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Characterization of plasma deposited poly(heptadecafluoro-1-decene)

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ABSTRACT

Fluorocarbon coatings were deposited by plasma polymerization of 1H,1H,2H-perfluoro-1-decene (HDFD). Chemical and morphological characterization of coatings obtained from different process parameters was performed by means of Attenuated Total Reflectance Fourier Transform Infrared (FTIR/ATR) spectroscopy, Energy Dispersive X-Ray analysis (EDX) and Atomic Force Microscopy (AFM). Hydro- and oleo-repellency were evaluated by contact angle measurements with different liquids. Optical properties were investigated by acquiring the transmittance spectra in the region 300–900 nm. Finally, evaluation of the mechanical properties was performed by means AFM nanoindentation. By increasing the Yasuda factor (the energy consumed per mass of monomer), coatings with lower retention of fluorocarbon chains were obtained. The F/C ratio, measured by means of EDX analysis, decreased from 0.85 for coatings deposited at 10 W to 0.69 for coatings deposited at 100 W. As a consequence of the lower retention of fluorocarbon chains, coatings deposited at high Yasuda factors displayed lower hydro- and oleo-repellency. In addition, these coatings contains large amount of unsaturated groups (CF═CF, CF═C═CF, …), as assessed by ATR analysis. This led to a lower transparency, due to radiation absorption in the visible region. On the other hand, the mechanical properties (and hence the durability) of the coatings increased with the energy consumed per monomer molecule.

1. Introduction

Plasma polymerization is a simple, one-step technique which allows the deposition of a variety of nanoscale organic thin films on any type of substrate material, generally without the need for additional surface preparation. Since this technique does not require solvents or initiators, does not create liquid organic wastes and uses minimal monomer quantities, it is considered as cost effective and environmentally friendly [1].

Fluorocarbon coatings are important for many everyday applications, due to their low dielectric constant, high hydro- and oleo-repellency, high chemical inertness and low friction coefficient. Fluorocarbon thin films can be obtained by RF plasma sputtering using polytetrafluoroethylene (PTFE) targets [2,3] or by plasma polymerization of different fluorinated monomers [3–10]. In the latter contest, besides the classically employed low molecular weight precursors (CF_4, C_2F_6, C_3F_8, C_3F_6O, CH_2F_2, CHF_3, CF_3CHF_2, C_4F_8), recent studies focus on the production of fluorocarbon polymer coatings by plasma polymerization of high molecular weight organic molecules. In general, these precursors contain a polymerizable unsaturated end group and a perfluoroalkyl pendant chain (examples are 1H,1H,2H,2H-perfluorodecyl acrylate [11] and fluorinated alkenes of the type $C_nF_{2n+1}CH{=}CH_2$ [6–10]). While the long perfluoroalkyl chain confers high liquid repellency (oleophobicity and hydrophobicity), the unsaturated end group allows fast polymerization also in mild plasma conditions.

In this work, fluorocarbon coatings were deposited onto different substrates by plasma polymerization of 1H,1H,2H-perfluoro-1-decene ($C_8F_{17}CH{=}CH_2$, HDFD). In literature, HDFD plasma coatings are generally deposited in mild conditions (low power inputs eventually combined with pulsed plasma polymerization). In such conditions, the retention of the monomer structure (and, as a consequence, the hydro- and oleo-repellency of the coatings) is maximized. In this work, depositions were performed in more extreme plasma conditions (continuous wave mode, high power inputs). These conditions were chosen in order to improve the mechanical properties of the fluorocarbon coatings, which are important for a number of applications (for example, when they are deposited as protective layers or for their use in the biomedical field). Chemical characterization of the coatings deposited with different process parameters was performed by means of attenuated total reflectance Fourier Transform Infrared (FTIR/ATR) spectroscopy and Energy Dispersive X-Ray analysis (EDX). The morphological characterization was performed by means of Atomic Force Microscopy (AFM). Hydro- and oleo-repellency were evaluated by contact angle measurements with different liquids. Optical properties were investigated by acquiring the transmittance spectra in the region 300–900 nm. Finally, a qualitative evaluation of the mechanical properties was performed by means of AFM indentation.

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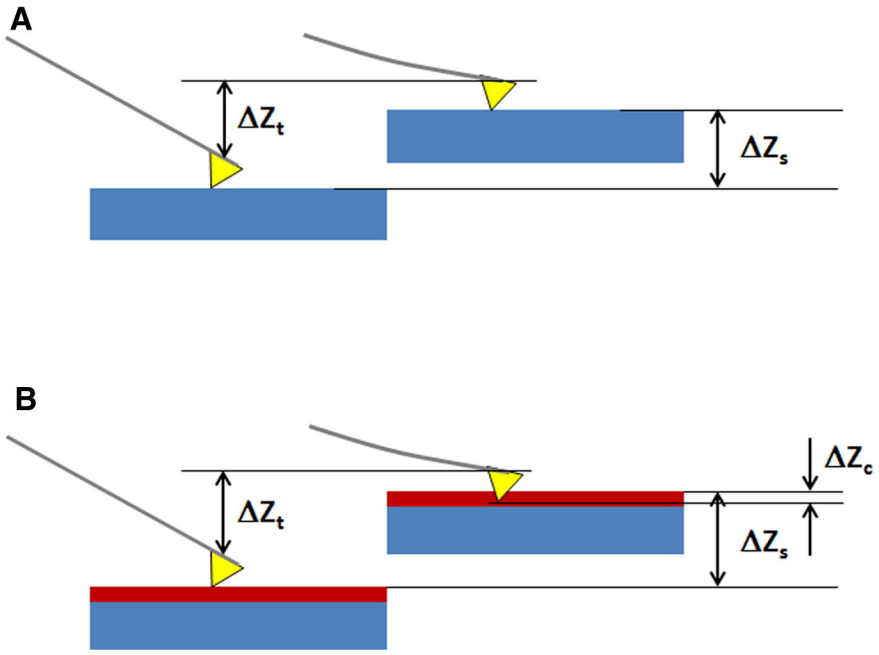

Fig. 1. Depiction of the AFM cantilever approach to rigid (A) and deformable (B) surfaces.

2. Experimental part

2.1. Materials

1H,1H,2H-perfluoro-1-decene (HDFD, 99%, Fluka) was used as received without any further purification. Plasma depositions were performed onto commercial aluminium foils, glass microscope slides (Carlo Erba Reagents, Italy) and silicon (100) wafers. All these substrates were washed in ethanol before use, in order to remove the contaminants from their surfaces.

2.2. Plasma polymerization of HDFD

A low pressure plasma of pure HDFD vapour was produced inside a cylindrical stainless steel vacuum chamber (diameter 30 cm) with a parallel plate configuration (two electrodes of 15 cm in diameter, placed at 8 cm far away from each other) [12]. The HDFD vapour was uniformly distributed in the reactor by the upper showerhead electrode (with pinholes diameter of 2 mm). This electrode was externally connected, through a semi-automated matching network (Advanced Energy ATX-600), to a 13.56 MHz RF power supplier (Advanced Energy RFX-600) which provided an RF voltage with respect to the grounded chamber. The specimens were positioned on the lower grounded electrode. Before operating the discharge the device was evacuated to 10^{-3} Pa by means of a rotary pump (Varian SD-300) combined with a turbo-molecular pump (Leybold RS232), while during the plasma deposition the chamber was evacuated by means of the rotary pump. The deposition time was fixed at 10 min. HDFD plasma depositions were performed at two different monomer flow rates (1 sccm and 0.5 sccm), varying the RF power input between 10 and 170 W.

2.3. Characterization techniques

Chemical composition of the plasma-polymerized HDFD (pp-HDFD) were determined by means of a Fourier transform infrared (FT-IR) spectrometer (Nicolet Avatar 360) equipped with a PIKE MIRacle ATR sampling accessory, suitable for the collection of spectra in the range between 650 and 4000 cm^{-1}. For each spectrum 32 scans, with a spectral resolution of 2 cm^{-1}, were recorded.

EDX analyses were performed with a Scanning Electron Microscope Zeiss EVA 50 EP using a primary electron beam with energy of 10 kV, coupled with a complete energy dispersive X-ray system (EDX Oxford Inca Energy 200) and with the INCA software program. No metal was deposited on the surface of the fluorinated coatings to minimize the number of treatments. EDX analyses were performed in three different zones (50 μm × 50 μm) of each sample and the mean results are presented.

Thickness of the HDFD coatings was measured with a Veeco dektak-8 stylus profilometer. An adhesive tape was used to mask a portion of the silicon wafer. After the deposition, the adhesive mask was removed and the HDFD coating thickness was measured.

Contact angles of water, α-bromonaphtalene and tetradecane were measured onto the coated glass slides with a Dataphysics OCA 20 (Dataphysics) instrument at room temperature. All the contact angles were determined by averaging the values obtained at 5–6 different points on each sample surface.

UV/VIS transmittance spectra in the spectral region 300–900 nm were acquired with a Shimadzu UV-2101 PC spectrophotometer.

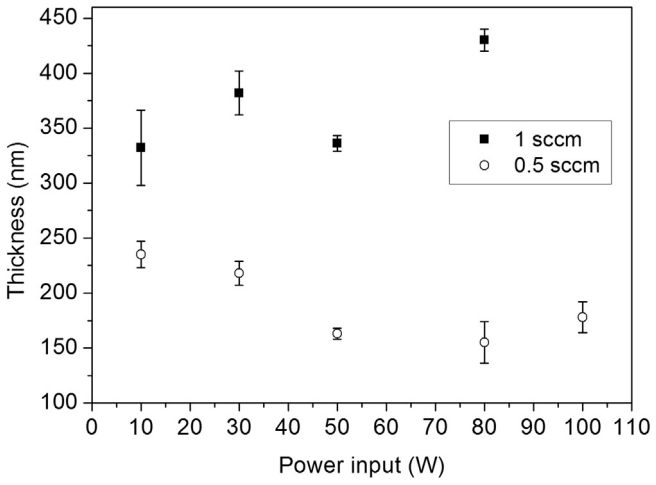

Fig. 2. Thickness of coatings deposited in different operative conditions (deposition time 10 min).