

# SUMMARY

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## Introduction

Fabrication of polymeric microfluidics has attracted much scientific research attention lately, due to the numerous of analytical applications. Their functional and commercial feasibility depends strongly on the fabrication procedures, some of which are typical microelectronic processes. Plasma processing may be utilized not only to pattern a surface, as in microelectronics, but also to modify its physicochemical properties.

## Objective

In this work we study the application of plasma processing in microfluidics fabrication and their surface modification. We focus on poly(methyl methacrylate)-PMMA.

The micro-channel is engraved on PMMA by employing Oxygen plasma etching, through a patterned Si-containing, e.g. poly(dimethyl siloxane)-PDMS, photopolymer (in situ mask) in a bilayer lithography scheme. The differential plasma etching rate (ER) of PMMA and PDMS ( $ER_{PMMA} > ER_{PDMS}$ ) enables pattern transfer (selective etching), while the PMMA surface is simultaneously modified.

The objectives are to (a) study and understand the Oxygen plasma etching mechanisms for the Si-photopolymer etching, that should provide increased plasma etching resistance, and for PMMA etching, that should be etched-off as fast as possible, in order to minimize the total plasma process time. (b) Study the plasma-polymer interactions and their effects on surface modification of PMMA, which will be in contact with the biofluids. Surface roughness measurements are carried out towards the control of surface topography, chemical composition variations are monitored via X-ray Photoelectron Spectroscopy (XPS), and wetting phenomena are recorded by means of contact angle (CA) measurements. Finally (c) a standard microfluidic device is fabricated and characterized with regard to its electrokinetic performance (electroosmotic flow etc.) and the surface state effect on such parameters. The aim is to couple the microfluidic fabrication, characterization and application along with a basic study of the plasma-polymer interaction mechanisms.

## Results

### (a) Oxygen plasma etching mechanisms

#### *a1. Si-containing photopolymers, increased etching resistance*

ER measurements of Si-containing polymers and copolymers were recorded by means of in situ spectroscopic ellipsometry (SE). The etching resistance of such polymers in

Oxygen plasmas comes from the development of a  $\text{SiO}_x$  ( $x \sim 2$ ) layer on the sheath-polymer interface, which is etched slowly only through sputtering processes. The pertinent mechanism is further understood within the frame of the shrinking core model, properly modified to embody special aspects due to the plasma environment. The main difference of our model compared to others published before is the addition of a term to model the ion-enhanced oxidation component. In this term the projection range of the Oxygen ions is inserted. This model was adequately fitted to the experimental data, while the fitted projection range was close to the theoretical value.

#### *a2. Organic polymers (PMMA), high ER*

PMMA etching was studied both experimentally and theoretically. The first aim was to maximize the ER value, by tuning the plasma power and the plasma vessel pressure so as to decrease the time needed to engrave the micro-channel. In our reactor with a maximum source power of 2000 W, the max ER value was found to be  $\sim 1.5$   $\mu\text{m}/\text{min}$  (in situ SE), meaning that for a  $\sim 30$   $\mu\text{m}$  deep trench the process time is  $\sim 20$  min. ER variations were followed by gas phase characterization, namely optical emission spectroscopy and actinometry, and ion flux measurements. These measurements were introduced to the PMMA plasma etching kinetics model with or without a chemical etching term. Pertinent analysis yielded etching constants, which turned out to depend also on the polymer Molecular Weight (MW).

Plasma ER of thin and ultra-thin polymeric films was in situ monitored, and systematic variations with time and thickness were recorded. The final steps of etching, due to the surface roughness formation may be exploited as an alternative RMS roughness measurement.

### (b) Surface modification in Oxygen plasmas

#### *b1. Formation and evolution of surface roughness*

Oxygen plasma treatments induces surface roughness, that was recorded by both AFM (Atomic Force Microscope), and in situ and ex situ SE. For Si-containing polymers we support that surface roughness is formed during the plasma process and not during the sample unload and subsequent cooling, as it is reported in the literature. The electrode temperature ( $T_{\text{electr}}$ ) and the bias voltage effect was also studied.

However crucial for the microfluidic device is only the PMMA surface state, since PDMS is removed after the fabrication procedure. Surface roughness is also formed on the PMMA surface and increased with the process time and the energy of the ions impinging on the surface. After 2 h processing, surface roughness range is  $\sim 8$   $\mu\text{m}$ . We studied the effect of  $T_{\text{electr}}$ , MW and the  $\text{SF}_6$  addition on the gas phase on the surface roughness by means of AFM. The RMS/etched depth ratio which is the crucial parameter

in the microfluidic identification, decreases only with the use of lower MW PMMA or the addition of O<sub>2</sub>/11% SF<sub>6</sub> gas mixture.

XPS measurements revealed the presence of metal species on the PMMA surface, after the Oxygen plasma treatment, to which the surface roughness may be partially attributed (micro- nano- masking). Moreover XPS recorded the oxidation of the PMMA surface and the slight increase of the Oxygen surface concentration.

### *b2. Study and control of the wetting phenomena on PMMA*

The above mentioned variations are reflected to the wettability of the PMMA surface. Oxygen plasma etching renders the PMMA surface highly hydrophilic with a water CA < 10° (fully wetting), within less than 5 min of processing. This highly hydrophilic character gradually recovers due to ageing (hydrophobic recovery).

Exploiting both the surface roughness formed and the possibility to plasma deposit fluorocarbon coating, we modified the PMMA surface into a super-hydrophobic (SH), attaining CA ~ 150° and CA hysteresis < 10°. Thus, plasma processing may be utilized not only to engrave the micro-channel but also to modify their surfaces with high flexibility. SH fabrication process was optimized to yield simultaneously SH and optical transparent surfaces, by controlling the surface roughness range. Pertinent optical measurements proved that these surfaces are also anti-reflective.

### (c) Fabrication and electrochemical characterization of microfluidic devices.

Following the processes described before (in a and b) we fabricated and properly modified standard devices for capillary electrophoresis.

The engraved part was sealed against a PMMA lid, by means of thermal bonding. With this technique the micro-channel is effectively sealed, quickly, in low temperature, without using other adhesives, of altering the geometrical characteristics of the channel.

Finally, these devices were characterized with regard to their electroosmotic mobility ( $u_{EOF}$ ). The  $u_{EOF}$  was measured for different pH buffers, channel cross-sections, time after the fabrication and finally the effect SH on the  $u_{EOF}$  was also explored.  $u_{EOF}$  is virtually constant in the pH range from 5.5 to 9 and decreases as the cross-section of the micro-channel decreases. In almost all of the cases the  $u_{EOF}$  is higher than that of respective micro-channels fabricated by conventional techniques, due to the surface modification during plasma treatment. For a specific micro-channel  $u_{EOF}$  decreases with the use and stabilizes, a variation that was followed by CA measurements. SH increases the  $u_{EOF}$ .

Finally we conducted electroinjection and electrophoresis of a negatively charged fluorescent dye (Eosin) and recorded it under the fluorescent microscope. When  $u_{EOF}$  is

higher than the electrophoretic mobility of Eosin, the negatively charged dye moves towards the cathode (negatively biased electrode).

**Keywords:** Etching, Si-containing polymers, PMMA, Oxygen plasma, Surface roughness, Nano-texture, Hydrophilicity, Super-hydrophobicity, Microfluidic devices, Electroosmotic flow, Spectroscopic ellipsometry