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Fouling and non-fouling surfaces produced by plasma polymerization of ethylene oxide monomer

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Abstract

This paper presents the results of plasma polymerization using diethylene glycol dimethyl ether as a precursor in a capacitively coupled radio frequency system. The chemical structure of the coatings was characterized using several analysis techniques (X-ray photoelectron spectroscopy, Fourier transform-infrared spectroscopy, ellipsometry), while the biological response of these coatings has been tested by protein adsorption and cell culture experiments. The modulation of the input plasma power controls the concentration of polyethylene oxide groups in the coatings and allows the production of films with opposite protein and cell repellent properties. The study of the stability of these coatings in different media (water, acetone, phosphate-buffered saline) reveals that these films could be involved in classical lift-off processes for the production of patterned surfaces.

Keywords: Plasma polymerization; Fouling and non-fouling coatings; Protein and cell adhesion

1. Introduction

The production of anti-fouling films is a key element in the development of biomedical materials, such as medical devices, implants, and in vitro tests [1]. Such coatings favour the biological integration of these tools by limiting the interactions between the implants and physiological fluids [2,3]. The control of the biological response of medical devices without altering their bulk properties is a challenge which can be taken up by tailoring their interfacial properties thanks to anti-fouling surfaces. Also, the development of coatings with patterned surfaces is a fundamental step for the construction of biosensor materials. The surface of such biosensors is composed of periodic domains with alternate fouling (i.e. reacting with specific target molecules) and anti-fouling properties [4]. Moreover, patterned surfaces containing cell or protein adhesive and non-adhesive functionalities provide a very useful tool in a large range of research areas, such as tissue engineering [5], investigations of cell behaviour [6], co-cultivating of different cell types [7], and artificial growth of neuron networks [8].

Poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) compounds are known for their ability to reduce adsorption of biomolecules [9] and cell adhesion [10,11]. The exact mechanism of PEO coatings that leads to protein resistance is not yet fully understood and several parameters seem to be involved (chain density, chain length, chain conformation) [12–14]. However, the non-fouling properties of PEO films are mainly due to a self-repulsion of the chains in water. This reaction initiates a dynamic sweeping process, which limits the adsorption of proteins on the surface [15]. Several approaches can be used to produce PEO layers: physical adsorption [16–19], radiation and chemical crosslinking [20–22], self-assembled monolayers [23], spin coating stabilized by ion beam treatment [24], covalent immobilization [25], chemisorption of PEO thiol on gold surfaces [26] or plasma polymerization

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of ethylene oxide [27,28]. Compared to the other methods, plasma polymerization allows coatings on a large variety of substrates. Moreover, the deposition occurs in one step and can be performed on three-dimensional surfaces. Plasma polymerization is a low pressure and low temperature process induced by a glow discharge via a pure organic vapour or a mixture of an organic vapour and a reactive or non-reactive gas. During deposition, two processes occur simultaneously: the ionization of gaseous species (inducing the plasma creation) and the fragmentation/recombination of particles (polymerization). These two processes have a strong influence on the properties of the deposited film and can be controlled by tuning the deposition parameters. Moreover, the films deposited by plasma polymerization have different physical properties than films elaborated directly from the monomer (by spin coating for example). These physical properties depend on the film microstructure (i.e. the chemical composition and the atomic organization) and can be monitored by the operating conditions.

In this work, we study the tuneable properties of PEO-like coatings obtained by plasma polymerization of diethylene glycol dimethyl ether (DEGDME) vapour on different surfaces (polystyrene, silicon wafers and quartz crystal covered with SiO_2). The stability of coatings in different media (water, acetone, phosphate buffer solution) and the possibility of involving them in the fabrication of patterned surfaces by a lift-off process are discussed. Biological properties of these coatings (towards cells and protein adhesion) have been investigated by several complementary techniques.

2. Materials and methods

2.1. Film processing

The plasma device used in this study is a homemade stainless-steel reactor (vessel size: $300 \times 300 \times 150$ mm) with two symmetric internal parallel-plate electrodes (diameter of the electrodes: 140 mm, distance between the two electrodes: 50 mm). The plasma was generated by a radio frequency (RF) generator (13.56 MHz) connected to the upper electrode, whereas the bottom electrode was grounded and used as sample holder. Experiments were carried out with a power ranging from 1 to 15 W. The reflected power was adjusted to its minimum value (<1% of incident power).

A mixture of DEGDME $(CH_3OCH_2CH_2)_2O$ vapour (Sigma Aldrich, used as received) and argon (15% of DEGDME in argon) was used as gas feed for the deposition of poly(ethylene oxide) films (subsequently called PEO-like films) at a working pressure of ~20 mTorr. Gas flow rates were regulated by MKS mass-flow controllers and the pressure was monitored by a MKS baratron. The low pressure in the chamber was maintained by a rotary pump. Between each deposition, the plasma chamber was cleaned for 30 min by a pure oxygen plasma (~25 mTorr, 15 W) followed by 10 min of a pure argon plasma (~25 mTorr, 10 W).

2.2. Film characterization

2.2.1. Fourier transform-infrared (FT-IR) spectroscopy

The FT-IR spectra (coatings were deposited on silicon wafers polished on both sides) have been recorded by using a Bruker model Vector 22 Fourier transform spectrometer, equipped with a Globar MIR source with a DTGS detector (resolution 2 cm^{-1}, 28 scans). The background correction was made before each measurement in order to avoid all contributions from the atmosphere. The absorbance spectrum of an untreated silicon wafer gives a flat signal centred on 0 with a noise of ± 0.0002. For each coating, a minimum of three spectra were recorded at different positions.

2.2.2. Ellipsometry

Ellipsometric data were acquired with a variable angle single-wavelength imaging ellipsometer (model EP^3 supplied by Nanofilm Surface Analysis GmbH). All measurements were performed in air at room temperature for different angles of incidence (80 measurements between 40° and 80°), a low-capacity laser with a wavelength $\lambda = 532$ nm was used as the light source. A conventional PCSA (polarizer–compensator–sample–analyzer) null-ellipsometric procedure is used to obtain the Δ and Ψ angles. The thickness and the complex refractive index $(n + ik)$ are calculated from these two angles using the software EP^3 View provided with the instrument. For these experiments, silicon wafers have been used as substrates.

2.2.3. XPS analysis

X-ray photoelectron spectroscopy (XPS) measurements have been performed with an AXIS ULTRA Spectrometer (KRATOS Analytical, UK). The instrument was calibrated using a clean Au/Cu sample (99.99%), by measuring the positions of the Au $4f_{7/2}$ and Cu $2P_{3/2}$ lines and setting them at 84.00 ± 0.02 eV and 932.00 ± 0.02 eV respectively. The samples were irradiated with monochromatic AlKα X-rays ($hv = 1486.6$ eV, spot size 400×700 μm^2) and a take-off angle of 90° with respect to the sample surface. The base pressure in the analysis chamber was better than 8×10^{-10} Torr and the pressure during measurement better than 3×10^{-9} Torr. An electron flood gun was used to compensate surface charging and all spectra were corrected by setting the hydrocarbon component at 285.00 eV. For each sample, a survey spectrum (0–1150 eV) was recorded at a pass energy (PE) of 160 eV. In addition, one set of high-resolution spectra (PE = 20 eV) was also recorded for each sample. The total acquisition time was kept below 10 min to avoid any possible X-ray induced damage on the coatings. The data were processed using the Vision2 software (Kratos). The chemical surface composition was obtained from the survey spectra after linear background subtraction and using the relative sensitivity factors included in the software derived from Scofield cross-sec-

ID	Title	Pages
2582	Fouling and non-fouling surfaces produced by plasma polymerization of ethylene oxide monomer	8