

Plasma etching technology for fabrication and surface modification of plastic microfluidic devices

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Abstract: Plasma etching is investigated as an alternative technology for the fabrication of microfluidic devices made of PMMA, PEEK and PDMS. O₂ and SF₆ plasma conditions were optimized with respect to etch rate maximization for PMMA, PEEK and PDMS substrates. Simultaneous formation of plasma-induced nanoroughness was observed and utilized, in combination with plasma chemistry, in order to control surface wettability. Microchannels with controlled bottom nanoroughness were fabricated in PMMA, PEEK, and PDMS substrates, through optimized plasma etching and sealing processes.

Keywords: PMMA, PEEK, PDMS, Plasma etching, microfluidics

1. Introduction

In the last twenty years, a strong interest has arisen for the development of multi-functional miniaturized devices for applications in life sciences [1]. Diagnostic tests, chemical sensing and detection experiments have been simplified and can be realized using lab-on-a-chip devices. Miniaturization of devices leads to many benefits, including decreased cost in manufacture, use and disposal, decreased time of analysis, reduced consumption of reagents, increased separation efficiency and increased portability.

The materials that are mostly reported for the fabrication of microfluidic devices are silicon and glass, while wet and dry etching are the processes that are mainly conducted for their formation. A desirable approach is to use plastics as device substrates, which, in contrast to silicon and glass, are inexpensive, easy to handle and easily batch fabricated through molding, embossing and casting processes. Poly-methyl methacrylate (PMMA) is widely used as a structural material of microfluidic devices, routinely patterned with the hot-embossing technique [2] that employs a mold insert that is pressed into PMMA. Similarly to PMMA, thermocurable Poly-dimethyl siloxane (PDMS) is patterned with soft lithography, realized by means of rapid prototyping and replica molding. Other polymer materials used for the fabrication of microfluidics are the photosensitive PDMS [3], polystyrene (PS), polycarbon (PC), poly-ether ether ketone (PEEK) [4], thermoset polymer films like the UV15 [5], the SU-8 photoresist [6], etc. Compared to Si or glass, polymers have the disadvantage that surface modifications are not permanent and more care must be taken to control their surface chemistry. Patterning of plastic substrates with plasma etching has been scarcely studied or used for the fabrication of microfluidic devices [7], although, combined with lithography, it constitutes a rather attractive planar technology [8], [9].

In this work, we present plasma-based patterning of PMMA, PEEK and PDMS substrates, with simultaneous

control of their physicochemical properties (composition, wettability, etc.), towards the requirements of the specific application. O₂ plasma is employed for the patterning of organic PMMA and PEEK substrates, while SF₆ plasma for the patterning of Si-containing PDMS. Plasma conditions are optimized with respect to etch rate maximization, and deep anisotropic etching is conducted, by choosing the appropriate material as an etching mask for each substrate, exhibiting a minimal or reduced plasma etch rate compared to the underlying substrate. As etching mask, a photosensitive silicon-containing polymeric mask (PDMS) [10] or inorganic-organic hybrid polymer (ORMOCER) is employed for the case of PMMA and PEEK substrates, while an aluminum layer or a photosensitive SU-8 film, for the case of thermocurable PDMS. PMMA, PEEK and PDMS microchannels were fabricated by plasma etching and control of their bottom roughness and wettability was achieved, by tuning the plasma conditions and/or by subsequent wet etching.

2. Experimental

PMMA is a cheap, widely used and highly transparent amorphous polymer with glass transition temperature $T_g \sim 119^\circ\text{C}$. PEEK is a semi-crystalline high performance engineering polymer with glass transition temperature $T_g \sim 150^\circ\text{C}$ and melting temperature $T_m \sim 340^\circ\text{C}$, which offers superior thermal stability, chemical resistance and excellent mechanical properties. Optically transparent 2 mm thick PMMA plates were purchased from IRPEN (Spain) and opaque grey 1.5 mm thick PEEK plates from RTP Company (USA). Thermocurable PDMS is a flexible, light transparent, non-toxic, chemically and biologically inert material. The commercial PDMS material with thermal curing (Sylgard 184, supplied by Dow Corning) was used. The prepolymer of PDMS was prepared by mixing the base and the curing agent at a mixing ratio 10:1. Thermal cross-linking was performed with baking at 150°C . Spin-coated films of thicknesses in the range of 10 μm to 100 μm were fabricated under a spinning speed

of 7000 rpm down to 500 rpm, respectively. Film thickness was estimated from the analysis of its UV reflection spectra.

As etching mask for PMMA, a Si-containing photoresist such as PDMS or inorganic-organic hybrid polymer (ORMOCER) was spin-coated on the PMMA and PEEK sheets, forming a $\sim 2 \mu\text{m}$ thick layer and was exposed through a photomask to UV light broadband at 365 nm. The soluble part of the Si-containing polymer was removed in MIBK (methyl-isobutyl ketone) and IPA (iso-propyl-alcohol). As etching mask for PDMS, aluminum was used, deposited on PDMS in a thermal evaporator at low deposition rates and at the largest possible distance of the PDMS substrate from the Al target, in order to minimize the formation of wrinkles on the Al/PDMS surface. Photolithography with AZ 5214 was performed, followed by wet etching of Al to define the mask. Also, the negative epoxy type photoresist SU-8 3050 (purchased from Microresist) was used as an alternative etching mask, spin-coated on PDMS substrates and patterned. The non-exposed part of SU-8 was developed in PGMEA and IPA. The process for etching mask definition by lithography and the subsequent deep plasma etching of the exposed are summarized in Fig. 1 (a).

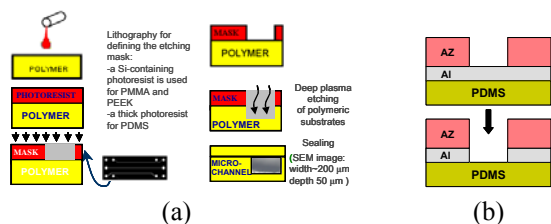


Fig. 1 Schematic of the fabrication process for plastic devices. Definition of the etching mask by lithography.

All plasma processing was performed in our Micro-machining Etching Tool (MET) from Alcatel, equipped with a helicon source (at 13.56 MHz) providing RF power up to 2000W. A second capacitively-coupled RF generator gives the ability to independently polarize the sample (situated on the electrode), and thus enhance the ion-bombardment, without affecting the ion-flux or the neutral species concentration. The process variables of this tool are: plasma power (in W), total process pressure (in Pa), gas flow (in sccm), substrate bias voltage (in V) and substrate temperature (in $^{\circ}\text{C}$).

Plasma ER measurements were performed on spin-coated PMMA films on Si wafers, in order to monitor the thickness variation via in situ spectroscopic ellipsometry (J.A. Woolam M2000) and on spin-coated PDMS films on Si wafers, by means of laser interferometry, with a solid state laser emitting at 650 nm. Furthermore, to measure the etch rate of PEEK, several samples were simultaneously etched in O_2 plasma and the etching dura-

tion was varied with a 5 minute step, until the maximum time of 60 minutes. The etch depth for each sample was measured with a stylus profilometer. ER of PMMA was also measured in this way, by utilizing PMMA plates.

Atomic Force Microscope (AFM) images were obtained from a Nanoscope III Digital Instruments atomic force microscope, in the tapping mode. Roughness characterization was also performed by means of a FEI Company SEM scanning electron microscope (sample viewed top-down or at a tilt). Water contact angles were measured with a GBX-DIGIDROP at ambient atmospheric conditions. De-ionized water was used for all contact angle measurements, and specifically, droplets of $5 \mu\text{l}$ were formed for static contact angle measurements.

3. Results and Discussion

O_2 plasma was used as etching gas of the organic PMMA and PEEK materials, while for PDMS, which contains organic groups on an inorganic $-\text{[Si-O]}-$ backbone, SF_6 was chosen as the etching gas.

Plasma etch rate (ER) is a crucial parameter, related to the throughput of the proposed fabrication scheme: the higher the ER, the shorter the total time needed for the definition of deep microchannels. By varying plasma conditions, we observed that etching rates of PMMA, PEEK and PDMS increase with decreasing chamber pressure, increasing plasma power and increasing bias voltage, revealing ion-enhanced anisotropic processes, Fig. 2. Optimized plasma conditions for PMMA and PEEK etching, achieving a maximum etch rate of $\sim 1.5 \mu\text{m}/\text{min}$, were 100 sccm flow of O_2 , 0.53 Pa chamber pressure, 2000 W plasma power, -100 V voltage applied on the substrate and temperature of 15°C , while for the case of PDMS, achieving a maximum ER of 800 nm/min, were 200 sccm flow of SF_6 , 1.33 Pa chamber pressure, 1900 W plasma power, -100 V voltage applied on the substrate and temperature of 15°C .

Under the conditions of anisotropic etching mentioned above, plasma treatment of PMMA [11], PEEK and PDMS [12] surfaces results in the formation of columnar nanostructures on etched areas. The formation of roughness is attributed to the presence of etch inhibitors on the etched PMMA, PEEK and PDMS surfaces, originating mainly from sputtered alumina from the chamber walls, while etch-resistant polymer components, such as Si impurities in PMMA plates or the inorganic siloxane backbone $-\text{[Si-O]}_n-$ of PDMS, may also contribute to nanoroughness development. Control of the height of nanoroughness can be achieved by tuning the plasma etching duration, when alumina sputtering occurs. The nano-column height increases linearly with plasma treatment duration with a rate of 300 nm/min for the case of PMMA and PEEK substrates and 400 nm/min for PDMS, as observed in Fig. 3.

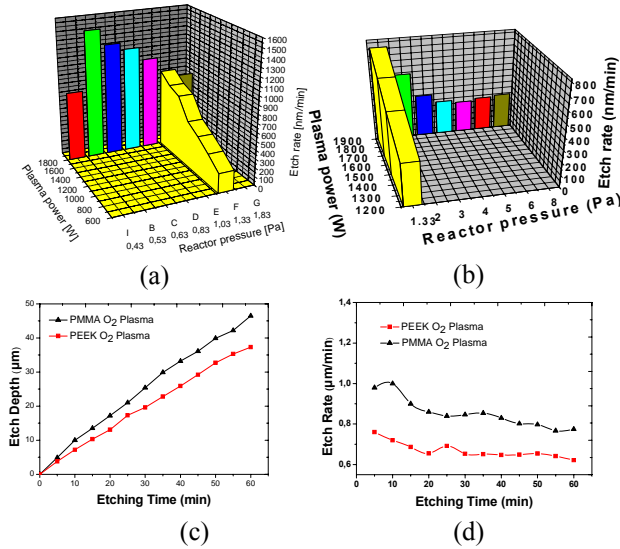


Fig. 2 O₂ and SF₆ plasma ER measurements of PMMA (a) and PDMS (b) films respectively, as a function of plasma source power and chamber pressure. O₂ plasma etch depth (c) and etch rate (d) as a function of etching time of PEEK and PMMA plates are presented under etching conditions: electrode temperature of -20°C, bias voltage of -120 V, O₂ flow of 100 sccm and chamber pressure of 0.75 Pa.

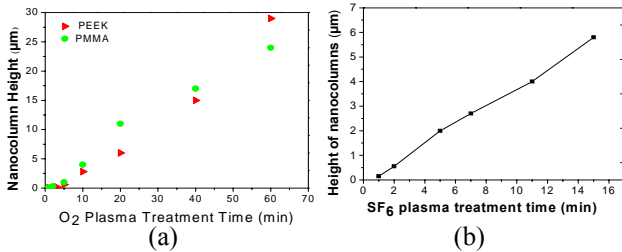


Fig. 3 Dependence of the nanocolumns height of PEEK, PMMA (a) and PDMS (b) on O₂ and SF₆ plasma treatment time, respectively.

Nanocolumns aggregate with increasing plasma treatment and islands of increasing size are formed, as shown in Fig. 4.

Control of nanoroughness can also be obtained by wet chemical treatment. For example, immersion in buffered HF (BHF) solution –a known SiO₂ etchant- of an untreated flat PDMS surface results in wet etching of PDMS at a rate of 32 nm/min, while immersion of a plasma roughened PDMS surface results in rapid reduction of nanoroughness. Consequently, we can even eliminate plasma created nanoroughness by tuning the duration of wet etching in BHF, depending on the SF₆ plasma duration. In Fig. 5, the evolution of a 2-min SF₆ plasma-induced roughness of 114.7 nm (rms value) is presented, as a function of the immersion time in BHF solution. A 4 min immersion in BHF solution is appropri-

ate for decreasing sufficiently the surface roughness. This way, we can obtain almost smooth PDMS surfaces after SF₆ plasma etching.

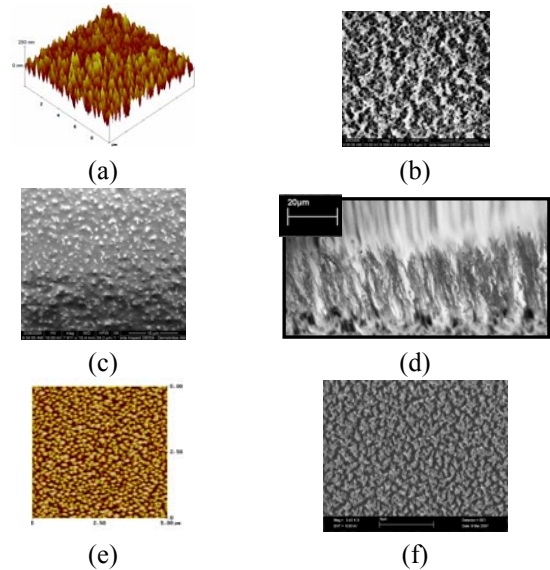


Fig. 4 3D AFM (a) and top-down SEM (b) images of a 2 min and a 20 min O₂ plasma treated PMMA surface, respectively. Also, SEM images of a 5 min (c, top-down) and a 60 min (d, tilted) O₂ plasma treated PEEK surface are shown. Finally, top-down AFM (e) and SEM (f) images of a 2 min and a 8 min SF₆ plasma treated PDMS surfaces are presented, respectively.

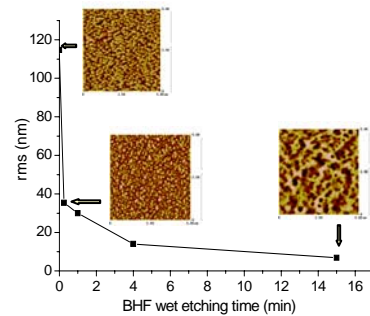


Fig. 5 Reduction of rms surface roughness of a 2-min SF₆ plasma etched PDMS surface with wet etching in BHF.

Moreover, plasma etched PMMA, PEEK and PDMS microchannels can be fabricated, with controlled bottom nanoroughness. In Fig. 6 (a) an open 45-min SF₆ plasma etched PDMS microchannel is observed, of a 23.4 μm depth, a 150 μm width, and a 18.9 μm high bottom roughness. A wet etched Al mask was used for plasma etching and was removed afterwards by means of immersion in BHF solution for 3 minutes. Simultaneously, bottom nanoroughness was reduced to 3.7 μm. The top surface of PDMS was smooth after the removal of Al mask and sealing of such PDMS microchannel with a flat PDMS cover

was achieved through O₂ plasma treatment in a RIE reactor (under mild conditions: 100 mT, 100 W and 50 sccm of O₂ flow). The as-sealed PDMS microchannel is also shown in Fig. 6 (a). In Fig. 6 (b), a 20-min O₂ plasma etched PMMA channel of 20 μm depth is shown, exhibiting plasma-induced bottom roughness. In Fig. 6 (c) and (d), PMMA and PEEK O₂ plasma etched microfluidic channels are shown respectively, before and after sealing. The latter was accomplished with solvent and thermal bonding, by means of a thermal press (Carver Inc. 3850 CE). Details of the microchannel by optical microscopy and top down SEM images reveal the surface roughness after O₂ plasma treatment. The etching mask of PMMA and PEEK channels was removed by means of SF₆ plasma etching.

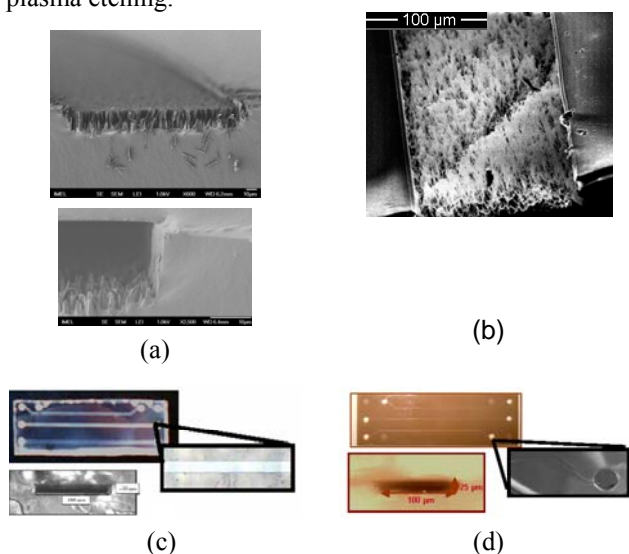


Fig. 6 An SF₆ etched PDMS microchannel before and after sealing (a), an O₂ etched PMMA microchannel (b) and O₂ etched PMMA and PEEK microchannels, before and after sealing, are presented.

Plasma etching also affects the surface chemical composition which, in combination with surface nanotexturing, determines the surface wettability. Plasma treatment in SF₆ renders PDMS surfaces hydrophilic, Fig. 7 (b), while subsequent treatment in O₂ plasma under mild conditions in RIE reactor, renders them superhydrophilic, Fig. 7 (d). O₂ plasma treatment alters PMMA and PEEK surfaces to superhydrophilic. PDMS, Fig. 7 (c), PMMA and PEEK surfaces become hydrophobic and superhydrophobic, with appropriate ageing. In all cases, surfaces with increased surface roughness delay their hydrophobic recovery, compared to smooth plasma treated surfaces. This is a favorable effect of the plasma patterning of polymeric substrates. In Fig. 8 (e), ageing of O₂ treated PMMA surfaces is illustrated. Lightly roughened surfaces return to their initial wettability much faster than all highly nanotextured surfaces, which eventually reach hydrophobicities much higher than the initial ones.

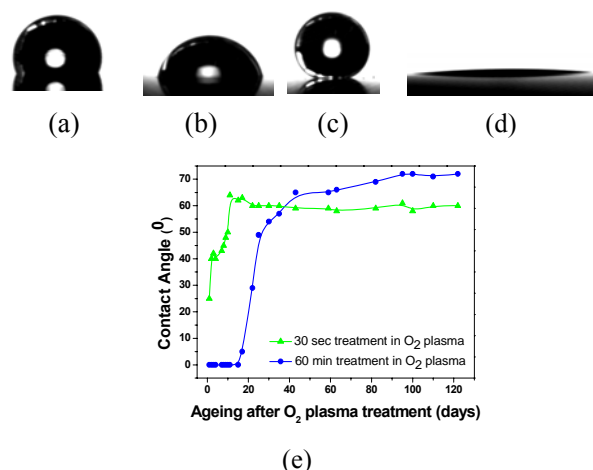


Fig. 7 PDMS surface untreated (CA=110°) (a), fresh SF₆ treated (CA=75°) (b), three-month aged 6-min SF₆ treated, exhibiting superhydrophobicity (CA=145°) (c), 6-min SF₆ treated, after a subsequent O₂ plasma treatment, exhibiting super-hydrophilicity (CA=5°). Ageing of O₂ treated PMMA surfaces is illustrated in (e).

4. Conclusions

A plasma-based technology is proposed as an alternative method for fabrication and surface modification of polymeric microfluidic devices. Anisotropic O₂ or SF₆ plasma etching is utilized to pattern PMMA and PEEK or PDMS substrates, with simultaneous control of their bottom nanoroughness and wettability. Devices of pressure-driven or electrokinetic flow with application in chromatography-based or electrophoretic separations can be thus realized.

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