Surface Nanostructuration: from Coatings to MEMS Fabrication

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ABSTRACT

We have developed a number of complementary methods using polymer self-assembly, sol-gel texturation and reactive ion etching techniques on a mix-and-match basis. The resulting nanostructured surfaces can have striking properties: super-hydrophobic, anti-fogging and anti-reflective to name but a few. Moreover, polymeric surface nanostructures are also very suitable as nanoscale etch masks for the transfer of the structure into the underlying material through reactive ion etching. This process leads to more durable nanostructures with aspect ratios of 10:1 in hard materials such as silicon, silicon nitride or quartz. Potential applications of these techniques include the fabrication of nanoporous membranes as well as the design of nanostructured surfaces for the analysis of the influence of nanotopographies on cell adhesion, orientation and growth properties.

Keywords: nanostructures, nanofabrication, self-assembly, polymer, membranes

INTRODUCTION

The systematic creation of nanoengineered surfaces with controlled nanoscale topographies (containing at least one dimensional feature below 100nm) is seen as an essential step for obtaining surfaces with radically new and unique size-dependent chemical or physical properties.

The continued development of lithography technologies allows the production of surface patterns with features sizes well below 100 nm. However, the increasing cost and complexity of standard top-down nanolithography techniques (e.g. deep UV, e-beam, Focused Ion beam) makes difficult their integration for mass production in an industrial environment. Only few examples, where the expensive nanofabrication processes are compensated by replication techniques (e.g. hot embossing, nanoimprint lithography) could find industrial applications. A prominent replication process that allows one to produce highly controlled surface topographies with structure sizes below one micrometer is the production of compact discs (CDs). The next generation of ultra high-density optical storage, Blu-Ray Discs is currently reaching patterning in the sub-micron region with track pitch and pit length of 320 and 140 nm respectively, but again the master fabrication is expensive and time consuming.

Other ways of creating surface structures in the ~10-100 nm range may represent alternatives if they offer advantages in reduced production cost, smaller feature sizes, or more flexibility regarding the morphology and size of nanometric structures. Systems that show ordering and pattern formation through self-assembly may offer some of these advantages. Among these nanopatterning approaches, surface structuring using polymer, block-copolymer and sol-gel self-assembly are currently attracting great attention.

POLYMER SELF-ASSEMBLY

Polymer demixing uses the phase separation properties of polymers. The resulting structures are generally larger than the length of the polymer chain (micrometre, sub-micrometre range) and have peculiar morphologies (worm-like or "dots") depending on the processing conditions. They are stochastic with respect to shape and order but present a well-defined length-scale. Various parameters can be used to tune the size and shape of the structures (Figure 1)**.** The length-scale of the structures can easily be controlled by modifying the solution-concentration or of the rotational speed during spin coating.[1] To modify the morphology of the features, the ratio between both polymers can be adjusted.[2] For symmetrical blends, the system phase-separates via spinodal decomposition, leading to the typical worm-like structures. In the case of very asymmetrical blends, the phase separation follows a nucleation and growth process, leading to the "dots in a matrix" pattern.
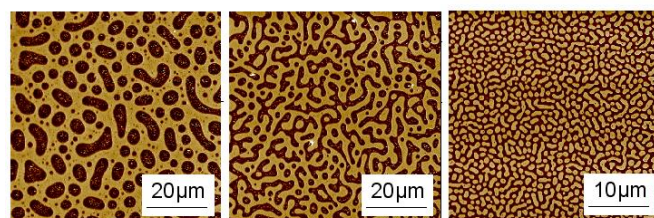

Figure 1: AFM images of phase-separated PS/PMMA thin films for different solution-concentrations (CSEM).

In order to create even smaller structures, we also investigated self-organization of block-copolymers (BC). BC is a special class of polymer with two or more polymer chains (or blocks) chemically bound to each other covalently. When deposited on a surface phase separation occurs intermolecularly and the two blocks can only separate to a distance compatible with the size of the chains. This constraint leads BC to separate into periodic microphases, i.e. into domains that are each rich in one of the constituent blocks. The size of the domains is on the order of the size of the macromolecules, i.e. ~10-100 nm. The properties of the constituent polymers, the number of monomeric units in each block, along with the relative proportion of the polymers within the BC determine the resulting equilibrium morphologies (gyroid, cylindrical or spherical domains). The characteristics of the pattern are significantly influenced by parameters such as the film thickness, solvent-selectivity and substrate influence, in relation to the BC molecular characteristics. The primary means of realizing this has been through (i) changing the relative lengths of the blocks, and (ii) the total BC molecular weight.[3-4] Tunability of micellar nanostructures obtained by dissolving BC in selective solvents has been shown for their size and spacing in a systematic manner (Figure 2).[5]
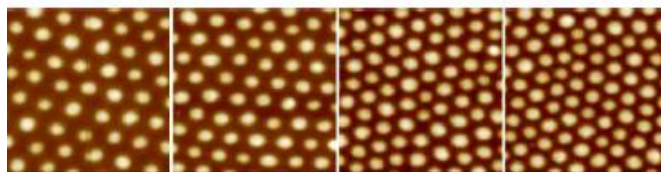
Figure 2: AFM images of arrays of BC micelles spin-coated onto silicon substrates. The spacing of the features can be tuned by using solutions of micelles of different concentrations. All the images are of 50 nm z scale and 1 μm x 1 μm scan size (CSEM).

This very flexible process of polymer self-assembly was already used for various applications where surface structuring plays a major role. Wahleim *et al.* for instance showed that it can be used to fabricate antireflective coatings.[6] Among potential applications of BC surface nanopatterns already identified are isoporous membranes.[7] However, a direct use of polymer nanostructured thin films is not always possible since the structures produced are easily damaged through mechanical wear and present often small aspect ratios. To overcome this problem, we used nanostructured polymer thin films as etch-masks for the transfer of the polymeric structures into the underlying substrate (hard material such as Si or quartz) using standard etching processes (Figure 3). This leads to more durable nanostructures in the form of arrays of evenly spaced pillars with aspect ratios of up to 1:10 in hard materials of technical importance such as silicon, silicon nitride or quartz.
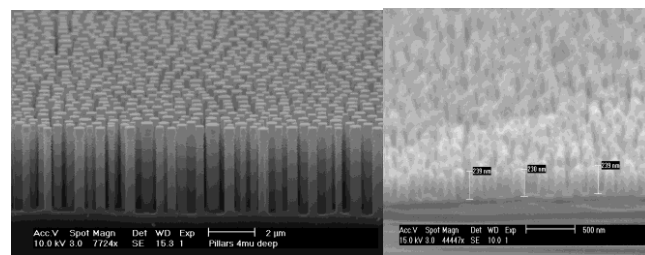
Figure 3 : SEM images of polymer/BC structures transferred into Si by DRIE (CSEM).

The main advantages of this approach are the fabrication of durable surface structures with lateral sizes controlled via the polymer self-assembly, while the depth of the structures is defined by the etching process (from few tens of nm to few μm). Three potential applications of such nanostructured surfaces have been identified.

First, subsequent surface functionalisation with perfluoro silane leads to a substantial reduction in surface wettability. The water contact angle increases from 111° on flat surfaces to 150° in the case of the pillar substrates thus demonstrating the surface roughness induced enhancement in hydrophobicity (Figure 5).
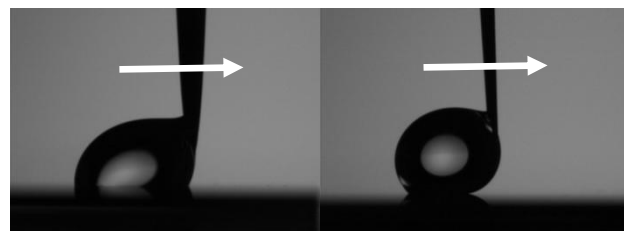
Figure 4 : Photographs of a 10μL water droplet moved on a flat (left) and nanostructured (right) silicon surface silanized with a perfluorosilane. The arrows indicate the direction of the movement (CSEM).

Based on previous work [8] a second application currently under investigation at CSEM is the control of biological cell growth on structured surfaces. For instance, Gallagher et al. have shown that cell growth can be completely inhibited by nanostructuring the surface. [9]

Third, CSEM has recently developed a silicon based freestanding nanoporous membrane in which the pore diameter can be tuned between 10 and 20 nm. The membrane is 60 nm thick and has been fabricated by combining standard microfabrication processes and block-copolymer lithography (a nanostructured block-copolymer thin film is used as etch mask for the transfer of the self-assembled structure into the underlying material by deep reactive ion etching). With this technology, the formation of pores with aspect ratios up to 1:5 could be demonstrated (Figure 5). [10] The nanoporous membranes are fabricated with a support structure in order to facilitate their manipulation and integration in macroscopic devices.
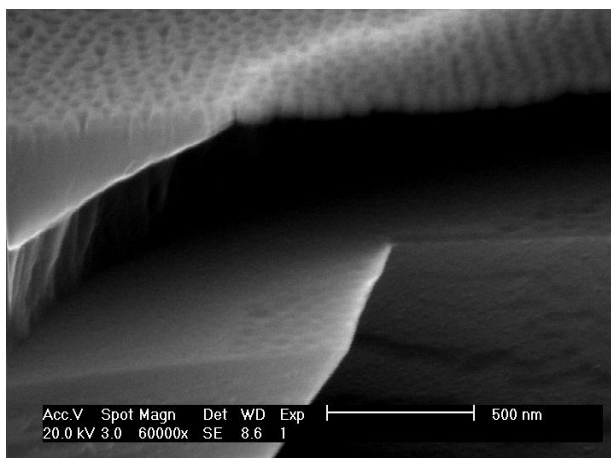
Figure 5 : SEM image of reinforced nanoporous membranes (CSEM).

Applications including ultrafiltration and prevention of particle emission are currently evaluated. Extension of this fabrication processes to the development of nanostructured metal thin films for plasmonics applications is currently under investigations. Present technical developments are concerning the fabrication of thicker suspended membranes with higher aspect ratio pores, narrow pore size distribution and improved mechanical robustness.

SOL-GEL NANOSTRUCTURATION

Complementary to polymer self-assembly, sol-gel processes are very versatile and well-suited for the formation of layers with controlled homogeneity, thickness, porosity and associated surface structures. Thin films with highly ordered structures can even be obtained by templating the gelation process by selected surfactants or block-copolymers. The control of surface properties such as the morphology and crystallinity of sol-gel derived thin films is of great importance for practical applications such as antireflection, photocatalysis, abrasion resistance, water-repellency, electric conductivity, and gas barrier properties for various substrates. A simple scalable method has been developed for the preparation of controlled 'grass-like' nanostructured surfaces with promising antireflective and wettability properties.

The preparation of precipitated "grass-like" thin films with a roughness of around 100 nm has been reported[11] for Al_2O_3-based coatings on a large variety of substrates (glass, ceramics, metals, plastics). Our approach uses the design of sol-gel surface nanostructures tailored to give outstanding properties for a specific application. The first experimental step consists of synthesizing an alcoholic sol of alumina nanoparticles by the controlled hydrolysis of alkoxide precursors stabilized by strong chelating agents. The sol can then be deposited on glass, silicon or polymeric substrates, typically using spin- or dip-coating processes. After annealing, transparent and crack-free alumina thin films are

obtained. Subsequent immersion of the dried alumina films in hot water, at a temperature between 50 to 100°C, leads to the formation of "grass-like" surface nanostructures that are caused by successive dissolution-precipitation steps of the initial alumina-based film (Figure 6). The depth of the nanostructures can be easily controlled by varying the immersion time.
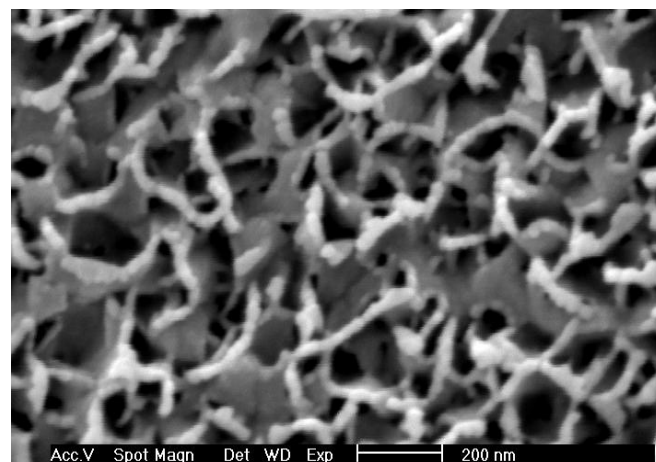

Figure 6: Scanning Electron Microscopy (SEM) picture of an alumina-based coating after hot water treatment (CSEM).

The optical properties of the nanostructured sol-gel layers have been intensively investigated. For most structures, the reflection spectrum at normal incidence shows a strong reduction of intensity for wavelengths in the range 400-1200 nm. The lowest reflectivity is 5.5% for a glass slide coated on one side. Moreover no significant variation in reflectance was observed on varying the incidence angle: a slightly increase from 5.5% at normal incidence up to 7% at 45° was obtained. In addition, colorimetric characterizations of both transmitted and reflected light demonstrate a very color-neutral behavior on changes of incidence angles when compared with bare glass sample.

While intrinsically super-hydrophilic (water contact angle smaller than 5°), such highly nanotextured metal oxides surfaces become super-hydrophobic and self-cleaning upon silanisation with perfluorinated silane (water contact angle 160°, hysteris <10°, roll off angle <10°; as evidenced in Figure 7).
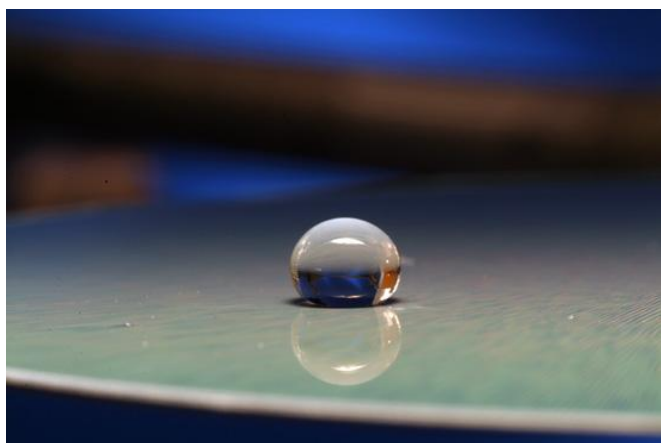
Figure 7: Picture of water droplet on a superhydrophobic nanostructured alumina surface (CSEM).

CONCLUSION

The self-assembly of polymer systems and controlled sol-gel texturation processes are promising strategies to create structures on the nanometer scale. As we gain a deeper understanding of the structuring processes, we will achieve better control of feature size/morphology and resulting properties. The simplicity of this very versatile toolbox, along with its potential low-cost for generating small features over large areas, makes it very attractive for applications in various different fields.

ACKNOWLEDGMENT

REFERENCES

[1] DalnokiVeress K., Forrest J.A., Stevens J.R., Dutcher J.R., *Physica A*, 239, 87, **1997**

[2] DalnokiVeress K., Forrest J. A., Stevens J.R., Dutcher J.R., *Journal of Polymer Science Part B-Polymer Physics*, 34, 3017, **1996**

[3] Wu C., Gao J., *Macromolecules*, 33, 645, **2000**

[4] Milchev, A. Bhattacharya, Binder K., *Macromolecules*, 34, 1881, **2001**

[5] Krishnamoorthy S., Pugin R., Liley M., Heinzelmann H., Brugger J., Hinderling C., *Adv. Func. Mater.*, 16, 1469, **2006**

[6] Walheim S., Schaffer E., Mlynek J., Steiner U., *Science*, 283, 520, **1999**

[7] Peinemann, K.V., Abetz V., Simon, P.F.W. *Science*, 6, 992, **2007**

[8] Dalby M.J., Giannaras D., Riehle M.O., Gadegaard N., Affrossman S., Curtis A.S.G., *Biomaterials*, 25, 77, **2004**

[9] Gallagher et al, *IEEE Trans Nanobio*, Vol1, **2002**

[10] Hoogerwerf A., Hinderling C., Krishnamoorty S., Overstolz T., *CSEM Scientific reports* , **2006**

[11] Tadanaga K., Katata N., Minami T., *J. Am. Ceram. Soc.*, 80, 1040, **1997**