µPlasmaPrinting deposition of amine-containing polymers by means of 3-aminopropyl trimethoxysilane and the application in metal-nanoparticle immobilization

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## Abstract

The modification of polymer surfaces by the introduction of specific functional groups, such as amine (-NH<sub>2</sub>) groups, allows exploring the potential of the modified surfaces, among others, a higher wettability, an improved adhesion to metal and coupling to biological cells, proteins and antibodies through the use of spacers. Here we present the plasma polymerization of amine-containing polymer films from 3-aminopropyl trimethoxysilane (APTMS), deposited by means of a µPlasmaPrint setup on fluorocarbon polymers. The uPlasmaPrint technology utilizes a multipin-to-plate dielectric barrier micro-discharge at atmospheric pressure and enables area-selective functionalization by means of a dot-wise patterning of the plasma treatment/deposition with a resolution down to 200 mm, according to a pattern which can be digitally programmed and changed. The present study addresses the identification of the chemical structure of the polymerized APTMS films as well as the interface development between the APTMS polymer and the fluorocarbon substrate using x-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry and surface energy analysis on layer-by-layer printed/deposited APTMS polymer. The layer-by-layer deposition and analysis of the APTMS polymer film by means of XPS has allowed determining their stoichiometry and chemical structure, predominantly consisting of siloxane chains with a relatively large retention of the amino-propyl chain, i.e. up to 70% for a single, printed layer. A detailed analysis of the F1s XPS peak has pointed out the interface formation between the APTMS polymer and the FEP substrate through Si-O-C bonds and partial etching of F/CF<sub>x</sub> functionalities. Fluorine is detected in the layer up to a number of layers equal to 5 and it is considered responsible for the limited oxidation occurring in the layers up to 5 printed layers. The analysis of the C1s and N1s peaks for an APTMS film deposited at 20 printed layers show that oxidation involves the hydrocarbon functionalities as well as the amine groups which are converted in amide-groups, thereby contributing to a decrease in surface energy of the FEP/APTMS samples. Digital, patterned microplasma treatment can be applied to achieve a variety of surface engineering solutions for application in microfluidics, printed electronics, tissue engineering and biosensors. As an example the immobilization of metal-nanoparticles to enable electro-less deposition of nickel on patterned amine-containing polymer will be addressed.