

Stimuli-Responsive Polymers in MEMS Devices

F. Montagne*, R. Pugin*, A. M. Popa*, A. Hoogerwerf*, T. Overstolz*, H. Heinzlmann*

*Swiss Center for Electronics and Microtechnology (CSEM SA)
Nanotechnology and Life Sciences Division

Jaquet-Droz 1, Case Postale CH-2002 Neuchâtel, Switzerland, franck.montagne@csem.ch

ABSTRACT

Due to their unique properties, stimuli-responsive polymers have been attracting considerable attention in biotechnologies and successful applications have already been demonstrated in sensing, intelligent textiles, bio-separation and drug delivery systems. In this paper, as an illustration of CSEM activities in the field of smart surfaces, we present examples of real case applications of responsive coatings, and in particular, we show their possible integration into Micro-Electro-Mechanical Systems (MEMS). Thus, we successively describe the use of stimuli-responsive block copolymer micelles for the fabrication of nanostructured surfaces and for the preparation of suspended nanoporous membranes. We also discuss the preparation and the use of thermally-responsive silicon-based surfaces obtained from poly(N-isopropylacrylamide) (PNIPAM) for application in biomedical microdevices.

Keywords: Responsive polymers, MEMS, nanoporous membrane, PNIPAM.

INTRODUCTION

Stimuli-responsive polymers, also referred to as “smart” polymers, are a very interesting class of materials since they exhibit marked and rapid conformational changes in response to external stimuli such as temperature, pH, electric field or ionic strength. When coated onto a surface, they confer to the resulting materials some unique properties and offer the possibility to achieve control over biocompatibility, wettability, permeability or adhesion, for instance.

During the last decade, the Micro-Electro-Mechanical Systems (MEMS) community started to integrate responsive polymers in fabrication processes, since it was demonstrated that such polymers could be easily coated, and even chemically grafted in a controlled manner onto silicon and metals, which are major materials in micro-electronic and biotechnology.

In this paper, we aim at showing example of application of stimuli-responsive polymers for the design of new components for the MEMS industry. First, we report the use

of responsive block copolymer micelles for the fabrication of nanostructured surfaces and the preparation of suspended nanoporous membranes. Then, we present the functionalization of silicon surfaces with thermally-responsive PNIPAM and discuss their integration in biomedical microdevices.

RESPONSIVE BLOCK COPOLYMER MICELLES FOR THE CREATION OF NANOSTRUCTURED SURFACES

It is well-known that amphiphilic block copolymers can self-assemble into a wide variety of nanostructures (micelles) when dissolved in a selective solvent. As an example, Figure 1 shows an AFM image of a monolayer of poly(styrene-block-2-vinylpyridine) (PS-b-P2VP) (91500-b-105000 g/mol, PDI 1.1) reverse micelles which were spin-coated from a 0.5 wt% toluene solution on freshly piranha-treated silicon surfaces. In these conditions, periodic array of individual spherical micelles consisting of a P2VP core and PS shell with an apparent diameter of 65 nm and height of 11 nm was formed on the surface. We specify here that micelle dimensions and array periodicity can be easily tuned in a systematic manner by adjusting parameters such as molecular weight, polymer concentration, nature of solvent or spin-coating conditions [1].

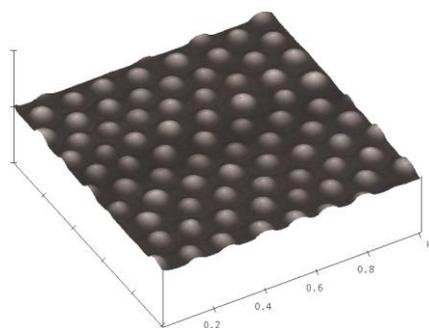


Figure 1. AFM tapping mode image of a monolayer of spherical micelles on a silicon substrate ($x=y=z$ div. 200 nm).

Interestingly, when exposed to polar solvent such as methanol, the micellar film undergoes a phase inversion, resulting in an array of holes with an average depth of 14 nm and the same periodicity than the initial spherical micelles (Figure 2). Core-corona inversion also leads to strong modification of surface properties as illustrated by the dramatic decrease of contact angle values.

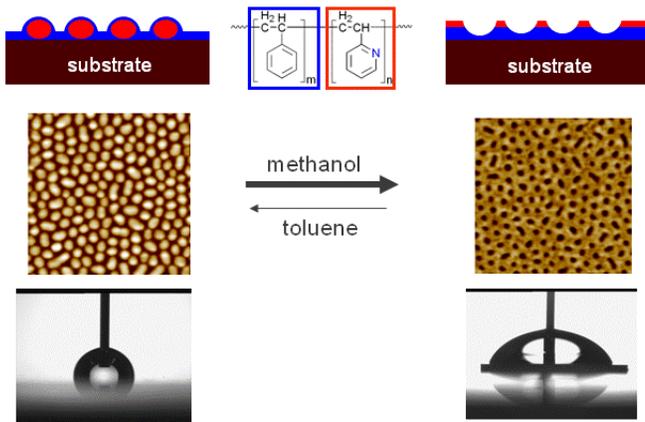


Figure 2. AFM micrographs of the PS-b-P2VP micellar film (left) as-coated and (right) after 30 s methanol treatment. Bottom are the corresponding optical images of advancing water contact angles on as-coated (adv90°/rec65°) micelles and on micelles transformed after methanol treatment (adv65°/rec <20°). The contact angle changes were found to be stable and reversible over several cycles of solvent treatment.

The attractive aspect of these responsive coatings is the reversible switchability of the micellar film between complementary nanotopographies and surface polarities, with switching times on the order of a few seconds. However, these polymer nanostructures are only physically deposited onto the surface and are easily damaged through mechanical wear. Therefore, polymeric nanotopographies are usually transferred into the underlying substrate, through etching for instance, in order to create ordered and periodic nanostructures [2]. Reactive ion etching allows the creation of more robust high aspect ratio nanostructures in hard materials. As presented in Figure 3, the transfer of polymeric masks using dry reactive ion etching (DRIE) led nanoscale pillars and cavities into substrates as technologically important as silicon, silicon nitride, silicon dioxide or glass under conditions which are compatible with clean-room fabrication processes.

These nanostructures offer a wide panel of applications. Among them, we are particularly interested in the evaluation of the nanocavities for the immobilization of DNA or proteins and further biological reactions. We are also closely examining the cell behavior, e.g. proliferation, morphology, orientation, on these nanotopographies. First results indicated marked differences in cell spreading and proliferation depending on the topography, while tests of cell

differentiation also showed different levels of proteins characteristic of the differentiated state.

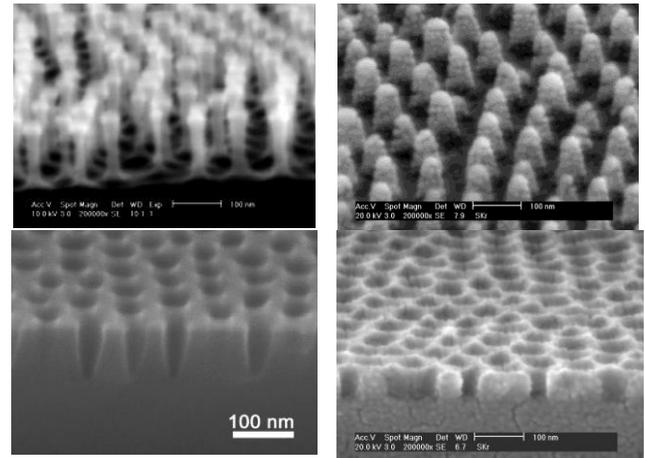


Figure 3. Scanning electron micrographs of arrays of nanopillars in silicon (top left) and silicon nitride (top right), as well as nanocavities in silicon (bottom left) and silicon oxide (bottom right) created using block copolymer micelles as etch mask.

NANOPOROUS MEMBRANES

Nanofabricated membranes are of considerable interest for many applications including ultra-filtration, osmosis, prevention of particle emission, high throughput DNA sequencing and biosensing. The fabrication of 2D nanopore arrays in ultrathin (freestanding) membranes can be accomplished by standard top-down fabrication techniques including Nano Imprint Lithography, Electron Beam Lithography and Focused Ion Beam-assisted etching; however, these techniques are currently still limited to structuring very small areas, and therefore, to prototyping.

A clean-room compatible approach has been developed at CSEM for wafer-scale fabrication of reinforced nanoporous membranes. The proprietary process is based on the combination of block copolymer lithography and standard microfabrication techniques and allows to produce thin inorganic membranes (thickness < 100 nm) with adjustable pore size ranging from 10 nm to 20 nm (Figure 4). Such membranes are made of silicon and are designed to withstand a differential pressure of few bars. Moreover, because of their large lateral dimensions (supported structure), such the membranes are easy to handle and are accessible without special equipment for their integration into different macroscopic devices.

SURFACE FUNCTIONALIZATION WITH THERMALLY-RESPONSIVE POLYMERS

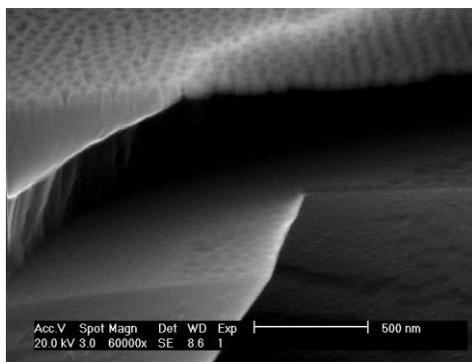


Figure 4. SEM picture of the suspended nanoporous membrane

Recently, the process has been optimised for the production of thicker membranes with improved mechanical robustness. Still starting with responsive block copolymer thin films, additional steps allowed to reach much higher selectivity, resulting in the formation of pores with aspect ratio 1:10. As shown in Figure 5, the pore channels are parallel throughout the membrane and are densely packed in a hexagonal configuration respecting the initial micelles self-assembled structures. The pore size distribution is very narrow and the mean coverage of membrane surface by pore openings is ~20-30% of the total area.

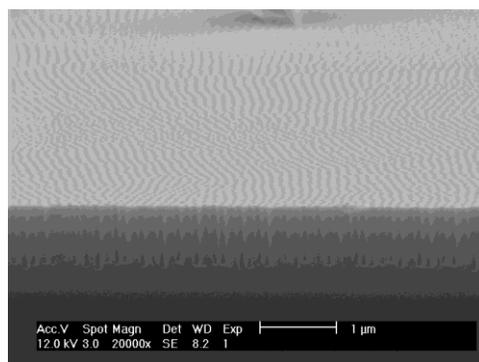
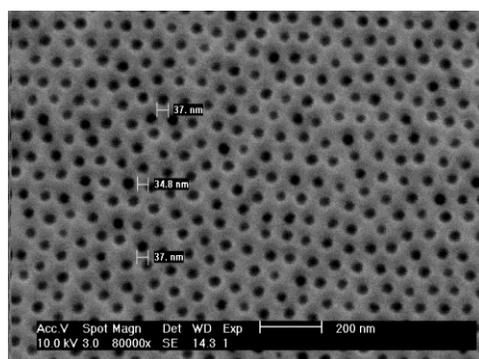


Figure 5. Scanning electron microscopy images (top view and transverse section) of silicon nanoporous substrate exhibiting 40 nm diameter pores.

The modification of MEMS compatible surfaces with thin polymer films is of considerable interest for the introduction of surface properties such as biocompatibility, antifouling, wettability or corrosion resistance in new generations of microsystems. As mentioned before in the case of block copolymer micelles, thin polymer films can be deposited from solution by dip-, spin-, or spray-coating but problems such as dewetting or delaminating often remain. In order to improve chemical and mechanical robustness and durable surface properties it is often preferred to covalently attach macromolecules via the formation of chemical bonds between reactive polymer functions and chemical groups on the surface. Of particular interest is the case where polymer chains are grafted by one end to the surface (tethering) at a high density in order to force the chains to stretch away from the surface and to adopt expanded structure. The resulting chain conformation is referred to as polymer brush and is usually obtained using “grafting from” techniques. Nevertheless, some authors also reported the preparation of dense polymer brushes using a “grafting to” method [3,4], which is usually much easier to adapt to large scale surfaces since it involves preformed polymers.

Using this last approach, we particularly focused our efforts on the development of thin thermally responsive poly(*N*-isopropylacrylamide) (PNIPAM) films onto silicon-based surfaces. Briefly, free PNIPAM chains exhibit a very sharp transition temperature in water, called LCST (Lower Critical Solubility Temperature), at about 32°C. At temperatures lower than 32°C, PNIPAM chains are hydrated and form expanded structures, whereas they are dehydrated and collapse at temperatures above the LCST. Because of these unique properties, PNIPAM-modified surfaces have been widely studied for tissue engineering [5], sensing or reversible capture/release of proteins [6] or cells [7]. However, it is a real challenge to preserve PNIPAM bulk properties when polymer chains are covalently attached to a surface in just a few nanometer thick films.

The grafting method that we developed consists in the covalent immobilization of end-functionalized PNIPAM under melt using reactive silanes as intermediate coupling agents (Figure 6). We mention here that the process can easily be adapted for the grafting of any kind of functional polymers onto various types of reactive surfaces (plane or colloidal). Extensive surface characterization using ellipsometry, infrared spectroscopy and XPS clearly evidenced the formation of dense and homogeneous PNIPAM layer whose thickness could be tuned by varying the grafting conditions. Surface morphology of PNIPAM-modified silicon surface shown in Figure 6 attests of the high grafting density. Preservation of bulk responsive property is evidenced by surface energy measurements showing an increase of the water contact angle when the temperature is raised above the LCST (Figure 6). Force measurements performed using AFM in a liquid environment confirmed

these results and indicated a clear change in the profile of repulsive forces below and above the theoretical value of LCST. Based on these results, patterned PNIPAM surfaces exhibiting responsive micro-domains ranging from $4\mu\text{m}$ to $200\mu\text{m}$ have also been produced using micro-contact printing and standard photolithography.

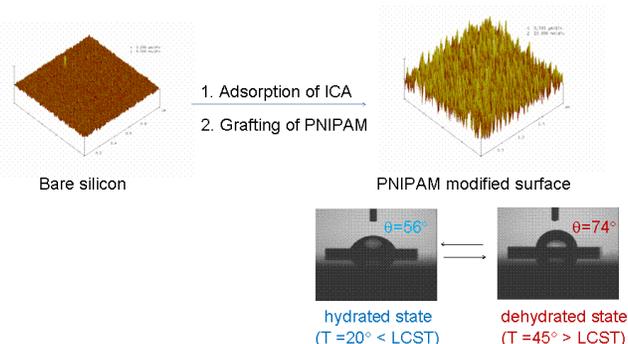


Figure 6. AFM pictures of PNIPAM-grafted silicon surface and evidence of the preservation of responsive properties (ICA is for intermediate coupling agent).

PNIPAM-modified surface were successfully evaluated at CSEM for reversible capture and release of cells (mouse fibroblast 3T3). Results showed adhesion and proliferation of cells above the LCST and a progressive release when the temperature was decreased to 27°C (below LCST). Integration of patterned responsive micro-components in automated biomedical systems is currently under investigation. We are also closely looking at the possibility to achieve post-functionalization of nanoporous membranes with thermally responsive polymers in order to create filtration systems with controlled permeability.

CONCLUSION

In this paper, we give examples of real case applications of stimuli-responsive polymers for the design of functional surfaces and their integration into MEMS devices. We first describe the use of the switchable properties of responsive diblock copolymer thin film to create complementary nanotopographies which are then transferred into underlying hard substrates to create ordered and periodic nanostructures, such as nanopillars or nanocavities. The same process is used, in combination with standard microfabrication techniques, to produce ultrathin suspended nanoporous membranes with controllable porosity. Finally, we report the functionalization of silicon substrates with thermally-responsive polymers and discuss their integration in biomedical microdevices.

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