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CHAPTER 14

NANO/MICROSTRUCTURING OF CERAMIC SURFACES BY UNCONVENTIONAL LITHOGRAPHIC METHODS

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Design of reproducible, simple and efficient nanofabrication routes has become a frontier topic in the emerging field of nanotechnologies. In this chapter we discuss the "state of the art" of ceramics micro- and nanofabrication techniques. We pay special attention to progress in this field made during the last five years.

In this chapter we will discuss about the progress on the use of lithographic tools to create nanoscale ceramic patterns or the potential of soft lithography to create ceramic structures by means of liquid ceramic precursors. The chapter also describes advances on the use of self-assembly and self organization to achieve nanostructured ceramic surfaces. In the final part, we discuss about the possibility of combining physical vapour deposition with micromolding techniques to obtain nanostructured ceramic subtrates.

Keywords: Ceramics; lithography; sol-gel; self-assembled monolayers, nanostructuring.

CONTENTS

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1. Introduction

The design and development of new and reproducible strategies for nano- and microscale patterning of materials surfaces has become one of the most relevant topics in the emerging nanotechnology. Physicists, engineers and materials scientists are being continuously challenged to discover new routes for creating small scale features in an efficient and accurate manner [1]. Pursuing this goal, different patterning methods with varying degrees of accuracy have been developed during the last decade. Moreover, researchers involved in the application and development of ceramic-based technologies work with the aim of minimizing the extremely high costs associated with the design, development and large production of ceramic-based micro- and nanodevices. Interaction between industry and academia provided the means for the creation of new strategies to be used as nanofabrication routes. However, many interesting patterning approaches did not reach the presumed technological impact as a consequence of lacking the required combination of reproducibility, accuracy, simplicity, and more important, suitability for large-scale fabrication.

This turned research on nanopatterning and nanomachining of ceramics and hard materials into a frontier topic of the current nanotechnologies. Ceramic materials combine unique properties [2] that make them extremely well suited for manufacturing diverse miniaturized devices, such as the microelectromechanical systems.

In this chapter, we will discuss the "state of the art" of ceramics micro- and nanofabrication techniques. In particular we emphasize the progress made in this area over the past five years, when nanostructuring ceramic surfaces was studied employing different techniques.

2. Writing Ceramic Patterns with the Aid of Lithographic Tools

Lithographic tools play a leading role in processing methods in the semiconductor industry. In the case of conventional lithography, a thin radiation-sensitive polymer layer is used as a resist [3]. Then a determined patterned region is exposed to the radiation in order to alter its solubility and remove it from the substrate using a chemical developer. Apart from the well-known photolithography using photoresists, they exist a vast range of lithographic methods and techniques with a varying degree of accuracy and sophistication. When making a choice between different hard lithographic tools, a typical problem is to find the compromise between four main variables: resolution, process complexity, costs and time. Working with lithographic tools in the nanoscale (<100 nm) often implies a sudden increase in process complexity, cost and time. Optical lithography is a very well-established tool commonly used in many laboratories. However, resolution of optical lithography is nearly the wavelength of the radiation thus limiting the use of optical lithography with nanolithographic purposes. Moreover, other problems that make the choice even more difficult concerns on the reproducibility, uniformity and suitability for large scale fabrication. Industry and academia converged to develop new members of the lithographic family in order to bring other alternatives fulfilling the demands of the ever growing nanotechnology-based industries. One clear example is the laser holographic printing [4] enabling the formation of gratings with a significant printing speed but lacking on the required versatility to be used as a general patterning method.

The final variable, and central to our chapter,is the material. Ceramics are commonly referred as "hard to machine" materials due to difficulties to transfer, write or print patterns onto their surfaces. Traditionally the problem for patterning ceramic surfaces was on the microscale. However, during the last few years different groups have started to explore novel and clever strategies using electron and ion beam lithography for patterning ceramics with nanoscale resolution. These techniques do not require mask making capability and the resolution is mainly determined by the spatial distributionof the deposited energy and the contrast of the developer.

Focused ion beam in combination with chemical vapour deposition (FIB CVD) has demonstrated to be very useful technique for the fabrication of 3D structures. Morita *et al.* [5] used this approach to fabricate nanostructures of diamond-like carbon materials with a very large Young's modulus (600 GPa). These authors used phenanthrene as the precursor to synthesize the diamond-like material. The experimental setup comprised two gas sources, in order to increase the gas pressure and to achieve uniformity around the sample, and a beam with perpendicular incidence to the substrate. Well-defined three dimensional structures were obtained by combining the lateral growth mode with the beam scanning.

Another very interesting approach was reported by Ruda and co workers [6]. These authors used electron beam lithography (EBL) with processible high resolution resists with high metal content, highly metallized cobalt-clusterized polyferrocenylsilane. The resists operate in a negative tone mode. The exposed regions witnessed a chemical change turning them insoluble in the developing medium. In other words, the regions exposed to the e-beam remains firmly adhered to the substrate while the unexposed metallopolymer is removed. The possibility of manipulating high concentrations of Co and Fe with a well defined stoichiometry was exploited for creating well-defined nanopatterned ferromagnetic ceramics. In the

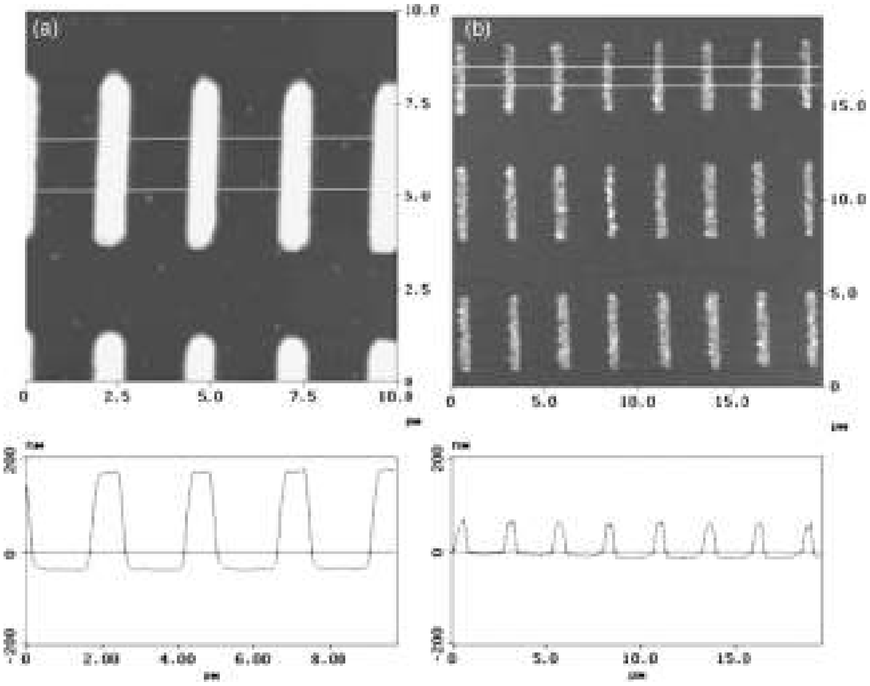

Figure 1. AFM imaging including cross-sectional analysis corresponding to lithographically patterned bars (A) before pyrolisis and (B) following 5 h the pyrolysis at 900 C. Reprinted with permission from [6] by VCH-Wiley.

case of the metallopolymer resist, the negative tone behaviour may result from crosslinking of polymer chins induced by e-beam. After EB nanopatterning, the substrate was pyrolized at 900°C during 5 h under a nitrogen atmosphere in order to obtain ceramics nanostructures containing Fe/Co nanoparticles. Thermal treatment did not introduce shape distortions but promoted an expected shrinkage in average height from 210 to 74 nm and in average width from 736 to 521 nm (Fig. 1).

On the other hand, Donthu *et al.* [7] used a different approach to fabricate ZnO nanostructures using e-sensitive polymers and sol-gel precursor. Firstly, a bilayer consisting of a high sensitivity methyl methacrylate-methacrylic acid (MMA-MAA) copolymer (at the bottom) and a low sensitivity PMMA (on top) was spincoated on the substrate. The polymer-coated substrates were irradiated and treated with oxygen plasma to improve the wettability of the subtrates. Then, a solution containing the sol-gel ceramic precursors was spincoated onto the patterned polymer surfaces and thermally treated at 150°C during 10 min. Finally, the substrates were soaked in acetone to dissolve the polymer resist and lift off the material deposited outside the patterned regions. This strategy enabled the fabrication of continuous and well-defined ceramic nanostructures with lateral resolution close to 40 nm (Fig. 2). A similar approach using this "soft EBL" approach has been recently reported for the fabrication of radially stacked heterostructures of multifunctional oxides [8].

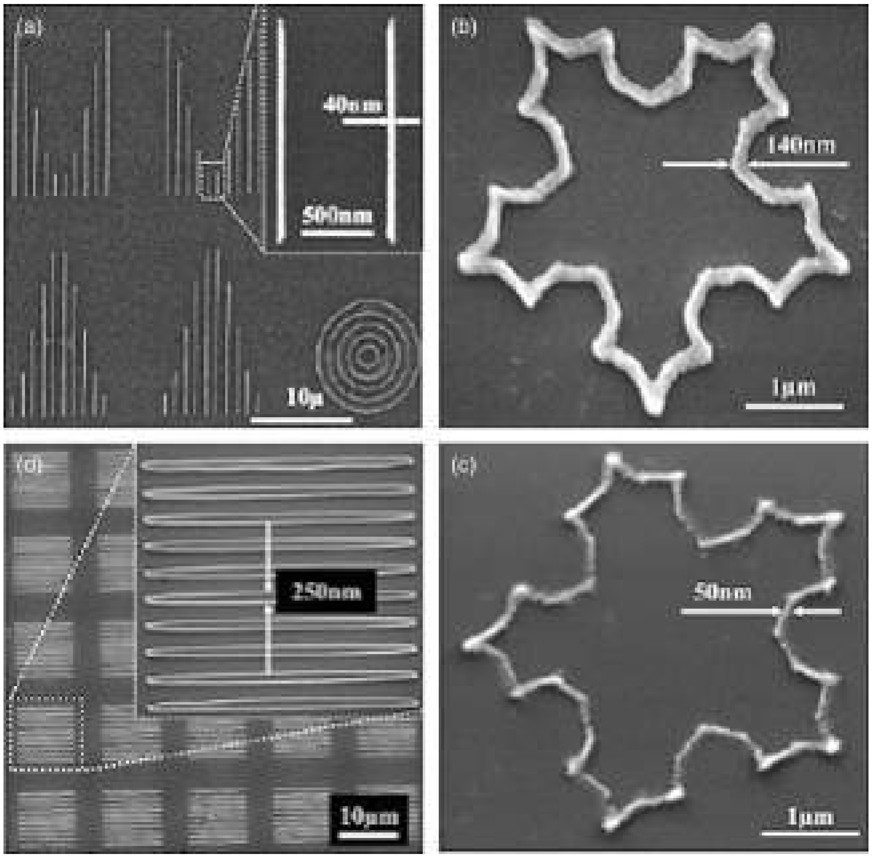

Figure 2. (a) Backscattered electron image of ZnO patterns on SiO_2 substrates annealed in air at 700 C for 20 min (b) secondary electron image before annealing, (c) secondary electron image after annealing at 700 C for 20 min in air and (d) secondary electron image of annealed patterns over large area. Reprinted with permission from [7] by American Chemical Society.

Well-defined nanorings of lead zirconate titanate were fabricated on a variety of substrates. These nanorings were used as nanoreservoirs and filled with a sol gel precursor of $CoTe_2O_4$ to generate radially stacked composite ceramic heterostructures.

Another rapidly growing fabrication method consists of laser processing of ceramic materials [9]. The main motivation for exploring this lithographic strategy was centered on finding a cost effective alternative for ceramic processing based on laser precision microfabrication. The principle lying behind this approach is based on the ablation of the substrate by the laser pulses [10]. When a determined surface is irradiated with an ultrafast laser, the irradiated substrate is melted and evaporated almost instantaneously. Submicrometer structuring of $LiNbO_3$ with periods of about 360 nm can be created by using picosend or femtosecond UV laser pulses [11]. This technique has been increasingly used for patterning a wide variety of substrates [12–22].

However, conventional UV, visible or IR lasers often promote significant damage in the hard material. The thermal stress built up in the materials during irradiation and the extensive cracking and exfoliation are deleterious effects of intense ns pulse laser irradiation. To overcome these problems, different approaches were developed. One is the use of vacuum ultraviolet and femtosecond lasers that has proven to be useful for high quality patterning of fused silica substrates [14]. Another novel approach for high quality patterned ablation is based on using hybrid lasers. In this case, another medium is introduced in the conventional nanosecond laser ablation system. The role of the medium is to enhance the absorption of the nanosecond laser beam by the materials. Sugioka and co-workers reported that simultaneous irradiation with the VUV laser beam which possess extremely small laser fluence and the UV laser beam has resulted in the accurate ablation of hard materials (VUV-UV multiwavelength excitation process) [23–25].

In this technique, the substrate is simultaneously irradiated by VUV and UV laser. The energy density of the VUV is only several tens of $\mathrm{J/cm^2}$. In contrast, the energy density of the irradiated UV laser beam is nearly $\mathrm{J/cm^2}$. The micropatterning process involves the irradiation of an unpatterned VUV beams on a broad area and the localized irradiation with the UV laser.

Another novel technique involving hydrid laser processing technique is laser-induced plasma – assisted ablation (LIPAA). In this technique, a single conventional pulsed laser lead to an effective ablation of transparent materials by coupling the laser beam to plasma generated from a metal target by the same laser [26,27]. An homogeneized beam is projected to the fused silica substrate. Since the silica is transparent in the UV range, the laser beam travels through the substrate and is absorbed by the Ag target placed behind the substrate. The interaction between the generated plasma and the laser beam produces and enhanced patterned ablation at the rear surface of the substrate.

Later on, Hosono and co-workers developed an holographic laser approach for patterning hard materials [28,29]. When two femtosecond pulses collide spatio-temporarily (overlapped region) the imprinting interference pattern results in the encoding of grating structures into the materials. This technique has been used to generate grating-like patterns on hard materials like diamond or sapphire. This is a promising technique which allows encoding gratings in almost all kinds of materials, irrespective of the photosensitivity.

3. Monolayer–Directed Patterned Deposition of Ceramic Thin Films

Modification of substrates with organic monolayers has been used as a very simple and powerful tool in the materials science community devoted to developing patterning strategies [30]. Currently, patterning self-assembled monolayers on a solid substrate is a routine procedure that can be accomplished in the laboratory without using expensive equipment [31]. Common procedures to achieve this goal in micrometer range are microcontact printing or masked photodegradation of the organic film. Self-assembled monolayers are used to introduce surface functional groups with the aim of influencing the interactions between the deposited ceramic oxides and the substrate.

On the other hand, soft solution processing provides a simple method for synthesizing ceramic materials with a determined structure, size, shape and orientation. In this approach surface chemistry plays a determinant role on achieving the patterning of the desired material. Deposition of ceramic oxides onto SAM-covered surfaces is governed by an interplay between the interfacial chemistry related to the SAM-particle system and the colloidal chemistry referred to the particle-solution system.

In most of the cases, ceramic oxides in solution are charged because of the adsorption of charged species on their surfaces and this determines characteristics like morphology, size and the charge of the depositing particles [32].

On the other hand, the substrate is modified with functional groups deliberately introduced in order to tailor the interaction between the particles and the surface. The functional groups provide a mean for triggering a controlled heterogeneous nucleation and growth of the ceramic film on the pre-patterned regions of the substrate. A clear example is the deposition of TiO_2 using titanium dichloride diethoxide precursors onto methyl/silanol patterned domains. The silanol domains present a high selectivity for the nucleation and growth of the films leading to the formation of well-defined TiO_2 patterned domains (Fig. 3).

However, it must be noted that initial homogeneous nucleation of ceramic particles occur in solution where the solid phase is originated from the inorganic polycondensation derived from the hydrolysis of metal ions and the condensation of hydroxylated complexes [32]. The occurrence of these two processes, heterogeneous and homogeneous nucleation, is regulated by the net interfacial energy of the system. In other words, when the interaction between the ceramic particle and the substrate represents a system with a lower net interfacial energy, the system evolves in the direction of heterogeneous nucleation instead of the homogeneous nucleation. As a consequence, deposition from solution demands an accurate control of the reactive process in such a way of inducing nucleation and growth on the surfaces rather than in solution. Homogeneous nucleation can be suppressed working in a low supersaturation region, that is low solution temperatures or low concentration of metal ions can decrease the degree of supersaturation. On the other hand, heterogeneous nucleation can be achieved in an intermediate supersaturation region.

This strategy exploiting the versatility of solution chemistry in combination with chemically patterned substrates has been successfully used for patterning a wide range of materials such as: TiO_2 [33,34], ZrO_2 [35,36], SnO_2 [37,38], Y_2O_3 [39], ZnO [40,41], La_2O_3 [42], Ta_2O_3 [43], and different iron oxides [44–46]. In most of these cases, the ceramic films were synthesized by inorganic polycondensation and the growth from the substrate was induced using self-assembled monolayers

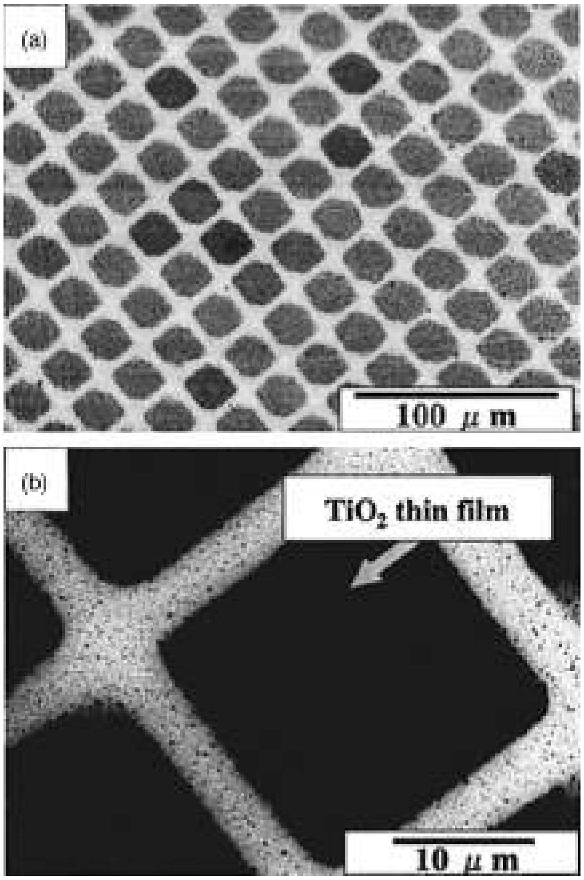

Figure 3. SEM micrographs of (a) a micropattern of TiO_2 thin films and (b) a magnified area of (a). Reprinted with permission from [33] by American Chemical Society.

functionalized with amino, phenyl or sulfonate terminal groups. The surface functional groups can strongly influence the deposition process due to the possible interactions between the depositing ceramic particles and the many different chemical entities on the substrate. A clear example is the growth of iron oxyhydroxide films onto SAM-modified substrates. It has been demonstrated that film growth is sensitively improved by using SAMs with sulfonate terminal groups in clear contrast with other surfaces modified with OH, CH_3, COOH and NH_2 terminal groups [47].

Another nice example is the growth of PbS films on different SAMs by using the chemical bath deposition method. The method consists on depositing PbS films by using a solution containing $Pb(ClO_4)_2$ and thiourea at room temperature. Interestingly, in this case the film formation is mainly governed by the pH. At low pH, the PbS film is preferentially deposited on SAMs with COOH and SO_3H terminal groups. Conversely, at high pH the film can be formed on surfaces bearing different terminal groups [48].

On the other hand, Koumoto *et al.* developed a method which consists of locally inducing supersaturation by using site-selective growth from a catalytic surface.

The authors used this strategy for patterning ZnO films on phenyl/ hydroxyl surfaces [41]. Initially, Pd catalyst is selectively immobilized from a Pd/Sn colloid solution on the phenyl groups domains on the surface. Then, the substrate is immersed in an aqueous solution containing $Zn(NO_3)_2$ and dimethylamineborane (DMAB) at 60°C. The catalyst induces the generation of hydroxyl ions near the substrate surface increasing the local saturation and promoting the heterogeneous nucleation. This approach has proven to be a useful procedure to create ZnO patterns with 1 μm in lateral resolution (Fig. 4).

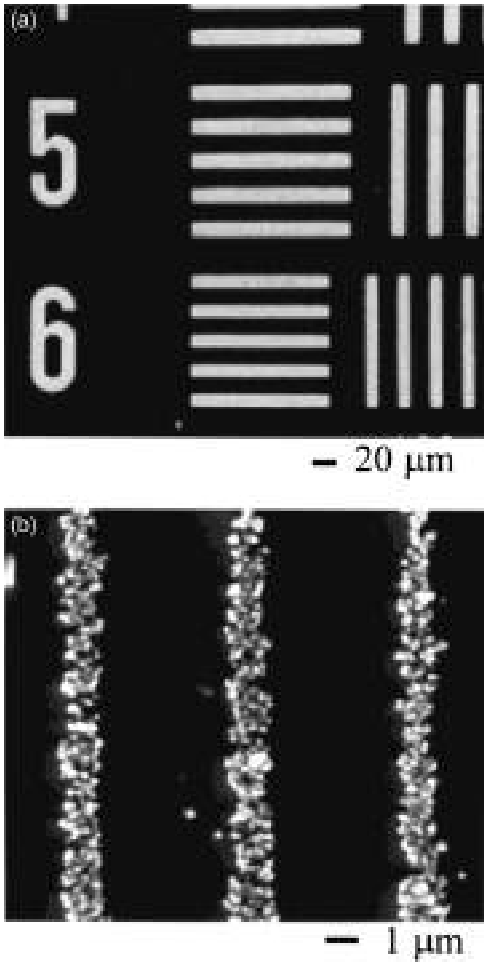

Figure 4. SEM images of the patterned ZnO. a) Large feature sizes area and b) 1 μm lines. Deposited particles are about 0.2 *μm* in diameter. Reprinted with permission from [41] by VCH-Wiley.

4. Soft Lithographic Patterning of Ceramic Surfaces Using Molecular Precursors and Solution Chemistry.

One of the main outstanding features of sol gel chemistry is its ability to elaborate solid materials beginning from molecular precursor [49]. The combination of inorganic polymerization process with organic chemistry offers a versatile alternative for materials synthesis. Currently, through soft chemistry processes, it is possible to design and control properties in ceramic materials in a predictable manner [49].

Sol gel techniques correspond to a process called hydrolytic polycondensation, where leaving groups at the metal are substituted by nucleophilic attack of H_2O. This process occurs at many metal centers in presence of many different leaving groups like halide, sulphide, alkoxide or nitride. Then, this process is followed by the elimination of the leaving group and formation of the metal hydroxide. This process leads to metal oxide bonds either by homo or heterocondensation. Finally, the solid phase is formed after a set of very complex steps involving precursors, oligomers, polymers, colloids, sol and gel [49]. Sol gel techniques have been employed as a cost effective and fast route to obtain ceramic materials with engineered properties. This choice is also based on their low temperature characteristics and good quality of the obtained films. For example, silica films, prepared by sol gel chemistry possess low optical loss and adjustable refractive index [50].

The first attempts to create patterned ceramic substrates using sol gel chemistry were based on the use of patterned substrates with different chemical domains. Nuzzo *et al.* used surfaces modified with patterned self-assembled monolayers for directing the deposition of Ta_2O_5 from sol gel precursors (tantalum ethoxide in absolute ethanol) onto different technologically important substrates [51]. These authors exploited the poor adhesion of ceramic films onto methyl terminated surfaces allowing delamination of oxide film from the functionalized regions. Sol gel deposition of Ta_2O_5 onto the functionalized substrates was followed by thermal treatment at 700 C and then by mild nonabrasive polishing. This process produced high quality patterned oxide on the patterned unfunctionalized regions.

Moreover, the antiadherent properties of SAMs have been exploited for direct patterning oxides surfaces by electrochemical oxide deposition [52]. The oxide film was deposited onto an alkanethiolate-modified Cu master from a plating bath and by applying a constant potential value at the electrochemical interface. After releasing the electrodeposited oxide film from the master, an accurate pattern transfer in the submicrometer scale was observed.

In order to fabricate ceramic microstructures from molecular precursor many research groups exploited the versatility and low cost of soft lithographic techniques. Soft lithography is a set of techniques that relies on molding and printing with an elastomeric stamp, polydimethylsiloxane (PDMS). This includes microtransfer molding, microcontact printing, and micromolding in capillaries (MIMIC) [53–55].

With soft lithography any material that can be derived from liquid precursor can be patterned, provided that the solvent used does not swell the elastomeric mold.

This makes soft lithography an outstanding alternative for molecular precursors to fabricate a wide range of complex ceramic architectures without using etching procedures.

Whitesides and co workers exploited this combination for patterning ceramic materials for high temperature applications. In particular, they worked with borosilicon carbonitride quaternary ceramics synthesized from several preceramic polymers [56]. A PDMS mold was filled with the preceramic and then a silicon wafer was pressed against the filled PDMS. After curing the preceramic during 1 hour at 200 C the mold was removed. The obtained polymeric microstructures were placed on top of a silicon wafer and transferred into a furnace and thermally treated at 1050 C. After thermal treatment samples evidenced a lateral shrinkage of 30%. The same research group following a similar strategy succeeded on achieving high quality accurate patterning of glass microstructures [57] (Fig. 5).

Cao *et al.* used a similar route to synthesize patterned complex oxide materials with important physical properties such as ferroelectricity, piezoelectricity or pyroelectricity. They synthesized the $Sr_2Nb_2O_7$ sol from inorganic precursors like strontium nitrate and niobium pentachloride using ethylene glycol as a cross linking agent and ethanol as a solvent [58].

Then they used a technique called micromolding in capillaries where the fluid is patterned by spontaneous filling of PDMS mcrochannels. When the elastomeric molds is placed in conformal contact with a clean silicon substrate, the channels of

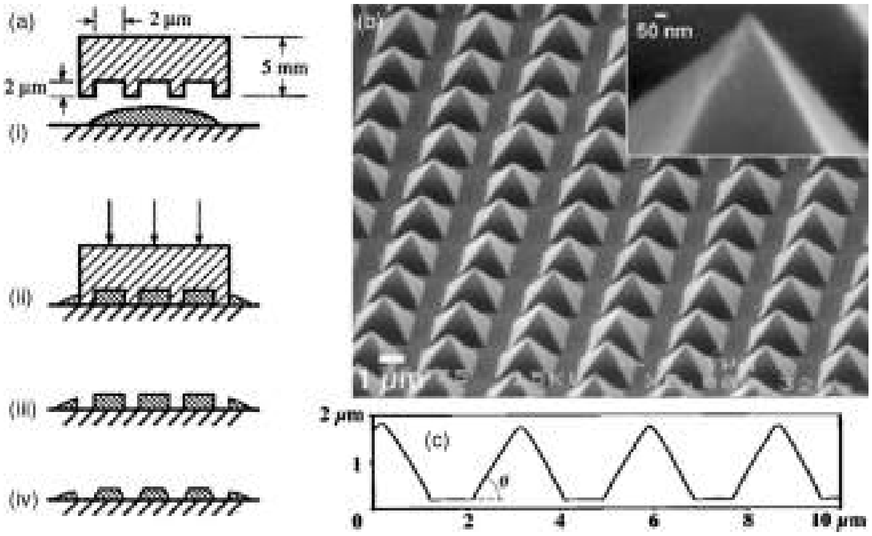

Figure 5. (A) Schematic describing the molding method to fabricate structures supported on a flat susbtrate. A droplet of precursor is compressed between the stamp and the surface (a,b). The high interfacial free energy of the solution promotes dewetting of the precursor where the stamp and the substrate were in contact (c,d). (B) SEM image and its AFM-derived analysis of a patterned piece of silica. Reprinted with permission from [57] by VCH-Wiley.

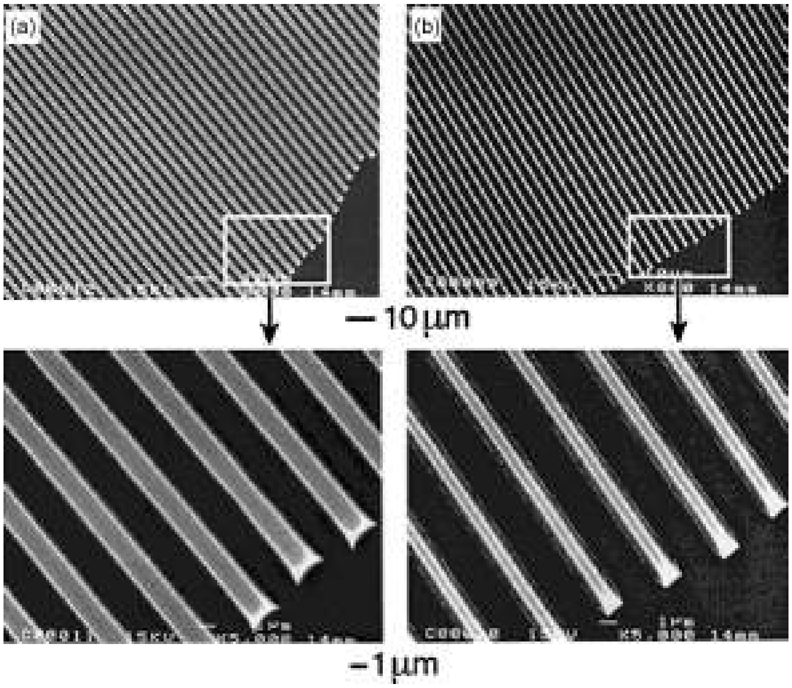

Figure 6. SEM images of MIMIC-patterned microstructures on a silicon substrate using an ethanol solution of the polymeric precursor to ZrO$_2$: (A) Prior thermal treatment firing, (B) after thermal treatment at 460 C for 4 h. Reprinted with permission from [59] by Materials Research Society.

the mold form capillaries with the substrate. The sol was deposited at the open end of these capillaries. Then the solvent was evaporated by placing the molds and the substrate in a drying oven at 100 C during one day. This process induces the condensation reaction promoting the cross linking and leading to the sol-gel transition. Finally, the molds were removed and the patterned samples were thermally treated at a 700–800 C for 30 min. The features evidenced a 46% shrinkage after densification by thermal treatment. Similar approaches were also applied for patterning other oxide ceramics such as zirconia and tin oxide [59], as shown in Fig. 6.

However, some problems may be present when dealing with MIMIC. Even considering that the filling process by capillary forces is thermodynamically favorable, infiltration kinetics can introduce some limitations for surface patterning by MIMIC [60].

Ideally the solutions suitable for MIMIC are powder free chemical solution with low viscosity and low solid loading. Within this scope we find liquid prepolymers and sol–gel precursors. In spite of lacking on these requirements, particulate fluids were used as a good alternative to obtain ceramic films by soft lithographic techniques.

Gauckler and coworkers used MIMIC for patterning 10 μm lines of SnO$_2$ ceramics using a 40 vol % suspension [61]. In most of the cases MIMIC patterning with ceramic suspensions involved the use of low concentration solutions with low viscosity in order to use the capillary forces to fill the channels [62,63].

To overcome this limitation, Moon *et al.* introduced a technique called vacuum-assisted microfluidic lithography [60]. A PDMS microfluidic device is used to fabricate ceramic microstructures employing ceramic suspensions of relatively high solid loadings, 42 vol %. The microfluidic device loaded with the suspensions is then placed in a vacuum chamber. The lower overall pressure allows releasing the gas contained within connected volumes of the channel networks. When the pressure is returned to atmospheric level, the suspensions flow in to fill the voids left in the channels. This technique also permits simultaneous pattern generation of multiple materials on the same substrate. Using mFL with suspensions of Al_2O_3 and NiO it is possible to fabricate interdigitated ceramic microstructures composed of two different materials on the substrate (Fig. 7).

Finally, Chou and co workers reported direct nanoimprinting of sol gel films for the fabrication of SiO_2-TiO_2 gratings [64]. The nanoimprinted samples shows excellent uniformity and smooth pattern profiles having 300 nm pitch and 80 nm linewidth. A 600 nm thick sol film was spin coated onto silicon substrates. Imprints were carried out immediately. During the imprinting process the mold and the gel

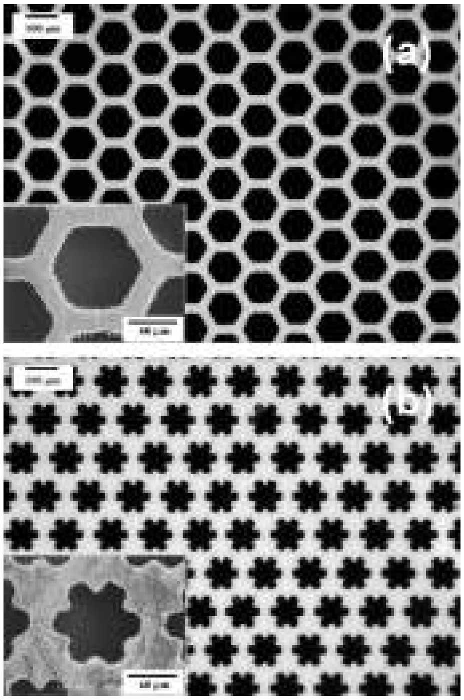

Figure 7. Optical micrographs of different patterned structures of Al_2O_3 on a Si substrate obtained by vacuum-assisted microfluidic lithography. The height of the structure was 25 mm. Reprinted with permission from [60] by Blackwell Publishing.

film were heated from 17 to 200 C. After releasing the mold, the patterned gel was thermally treated at 400 C evidencing a 61% shrinkage in the film thickness. The shrinkage was in the direction perpendicular to the substrate with no obvious shrinkage observed in the direction parallel to the wafer substrate. Similarly, Park *et al.* used nanoimprint lithography for patterning SiC-based ceramic patterns on Si substrates. In this case, a viscous polyvinylsilane was used as a ceramic precursor, followed by pyrolysis at 800 C under nitrogen atmosphere [65].

In most cases, the micromolding of pre-ceramics or ceramic suspensions shows considerable isotropic or ani- sotropic shrinkage after thermal treatment. Recently, Martin and Aksay [66] demonstrated that the micromolding of sol–gel films could produce unintended topographical distortions. This is as a consequence that during thermal treatment, a non-uniform shrinkage across the micromolded film is observed. In spite of the versatility of the method, this fact should limit the potential applications of the technique. Moreover, shrinkage has shown deleterious effects on micromolding ceramic suspensions where high drying shrinkage can lead to partial destruction of the patterned sample. This deleterious effect can be reduced (for patterning above the micrometer scale) by colloidal isopressing [67], a technique in which a pre-consolidated slurry is injected into an elastomeric mold and isopressed to rapidly convert the slurry into an elastic body that can be released from the mold without any distortion.

5. Fabrication of Nanopatterned Ceramic Substrates Directed by Self-Assembly

Most of the approaches discussed along this chapter consist of the so-called top down strategies. These are based on miniaturizing existing techniques which are already available at larger scales. An interesting alternative to these strategies is the bottom up approach. The philosophy of the bottom up strategies is the creation of nano- and microstructures through the use of smaller building blocks. These building blocks generate the desired structure through self-assembly without any external intervention when the process is carried out in the appropriate conditions [54].

The concept of self-assembly is very familiar to disciplines like biology. Different building blocks like molecules, macromolecules or nanoparticles spontaneously organize giving origin to well-defined structures stabilized by non covalent supramolecular interactions. Many biological processes, like membrane formation using phospholipids as building blocks, are based on the self-assembly principle [54].

One very important feature relies on the fact that the stabilized self-assembled structures are close to the thermodynamic equilibrium. As a consequence supramolecular aggregate present a very low level of defects. Biology has demonstrated that self-assembly is able to generate very complex and very small architectures. With this focus different researchers explored the use of self-assembly as a route to achieve well-defined patterned nanostructures [54].

Aksay and co-workers synthesized nanostructured ceramic materials by exploiting the templation effect of complex fluid systems [68]. These complex fluids, which are based on amphiphilic building blocks like surfactants, biomembrane lipids or block copolymers, can generate unique features in the 1–100 nm range through spontaneous self-assembly. By controlling the size of the building blocks and the interaction strength between them, self-assembly can be a very versatile strategy for the manipulation and generation of nanostructures at temperatures $<100\,\mathrm{C}$. Higher temperatures can lead to coarsening that is a strong limitation to retain the pre-designed nanostructured features [68].

This approach is based on exploiting to the weak interactions that determine the architecture of the supramolecular aggregates of the amphiphiles. Then by using inorganic precursors, the strategy relies on replicating the structures of the complex fluids into an organic/inorganic nanostructured composite material. Later the complex fluid portion is removed through solvent extraction or pyrolysis, converting the organic-inorganic hybrid into a 100% ceramic nanostructure. Materials obtained by this procedure received the name of self-assembled ceramics.

Chan *et al.* produced porous and relief ceramic nanostructures from self-assembling block copolymer (polyisoprene and poly (pentamethyldisilylstyrene)) precursors in a single step at low temperature [69]. In this case, the key factor is the careful selection of the relative volume fraction and phases. These authors showed that block copolymers can produce precursor materials with different symmetries and structures giving origin to highly ordered and complex nanostructures. The process consisted of a bifunctional oxidation to both selectively remove a hydrocarbon block and convert a remaining silicon-containing block to a silicon oxycarbide ceramic. Interestingly, the obtained nanoarchitectures only depend only on the volume fraction of the hydrocarbon block relative to the silicon-containing block in the block copolymer precursor. Moreover, double gyroid and inverse double gyroid morphologies were obtained by using two triblock copolymer precursors. However, treatments like ozonolysis or ultraviolet irradiation can affect the selective removal of the hydrocarbon block and the conversion of the silicon-containing block to a silicon oxycarbide ceramic. This strategy has been successfully used to synthesize nanorelief ceramic structures with interfacial areas of 40 square meters per gram.

Cooperative self-assembly of organic and inorganic materials can lead to a vast range of ordered morphologies. The combination of self-organization and soft lithography has been exploited as a simple route to generate hierarchically ordered ceramic materials over several length scales. Stucky *et al.* reported the preparation of porous silica, niobia, and titania with three-dimensional structures patterned over multiple length scales [70]. These materials show hierarchical ordering over several discrete and tunable length scales ranging from 10 nanometers to several micrometers (Fig. 8).

Another clear example where self-assembly and self-organization can lead to nanostrutured ceramics is the use of incompatible diblock copolymers. Diblock

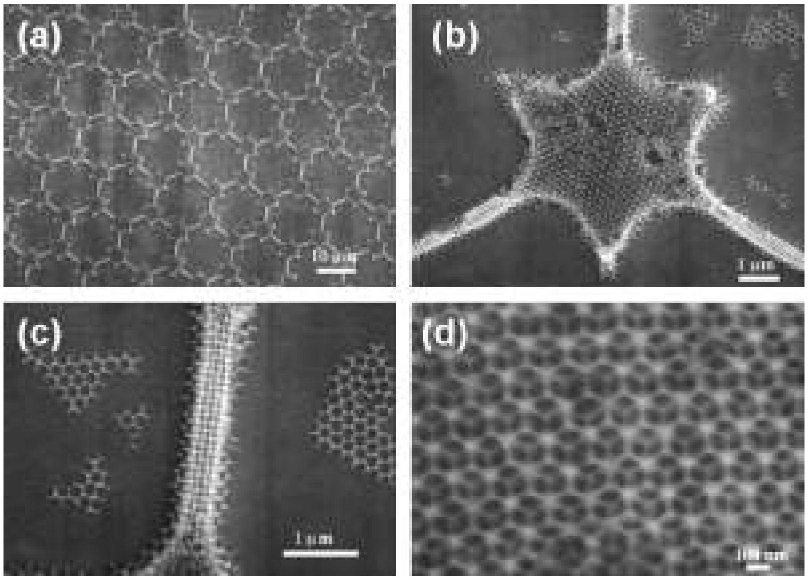

Figure 8. (A to D) SEM images, at different magnifications, of hierarchically ordered mesoporous silica displaying organization over three discrete characteristic dimensions. Reprinted with permission from [70] by American Association for the Advancement of Science.

copolymers are two chemically different polymer chains held together through covalent bond. The interplay between the connectivity constraints and the incompatibility between the blocks, leads to self-assembly into microphase-separated molecular–scale domains with ordered morphologies [71]. These macromolecular architectures can be supported on solid substrates forming a large variety of well ordered structures of molecular dimensions.

Following this framework, Park *et al.* proposed self-assembly in synthetic materials as a route for nanopatterning ceramic surfaces [72]. These authors fabricated dense periodic arrays of holes and dots on silicon nitride-coated silicon wafers using a method called block copolymer lithography. A monolayer of ordered microdomains was deposited on the surface by spin coating. These films consisted of diblock copolymer thin films, polystyrene-polybutadiene (PS-PB) and polystyrene-polyisoprene (PS-PI), with well ordered spherical or cylindrical microdomains.

Initially, the microdomain monolayer was exposed to ozone to selectively degrade and remove the PB spherical domains before treatment with reactive ion etching (RIE). Ozone attacks the double bonds in the PB domains producing a region that can be dispersed in water. This results in an array of voids in the PS matrix. Later, the sample was exposed to RIE producing holes in the substrate. The hexagonally ordered holes were 20 nm in diameter with a separation of 40 nm apart with polygrain structure. The fabrication of dots consisted of using the same microdomain monolayer but the PB domains were stained with OsO_4. Osmium-stained domains present a reduced etching rate during treatment with RIE. As a consequence, the

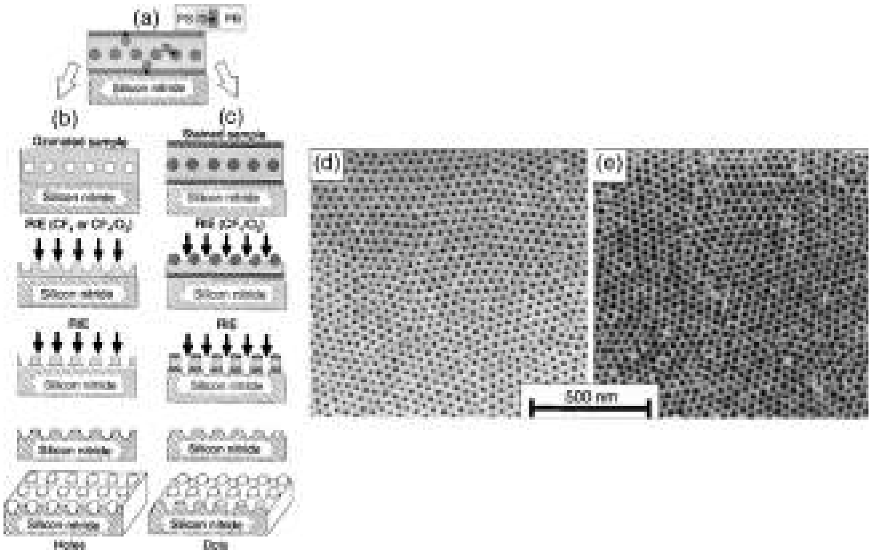

Figure 9. (A) Block copolymer film deposited on the silicon nitride substrate. (B) Schematic of the process producing holes in the silicon nitride. (C) Schematic of the process producing dots in the silicon nitride. (D) SEM image of a partially etched, ozonated monolayer film of spherical microdomains. (E) SEM image of hexagonally ordered arrays of holes in silicon nitride on a thick silicon wafer. The pattern was transferred from a copolymer film such as that in (D). The darker regions represent 20-nm-deep holes etched out in silicon nitride. Reprinted with permission from [72] by American Association for the Advancement of Science.

regions underneath the PB domains were partially masked from the RIE process, resulting in the fabrication of dots (Fig. 9).

6. Self-organization as a Route to Fabricate Nanopatterned Ceramic Substrates

Previously we have described different approaches for exploiting self-assembly in soft matter as a route to generate templates for nanofabrication. The spontaneous formation of different nanostructured materials through self-organization phenomena has attracted increasing interest through the last decade. Self-organization is now being examined extensively for large scale patterning at scales below 100 nm [73]. Concerning this latter, special emphasis was placed on using naturally occurring self-organization processes on hard matter leading to well-defined nanostructured solids.

A typical example is aluminum anodic oxidation producing self-ordered nanochannel arrays. This technique is a very promising self-organization method to obtain highly ordered and high aspect ratio periodic structures arrays in the nanometer scale. Anodic porous alumina is prepared by the anodic oxidation of aluminium in an acidic electrolyte. Recent improvements in the degree of ordering obtainable for a hole array has increased even more the attractiveness of such materials for nanofabrication [73].

Masuda *et al.* pioneered this very successful approach using nanostructured alumina as a host or template for fabrication [74]. The potential of this approach relies on the preparation of large area nanostructures with high aspect ratios. During the last years, nanostructured alumina has been widely used as a template for nanostructuring materials, including ceramics and other hard materials.

Takahagi *et al.* achieved the pattern transfer of an alumina template containing nanohole arrays to a Si substrate by RIE. Treating a nanostructured porous alumina/SiO_2/Si substrate with RIE using chlorine plasma is a very effective route for pattern transfer to Si [75].

On the other hand, Masuda *et al.* used a nanostructured alumina to fabricate nanoholes on a diamond substrate [76]. The nanostructured membranes were laid on top of the synthetic diamond films, and then deep holes were etched into the films using an oxygen plasma treatment. This approach leads to the fabrication of ordered diamond nanostructures over $1\,cm^2$ areas. The versatility of the method to fabricate different diamond surface architectures is based on the capability for electrochemically nanostructuring the membrane that is used as etching mask. It must be noted that anodic alumina has high resistance to oxygen plasma etching being able the generation of high-aspect ratio features.

7. Physical Vapor Deposition Meets Micromolding Techniques

Molding technology could be interpreted as a primary strategy to replicate features by sequential pattern transfer steps. This is commonly used to transfer surface-relief patterns on diverse functional materials. In spite of its simplicity, molding technology is still at the forefront as a simple and valuable tool for the next generation nanotechnologies. Different research groups have demonstrated how easily molding techniques can be applied in the nanoworld [77,78].

The molding and replication approach (micro- nanomolding) presents distinctive outstanding features: simplicity, high-resolution, low cost and high throughput. However, in spite of these advantages for transferring surface-relief patterns, micromolding strategies have been mainly focused on using polymeric materials.

By simple physical contact, the micromolding process is carried out by casting a pre-polymer or polymer against a master surface. Then, after polymerization or solvent evaporation, the polymer film is released from the master. In the case of replication, it involves two consecutive “relief-transfer” processes.

Molding and replication on polymer materials is widely used on large-scale fabrication of diffraction gratings or compact discs. Extending the concept of molding and replication to ceramic materials brings a straightforward route for patterning “hard to micromachine” materials.

In order to achieve this goal Auger *et al.* explored the direct micromolding of ceramic materials deposited by physical methods onto micromolds with no need for post-patterning treatments [79]. In this strategy, the relevant step of the molding

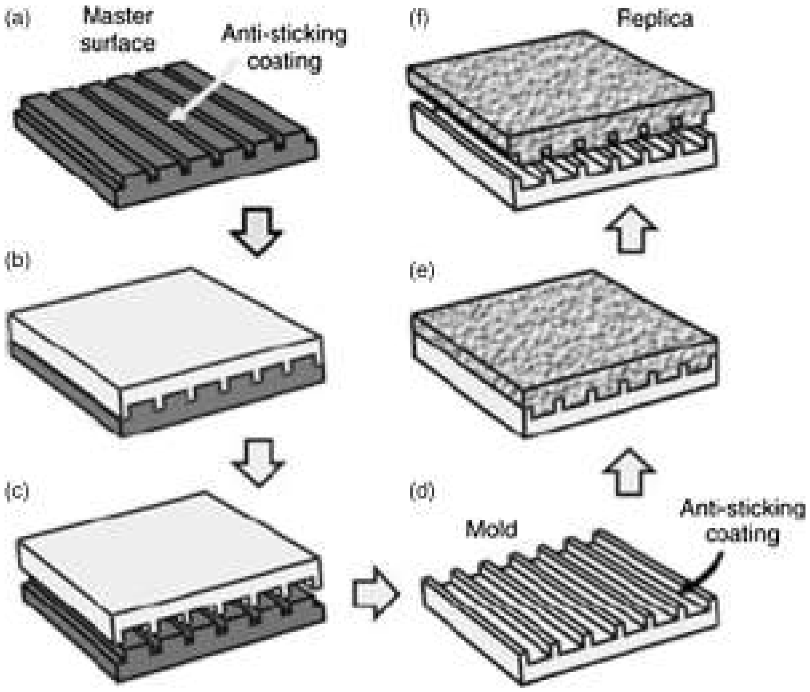

Figure 10. Schematic describing the molding and replication procedure used for transferring surface-relief patterns onto ceramic surfaces. A master surface (a) modified with an antisticking coating is used to fabricate the corresponding metallic mold (b) by thermal evaporation (c). Then, this negative replica (d) is used as a mold for the physical vapour deposition of the ceramic film (e). After detaching the deposited film a replica of the original surface is obtained (f). Reprinted with permission from [79] by VCH-Wiley.

process is to provide molds with good anti-sticking properties (Fig. 10). A low surface-energy layer on mold surfaces helps sensitively the release process and increases the mold lifetime by preventing further surface contamination. In this case, fluorine- or methyl-terminated self-assembled monolayers (SAMs) are the most commonly used anti-sticking layers [80]. These layers are built up by simple self-assemby on the surface. In addition, the molecular thickness of the monolayer enables pattern transfer of nanoscale feature due to the release layer itself.

However, direct micromolding of ceramic materials by depositing onto surface-modified molds is not so straightforward. It is well known that deposition conditions like temperature or particle energy, required to grow high-quality ceramic films, can introduce failure on the release process due to degradation of the anti-sticking coating.

These limitations can be avoided by introducing slight changes in the deposition conditions. For example, ceramic deposition by reactive sputtering involves the formation of high-energy species. Collision of these energetic species with the modified substrate produces immediate degradation of the SAM in the early stages of deposition. These detrimental effects can be overcomed by increasing the substrate-target distance (d), and by introducing an inert gas into the sputtering chamber, in such a way of "thermalizing" the energetic species arriving at the SAM-coated substrate.

Following this route micromolding of aluminum nitride surfaces deposited by reactive sputtering on metallic micromolds has been recently reported. Aluminum nitride (AlN) is a ceramic material that exhibits a wide bandgap with potential applications in constructing arrays of electro-optical and photonic devices. In spite of the promising properties of this ceramic material, little progress has been reported on the design of cost-effective and reproducible routes for the surface patterning of AlN.

Ceramic films were deposited onto surface-modified Cu micromolds by dc reactive sputtering of a pure aluminum target under specific experimental conditions. By the direct micromolding (deposition and release) of sputtered ceramic films well defined AlN gratings were obtained. In addition, ceramic gratings present a very low roughness (Fig 11).

Other techniques for depositing ceramic films involve the evaporation of the ceramic material itself, such as electron-beam evaporation. In those cases, temperature is a relevant factor that could affect the stability of the anti-sticking coating. The evaporated particles arriving at the substrate are low-energy particles, so the integrity of the antisticking coating is not at risk. By using the micromolding technique in combination with electron beam evaporation it was possible to fabricate patterned B_4C substrates from Au micromolds. The Au micromolds can be easily obtained by micromolding thermally evaporated gold films using copper micromolds as master surfaces. In the case of electron beam evaporation an incident 110 mA e-beam biased at 7 kV with a 1 cm^2 spot size was used to evaporate the B_4C films under vacuum conditions. Detrimental thermal effects on antisticking coating stability can be minimized by increasing the evaporating source-substrate distance. This change influences the growing rate of the evaporated ceramic material but no damage to the antisticking coating is promoted, thus promoting a successful relief transfer (Fig. 11).

Another very useful technique for depositing ceramic materials is pulsed laser deposition (PLD). The combination of PLD with micromolding techniques enlarged even more the variety of ceramic materials that can be micromolded using physical vapour deposition. One example has been recently reported by Zaldo *et al.* on the deposition of micropatterned ZnO films [81]. PLD was performed in a vacuum chamber at room temperature. A KrF laser ($\lambda = 248$ nm) was used to ablate sintered ZnO (99.99%) ceramic targets rotating at 50 rpm. The laser fluence J on the target was 10 J cm^{-2} and the pulse repetition frequency was 10 Hz. The target-substrate distance was 6 cm. One remarkable feature of PLD is that the kinetic energy of the species in the laser plasma can be easily controlled by introducing an inert gas on the deposition chamber. In order to avoid degradation of the antisticking coating,

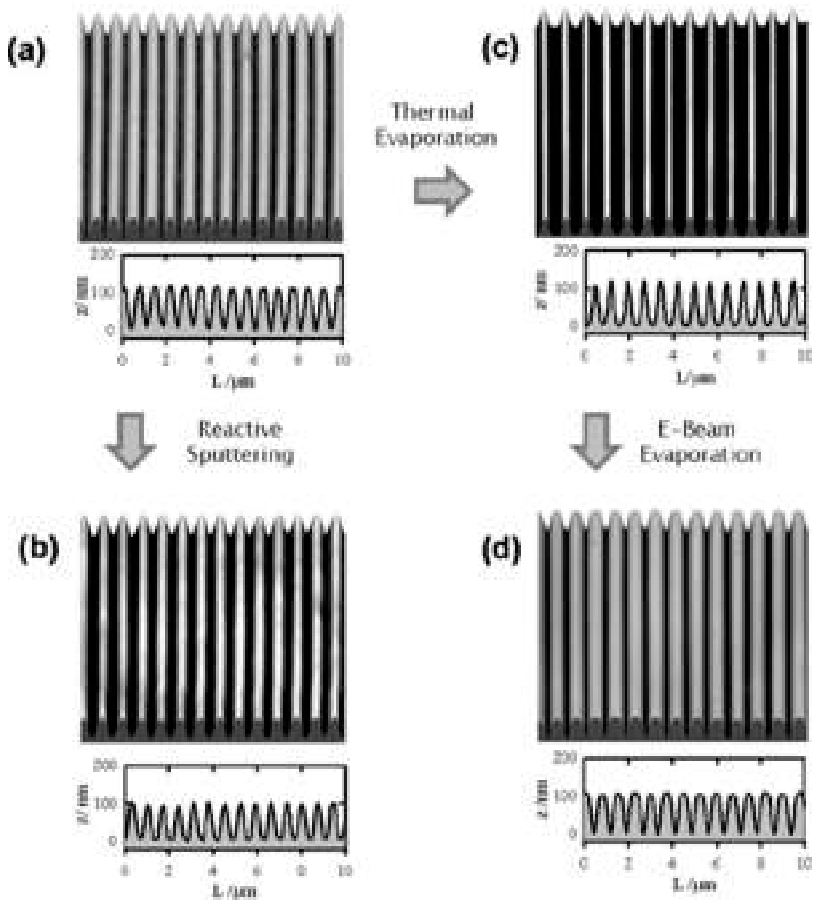

Figure 11. 3D AFM images ($10 \times 10\,\mu m^2$) and their corresponding cross sections showing: (a) a Cu micromold; (b) a micromolded AlN surface obtained by reactive sputtering onto the Cu micromold depicted in (a); (c) a Au micromold obtained by thermal evaporation using the copper surface depicted in (a) as a master; (d) a micromolded B4C surface obtained by electron-beam evaporation onto the Au micromold depicted in (b). Reprinted with permission from [79] by VCH-Wiley.

these authors introduced Ar as a background gas to thermalize the plasma. By using Cu micromolds grating-like patterned ZnO substrates were easily obtained.

One remarkable fact of using physical deposition techniques is that micromolded surfaces do not show significant shrinking effects. The amplitude of the sinusoidal relief structures transferred from the micromold to the ceramic film suffers a shrinkage of $< 5\%$, and the pitch shows only slight variations ($< 2\%$). This is a clear advantage of the direct micromolding procedure if we consider that in most cases, the micromolding of pre-ceramics or ceramic suspensions shows considerable isotropic or anisotropic shrinkage after thermal treatment.

Physical deposition methods can easily produce deposits with small grain sizes (< 30–$40\,\text{nm}$). Larger grain sizes can be serious limitation when it is intended to

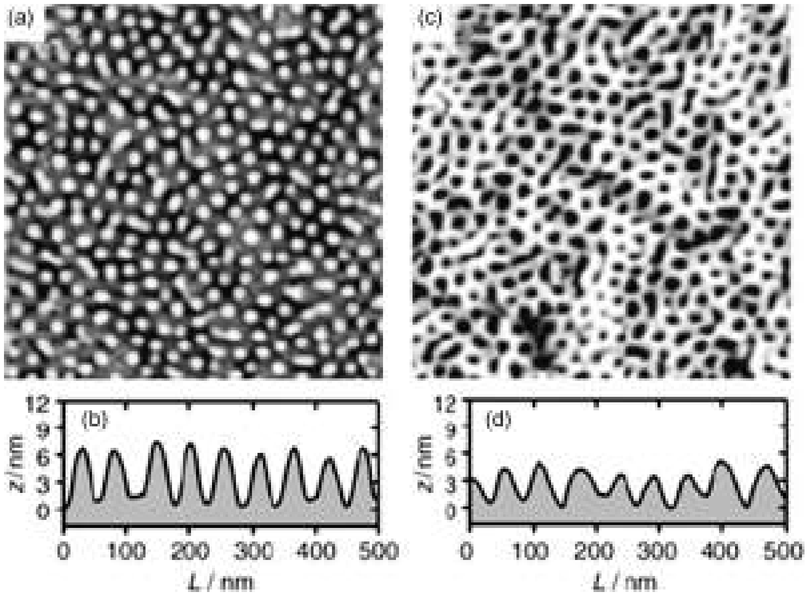

Figure 12. Top view AFM images ($1 \times 1\ \mu m^2$) with their corresponding cross-sectional analysis of a nanostructured SiO_2/Si surface (a,b) and a nanopatterned TiN surface (c,d). Reprinted with permission from [79] by VCH-Wiley.

downsize the micromolding scale with ceramic materials. In the case of ceramics micromolded by physical deposition methods, nanoscale resolution is easily obtained. A clear example is direct molding of nanostructured TiN surfaces deposited by reactive sputtering (Fig. 12).

8. Summary and Outlook

The research area related to the study of new patterning techniques suitable for ceramic materials is a growing field that has attracted the attention of a number of research groups. In contrast to polymer patterning, ceramics patterning still requires a considerable effort and creativity to find new methods capable of fulfilling all the industry demands. As is well-known, reproducibility, accuracy, simplicity and suitability for large-scale fabrication are very important features of the method to be developed. So far, there are no techniques fulfilling all these requirements. Hard lithographic techniques, like e-beam lithography, are very accurate but unsuitable for large scale fabrication as a consequence of being a time-consuming technique. Soft lithographic techniques in combination with sol gel chemistry are a very simple and inexpensive route. However, the significant shrinkage upon thermal treatment makes the approach unsuitable for accurate nanoscale patterning. On the other hand, micromolding in combination with physical vapour deposition enables accurate nanoscale patterning but the range of materials that can be patterned is rather limited. Self-assembly and self-organization seem to be a very powerful alternative.

However, much effort should be placed on achieving different predictable architectures in order to use them as reliable templates for large-scale serial fabrication.

All these efforts are completely justified if we consider the enormous implications of ceramic-based nanotechnologies on the production of high added value products. This review chapter describes with special emphasis the advance in the field during the last five years. It can be clearly seen that "true" nanoscale resolution can be reached by different methods. New high resolution resists, different families of self-assembling molecules, and many other approaches are supporting this point of view. The combination between complimentary disciplines and the creativity of scientific community will pave the way to different affordable techniques and methods for reliable accurate nanoscale patterning of different ceramic materials.

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