

Self-supporting nanofilms by plasma assisted technology

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Abstract: Freely suspended nanofilms (thickness < 100 nm) (fsNFs) have been a theoretical and experimental curiosity for several decades because, with macroscopic sizes and molecular scale thickness, they combine at the same time the properties of macroscopic materials along with individual molecules. In this paper plasma deposition of fsNFs will be discussed extensively as an innovative approach of synthesis which find application in several fields.

Keywords: Free-standing nanofilms, plasma deposition, conformal films

1. Introduction

Self-supporting membranes are of great interest for use in MEMS devices in the form of sensors or actuators, flexible skin displays and electronic tattoo, wound dressing and drug delivery systems. The recent miniaturization of perm selective membranes or of scaffolds for the 2D adhesion of cells has created a demand for thinner membranes with a broad range of properties, such as defect-free uniformness, macroscopic stability and elasticity together with nanometer thickness. However, the synthesis of materials with such conflicting features is still a challenge and largely remains to be explored. To date, several approaches have been implemented for the fabrication of free-standing nanoscale films from polymers and/or from inorganic materials: casting [1], layer-by-layer (LbL) assembly of polyelectrolyte multilayers [2], crosslinking of amphiphilic Langmuir–Blodgett [3] and self-assembled [4] monolayers, and assembly of triblock copolymers [5]. The main used manufacturing process flow of fsNFs follows the common manufacturing pattern: the thin film deposition of the fsNFs precursor onto a suitable sacrificial layer; dissolution of the sacrificial layer in an adequate solvent; leaving the fsNFs freely floating in the liquid; withdraw the fsNFs from the solvent and transferring it to a permanent frame. This final step remains generally a difficult issue.

So far proposed synthesis of fsNFS have some limits: a) time consuming; b) use of toxic solvents not compatible with bio-applications and not ecofriendly; c) limited versatility in terms of chemical/physical properties of the film synthesized. Therefore, the application of fsNFs is usually unsuccessful.

In this paper we propose an innovative approach based on plasma technology that is versatile, one-shot solventless and contaminant free and that, more importantly, guarantees the synthesis of fsNFS with chemical physical properties that are peculiar of the process applied (i.e. super-hydrophobicity, super-hydrophilicity etc. ...) [6].

This paper demonstrates that plasma technology could produce robust self-supporting membranes with dimensions and properties that have not been reported to date and performances similar and sometimes superior to that of films produced by casting.

2. Materials and Methods

The general procedure of the fsNFs fabrication is as follows. A sacrificial layer is formed on a flat silicon wafer by spin-coating, and a thin layer of PE-CVD coating is additionally formed with thickness of several tens of nanometer. First, silicon wafers were thoroughly cleaned with piranha solution (30min rinsing at 80° C) and then a layer of polyvinylalcohol has been spin coated (4000 rpm for 60 s) upon them. The PE-CVD process has been used to deposit a thin polymeric film on the prepared substrates. Plasma processes are carried out in a low pressure plasma reactor, equipped with a Pyrex glass cylinder (100 mm in diameter, 100 mm in height). The plasma was ignited by means of two external stainless steel electrodes: a ground ring-electrode (130 mm in diameter) wrapped around the glass cylinder, and a 13.56 MHz RF flat disc electrode (80 mm in diameter), placed at the bottom of the chamber. The RF electrode is connected to a power supply (Ceasar1010, Advanced Energy) through an home-made matching network. The reactor was fed CO₂, C₂H₄ and H₂ and mixture of them. The H₂ was produced by a hydrogen generator (CINEL RC100).

A double step process was carried out composed by a first step of deposition with a mixture of CO₂/C₂H₄ and a second step with CO₂/H₂ in order to modulate the chemical composition of the outermost layer of the deposited film. Several experimental conditions were investigated in order to tune the chemistry of the treated surface and to study the effect of plasma power, gas feed composition and process time.

In the first step, operating with a pressure of 600 mTorr for 10 min, the total C₂H₄/CO₂ gas flow was kept constant at 150 sccm. The input power was varied from 30 W to 100

W and the gas feed composition was changed from 100% C₂H₄ to a mixture of CO₂:C₂H₄ at 2:1.

In the second step, operating with a pressure of 600 mTorr and 10 W of input power, the gas feed composition was changed from 100% CO₂ (100 sccm) to 100% H₂ (50 sccm) and the process time was varied from 1 to 5 min. All the fsNFs were detached from solid substrate by immersion into double distilled water.

The films were analysed by means of a profilometer (Alpha-Step D-120 Stylus Profiler), FT-IR (VERTEX 70v FTIR Spectrometer), water contact angle (KSV CAM200 digital goniometer), XPS (PHI Versa Probe II XPS spectrophotometer), nanoindentation (TI 750 UbiTM, Hysitron triboindenter). The cytotoxicity of fsNFs was analysed by using two cellular lines: EA.HY926, endothelial human cells, and SAOS2, cells taken from human osteoblastoma. Silicon shards covered with a PVA layer and a PE-CVD film were placed in 60mm Petri dishes and covered with 200 µL of a cell suspension in cell culture medium (1×10^4 cells). The cell culture was carried out for 2 hours in an incubator at 37° C, 5% CO₂ atmosphere, in order to let the cells to adhere as much as possible on the films. After that the samples are completely covered with cell culture medium and left in the incubator for 24 h or 72 h. After the time set for their growth, cells were treated with paraformaldehyde (PFA) and coloured with Coomassie Blue Brilliant.

Results

A first optimization of plasma deposition processes has been carried out in order to make sure that the substrate is robust enough and easy to handle. The PE-CVD to produce the desired layers was accomplished with a double step approach. Considering the coatings deposited without the second grafting step, namely from ethylene/CO₂, the deposition rate resulted 5.2 ± 0.4 nm/min at a RF discharge power of 30 W, when the working gas mixture was CO₂:C₂H₄ at 2:1 ratio. Keeping constant the input power at 30 W, no relevant differences were observed in term of deposition rate, when the gas ratio was changed from 100% C₂H₄ to a mixture of CO₂:C₂H₄ at 2:1.

The chemical structure of the deposited C:H:O plasma polymer films was studied with FT-IR spectroscopy. The normalized adsorption FT-IR spectra of the plasma deposited coatings in a single step process, working at 30 W of input power and changing the gas ratio from 100% C₂H₄ to a mixture of CO₂:C₂H₄ at 2:1 show characteristic absorption of hydrocarbon coatings: a peak centered at 3500 cm⁻¹ corresponding to OH stretching and one centered at about 1710 cm⁻¹ typically attributed to C=O vibration. The intensity of these two bands increase with the percentage of CO₂ in the gas feed. Also the vibrations of other structural units were identified in the FT-IR spectra reported, such as the band around 2900 cm⁻¹ relative to CH stretching, the shoulder around 1630 cm⁻¹ attributable to C=C bonds, and the double band around 1450 cm⁻¹ and 1380 cm⁻¹, due to the bending of CH bonds.

The region below 1500 cm⁻¹, known as fingerprint region and unique each different bond structure, is characterized by the broadening of all the absorption peaks and by the evolution of complex bands, both connected with the random and irregular structure of a plasma polymer film with high crosslinking, especially when the content of CO₂ in the gas feed increases. The deposited C:H:O films were characterized also with XPS to study the elemental composition of their surfaces. Considering the single step deposition, as reported in the first part of the Table 1, the addition of CO₂ to ethylene in the gas feed mixture increased the O/C elemental ratio of the coatings from 0.057 ± 0.002 (pure C₂H₄) up to 0.195 ± 0.007 (CO₂:C₂H₄ 2:1), resulting in a higher incorporation of oxygen moieties in the structure of the growing film. When a post-treatment with CO₂ (100sccm, 10W, 600mTorr, 40s) has been used the outermost layer has a similar O/C ratio whatever the experimental conditions used for the first step (O/C: 0.273 ± 0.005). Immersion of this layered structure in double distilled water allows to collect fsNFs due to the dissolution of the sacrificial layer. A freely suspended fsNF can be easily seen after 5 minutes of water immersion (fig. 1a).

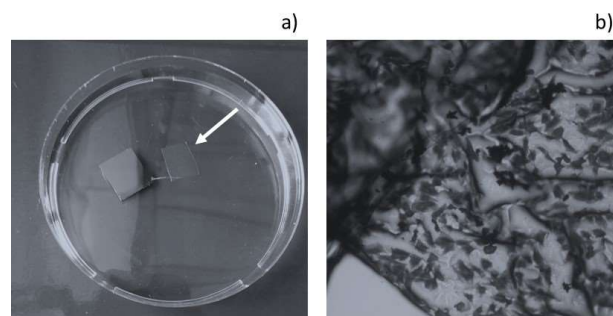


Fig. 1. a) Example of a self supporting fsNFs (white arrow) and of the same film covered by SAOS2 cells after 72h of cell culture

The XPS characterization performed on the bottom side of the film detached from the silicon shard and rinsed in water for three times shows the presence of a PVA-like layer that seems to be covalently attached to the bottom of deposited film. The resulting mechanical properties in the free-standing state are directly influenced by the thickness of the deposited films and chemical characteristics of the coatings in terms of oxygen content. In general, ultra-thin films show a smaller elastic modulus and higher adhesive properties compared with thicker films of similar chemical composition.

From biological point of view, it has been demonstrated that the material surface chemistry plays a key role in a series of cellular functions, including adhesion and proliferation. Films characterized by the highest O/C ratio are more suitable to promote cell adhesion and proliferation both for SAOS2 cells than films deposited in a single step approach with only C₂H₄ as gas feed. Similar results have been obtained for EA.HY926 cells. The fsNFs both as well and in presence of cells could be easily

manipulated in water with metal tweezers or pipettes, folded and unfolded multiple times without breaking.

3. Conclusions

Plasma processes developed in this research provide a simple, versatile and robust tool to synthesize ultrathin chemically asymmetric multifunctional free-standing coatings that are stable for at least 1 month of storage in air although they are rich of COOH groups. Plasma technology offers an opportunity to separately control chemistry, thickness and morphology of deposited coatings capable of overcoming some of the major concerns regarding synthesis of fsNFs by means of conventional methods, including the poor macroscopic stability and elasticity, together with nanometer thickness.

4. References

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