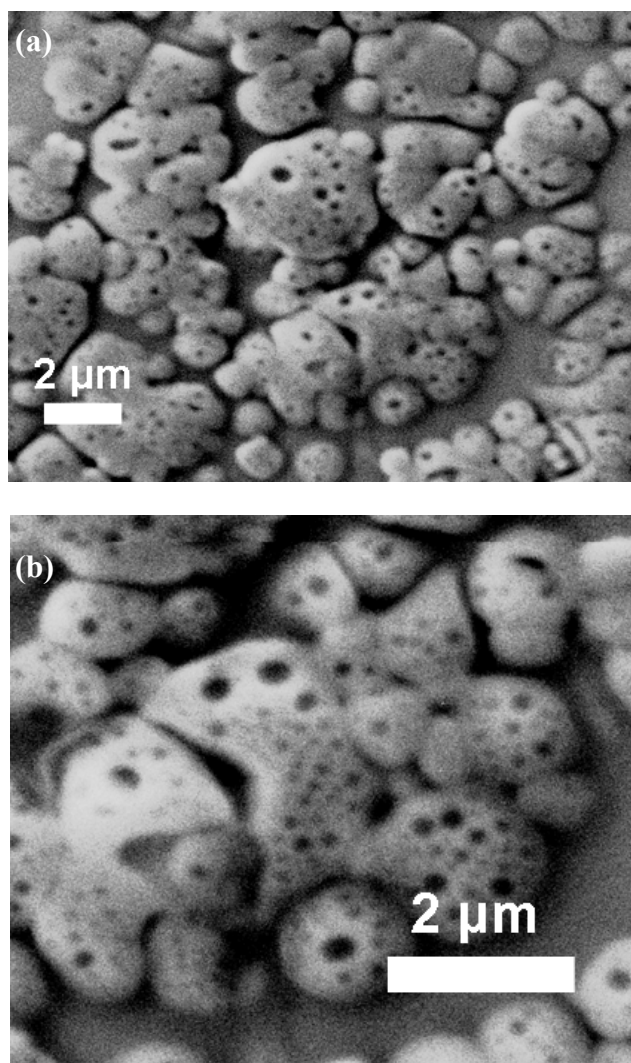


Fig. 2 (a) and (b) are the SEM micrographs captured at different magnifications, showing the surface morphology of the coating. The nano-texture of the coating is evident.

C. Characterization of the Nanolayers

The chemical and physical characterization of the nanolayer was performed using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Scanning electron microscope (SEM) imaging and contact angle goniometer. Different ratios of APTMS:PFTS were used to make the coatings. From the contact angle measurements, the surface energies of the nanolayers were calculated which showed very low values [15].

The biostability of the nanolayer was tested by immersing the coated silicon substrate into different pH solutions including deionized (DI) water. Five different silicon chips were coated with 2.5:1 ratio of APTMS and PFTS for 50 mins at a vacuum of 22 mmHg. These chips were immersed in solutions with pH values of 2, 4, 7 and 10.

The surface morphology of the coating was studied using contact angle goniometer and SEM before and after exposure to the pH solutions. When the surface was washed using DI water, there was no change in morphology and surface energy but when it was left in DI water for 24 hours, there was a slight increase in the surface energy. When the samples were immersed in different pH solutions for 15 hours, the coating was stable but the strength of the coating varied. For the chip immersed in pH 2 solution, it was found to have more surface energy for the coating, making it more hydrophilic and in addition, the nanolayer lost its continuity. For the samples which were dipped in pH 4 and pH 7, similar results were obtained where the nanolayer was stable and its surface energy did not change. The sample which was dipped in pH 10 showed results very similar to those for chip dipped in solution at pH 2.

D. Coating of 3D Structures

A conformal coating of organic nanolayers is a much sought-after property, which has potential applications in medicated implants, organic devices, surfaces of military assets, etc. As a proof of the power of the presented approach, a micropore structure was coated. MEMS devices, used as body implants or substrate carriers for controlled drug delivery, need medicated coatings that can be done with this approach. The morphology of the coating on angled, circular and uneven surfaces of the solid-state micropore was studied. The 2.5:1 ratio of combination of APTMS and PFTS was used for micropore coating at a controlled vacuum of 22 mmHg with a deposition time of 40 mins. Fig 3 shows the image of the coated micropore structure.

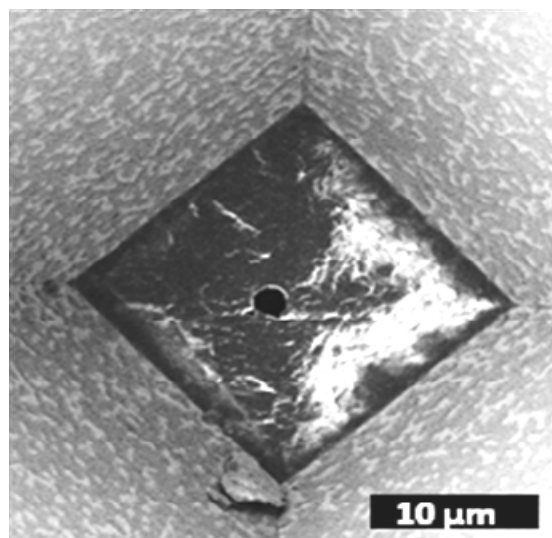


Fig. 3 SEM micrograph of a micropore coated with polymer nanolayer.

III. RESULTS AND DISCUSSION

Table 1 shows the calculated surface energy values. The plain SiO₂ surface energy calculations were in close agreement to reported free energy of interaction between SiO₂ and water [16]. The reduction in the surface energy depicted increased hydrophobicity of the surface. Such low energy and highly hydrophobic surfaces can enhance protein adsorption and better interfaces with biological environments [1].

TABLE 1
SURFACE ENERGY MEASUREMENTS

Sample	Ratio of APTMS:PFTS	Average Surface Energy (mJ/m ²)
1	No Coating	63.721
2	2.5 : 1	5.102
3	1 : 2.5	10.563
4	1 : 1	9.711

The FTIR results showed remarkable differences between samples made with 2:1, 1:1 and 1:2 ratios of APTMS and PFTS. For sample with 2:1 ratio of APTMS and PFTS (Table 2), a broad stretching in the range of 2500–3200 cm⁻¹ was observed which indicated the presence of O-H and C-H bonds. The -C=O bonds along with Si-O-Si were also observed with this concentration. Halogen peaks indicated the presence of fluorine which originated from PFTS. These groups can have high protein/cell adsorption due to their inertness and thermal resistance. Sample with 1:1 ratio of APTMS and PFTS showed similar results but the spectra of sample with 1:2 ratio of APTMS and PFTS showed the presence of halogens and C-H bonds, indicating the dominance of PFTS upon APTMS.

TABLE 2
FTIR PEAK DATA FOR NANOLAYER FORMED IN 2:1 RATIO OF
APTMS:PFTS

Sample #	O-H and C-H bonds (cm ⁻¹)	-C=O (cm ⁻¹)	Si-O-Si (cm ⁻¹)	Halogen Si-C/C-Cl (cm ⁻¹)
1	2630-3630	1635	1139-1010	749, 688
2	2645-3211	1701	1135-1006	670, 641
3	2649-3335	1652	1135-1005	782, 650
4	2573-3202	1506	1137-1013	755, 698

Presence of C, O, F, Si and Cl was seen in the XPS analysis (Fig. 4). The presence of C and O peaks in the areas of 280 eV and 520 eV, respectively, confirmed the film to be

organic. These peaks would have stemmed from the C-F bonds of PFTS indicating high percentage of fluorine.

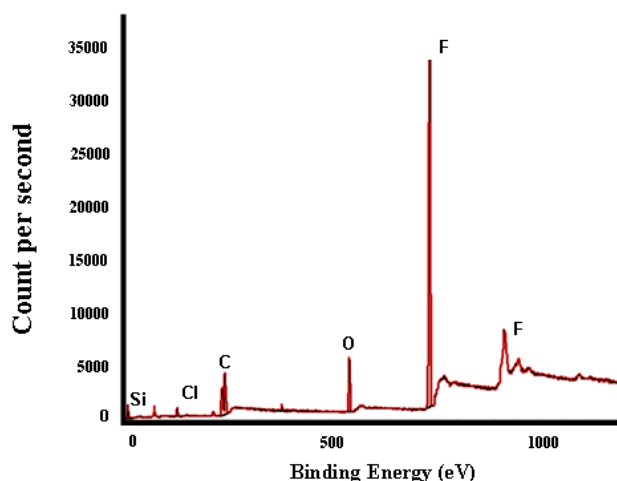


Fig. 4: Survey spectrum of the XPS analysis showing the peaks obtained due to the presence of Silicon, Chlorine, Carbon, Oxygen and Fluorine.

Controlling the morphology and conformality coverage of the polymer film are the critical factor which determine the feasibility of coating films in many biomedical MEMS devices. The thickness of the film was controlled by the concentration and the reaction time. Based on the data of Figs. 1 and 2, the sample with 2.5:1 concentration of APTMS and PFTS after a 60 mins deposition showed thick porous surface morphology. Based on the results obtained from characterization, the fluorinated nanolayers show their strong potential to coat devices and surfaces for wide ranging applications.

IV. CONCLUSION

This paper demonstrates the formation of a nanolayered organic polymer coating using a simple vacuum chamber instead of specialized equipment and need for trained users. The stability and the chemical composition of the nano film in different pH solutions indicate that the film can survive in strong chemical surroundings including the body pH. Though the control of the pore size of the film is still under study, our process of making low surface energy fluorinated polymer films can be used in many applications. .

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