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## Nanostructure of Nanoparticles, Self-assembled Inorganic Nanopatterns and Hybrid Sol-Gel Coatings in Surface Engineering

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## ABSTRACT

Aluminum, its alloys and ceramic nanopatterns-are widely used in the fields of engineering, aerospace and machine manufacturing because of their low densities, low thermal expansion coefficients, high strength and strain performance, which have drawn much attention from both researchers and engineers as promising materials for electrical appliances and the machine industry.

Sol-gel chemistry offers a flexible approach to obtain a diverse range of materials. It allows different chemistries to be achieved and offers the ability to produce a wide range of nanostructures. Sol-gel materials have been explored and found to hold significant potential. Sol-gel chemistry allows the combination of inorganic materials nanopatterns in a single phase and has led to the development of inorganic hybrid (OH) coatings for several applications.

Ceramic nanopatterns have been prepared on various substrates, through a simple fast, cheap, reproducible and easy to scaleup (bottom-up) approach, involving sol-gel dip coating, block copolymer self-assembly and thermal treatment. The patterns are composed of hexagonally-arranged nano-perforations through which the surface of the substrate remains accessible. They constitute novel ordered heterogeneous inorganic nano-patterns, which present a unique combination of thermal, mechanical and chemical stability with the very interesting characteristic of ordered nano-heterogeneity. This approach offers unique possibilities-of processing large-scale nanostructured surfaces finding applications in many nanotechnology and fabrication domains.

Sol-gel materials have been explored and found to hold significant potential. One of the interesting fields that has been developed recently relates to hybrid materials that utilize sol-gel chemistry to achieve unusual composite properties. Sol-gel processing allows the combination of inorganic and organic materials in a single phase and has led to the development of organic-inorganic hybrid (OH) coatings for several applications including corrosion mitigation. The advantages and disadvantages of using modified sol-gel polymer films and hybrid system coatings will be discussed here, as well as the methodologies for the chemical characterization and the feasibility of evaluating the mechanical properties of the coatings.

The principles of assembly are discussed together with the properties of nanoparticles and layer-by-layer polymeric assembly essential in building hybrid coatings. They constitute novel ordered heterogeneous inorganic nanopatterns (INP), which present a unique combination of thermal, mechanical and chemical stability with the very interesting characteristics of ordered nano-heterogeneity.

Key Words and phrases: Sol-gel methods and chemistry, dip-coating, nanostructures, nano-perforation coatings, nanofabrication, nanoparticles, polymers, layer-by-layer films, properties of nanoparticles and layer-by-layer polymeric assembly essential in building hybrid coatings, inorganic precursors in sol-gel methods.

### 1. Introduction

Surface nano-structurization, or nano-patterning, is gaining more interest in nanotechnology, since miniaturizing objects down to the nanoscale can lead to a considerable increase in device efficiency. Pushing feature size and spatial resolution down to sub-90 nm length scales has thus become a priority.

Alternative approaches that allow fabrication of robust high-resolution nanopatterns over large surfaces are essential for developing technologies compatible with industrial production requirements. A promising alternative that allows overcoming the resolution limitations of lithography is the bottom-up approach. This strategy is based on the self-assembly of molecules or pre-





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formed nano-objects on the surface, such as in the case of block-copolymer self-assembly or nanosphere lithography. These strategies have shown great potential in terms of pattern quality and resolution, but some issues concerning their processability and their chemical, thermal and mechanical stability are still unsolved.



Figure 1 - Domains of applications of sol-gel derived inorganic nanopatterns.

One strong candidate among the bottom-up techniques has emerged recently by the marriage between supramolecular self-assembly, sol-gel chemistry and controlled liquid deposition. The so-called inorganic nanopatterns (INPs) were obtained by the controlled cooperative self-assembly of inorganic precursors with supramolecular aggregations such as block copolymer micelles, which can be applied to elaborate 2D materials over large areas. Both structuring and precursor agents are usually dispersed in solution and then applied to a substrate by liquid deposition before curing to stiffen the inorganic phase and eliminate the structuring agent. This strategy allows the facile preparation of large surfaces, patterned with sub-90 nm periodical assemblies, overcoming the scale-up and resolution limits of most lithographic methods. Once deposited onto a substrate, these inorganic nanopatterns, bearing periodic physical and/or chemical heterogeneities can be exploited in many applications. This paper reviews the preparation of such INPs based on TiO<sub>2</sub>, ZrO<sub>2</sub> and NaTiO<sub>3</sub>, and how they have been exploited in nanofabrication or as a

functional component for different domains of nanotechnology as shown in Fig. 1.

In this paper, we will first describe how this novel generation of substrates is prepared and how one can perfectly control the morphology and the dimensions of the nano-perforation patterns. Some examples of how the ordered topography can be used to add new functionalities to the system will be shown. In particular, they have been used as controlled wetting surfaces, as photoactive layers, as growth directing substrates for the co-deposition of magnetic, semiconducting, photomagnetic and photoluminescent dots, as nanoelectrode arrays, as charge injection and as recombination enhancers in LED stacks. In addition, they have been combined with nanofabrication techniques such as reactive ion etching and deep X-ray lithography for the fabrication of even more complex nanostructures.

### 2. Controlled Elaboration of Inorganic Nanopatterns

### 2.1 Overview of the chemical/process strategy

Metal oxide inorganic nanopatterns were synthesized via a sol-gel based strategy, based on the codeposition by dip-coating of the inorganic precursors and block copolymer micelles, followed by a short thermal treatment. INPs can be made from almost any inorganic precursors, giving rise to a wide panorama of compositions, taking advantage of the versatility of sol-gel chemistry. In the following sections we will discuss the case of titania, calcium titanate and zirconia nano-patterns prepared with commercial polybutadiene-polyethylene oxide block-copolymers. Compared to others, this type of block copolymer has been chosen because it forms micelles in the typical ethanol/water system and it usually does not require other unfriendly solvents, such as THF or dichloromethane to adjust the medium polarity.<sup>10</sup> An overview of the typical INP preparation steps is illustrated in Fig. 2.

First, (a) the PB-PEO templating agent is mixed with water and with 4/5 of the total amount of ethanol. The solution is annealed at 70°C for 2-3 hours until dissolution of the block copolymer is complete (b). During cooling-to room temperature, homogeneous spherical micelles form with the hydrophobic PB chains; the core and the hydrophilic flexible PEO shell interact with the relatively polar solvent. The chloride salt precursors are then dissolved in the remaining portion of ethanol (c). Both inorganic and block copolymer solutions are then mixed. The Ti (IV) and Zr (IV) species are expected to remain in the PEO-hydro-alcoholic medium shell since the polar PEO units are hydrophilic and can form strong coordination bonds with the M (IV) metallic center through the interaction between the free electron pairs of O atoms and the vacant d-orbital of the metallic atoms (Lewis acid/base pair). After mixing the system for at least 3 hours, the substrate is dip-coated in the solution (d). Through the





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exact control of the deposited material, the surface is just covered by a monolayer of micelles surrounded by the inorganic species. The final step is the thermal treatment that enables the complete evaporation of the absorbed water, the decomposition of the block-copolymer, and eventually the condensation and potential crystallization of the oxide matrix (e).



Figure 2 - Schematic illustration of the preparation process of inorganic nanopatterns.

This protocol was followed for each of the prepared systems. Synthesis conditions and structural characteristics are reported in Tables 1 and 2. An example of titania INPs on a silicon substrate is shown in Figure 3.

	Structure		Solution compositions			Processing conditions		
	<b>D</b> nm	<b>b</b> nm	PB-PEO	m	c mmol/L	<b>u</b> mm/s	<b>T</b> Dipcoating	<b>TT</b> 5 min
А	9	15	8678	1.5	38.3	0.5	25-40°C	500°C
B	12	25	6605	1.5	38.3	0.5	25-40°C	500°C
C	14	40	3902	1.1	33.9	1.2	25-40°C	500°C
D	16	26	2753	1.5	38.3	0.5	40°C	500°C
E	17	34	3017	0.8	68.2	0.5	40°C	500°C
F	18	36	4755	1.5	34.1	0.5	40°C	500°C
G	17	44	3017	6	11.4	0.5	40°C	500°C
н	20	41	3017	3	22.7	0.5	40°C	500°C
1	24	35	3017	1.5	34.1	0.5	40°C	500°C
L	25	64	1945	1.5	50.3	1.2	60°C	500°C
M	32	42	2999	1.5	50.3	0.5	25-40°C	500° C
N	31	89	2231	1.5	49.1	1.2	40-60°C	500°C
0	42	75	3397	0.7	76.6	1.5	60°C	500°C
Р	51	79	3397	1.5	38.3	1.5	60°C	500°C
Q	53	81	3397	3	19.2	1.5	60°C	500°C
R	67	110	2325	1.5	34.1	2.5	60°C	500°C
		Table 2 -	Chemical and p	rocess parar	neters used to fat	pricate the TiO <sub>2</sub> I	NP.	
	Structure		Solution compositions			Processing conditions		
	<b>D</b> nm	<b>b</b> nm	PB-PEO	m	C mmol/L	<b>u</b> mm/s	T Dipcoating	<b>TT</b> 5 min

Table 1 - Chemical and process parameters used to fabricate the ZrO<sub>2</sub> INP.

	Structure		Solution compositions			Processing conditions		
	<b>D</b> nm	<b>b</b> nm	PB-PEO	m	C mmol/L	<b>u</b> mm/s	<b>T</b> Dipcoating	<b>TT</b> 5 min
A	9	16	8678	1.8	26.7	0.5	25-40°C	500°C
B	15	39	3902	1.8	37.5	0.5	25-40°C	500° C
С	17	33	2753	1.8	26.7	0.5	25-40°C	500° C
D	17	47	3017	10	5.75	0.5	25-40°C	500° C
E	20	42.7	3017	4	12.3	0.5	25-40°C	500°C
F	27	39	3017	1.8	21.5	0.5	25-40°C	500°C
G	29	43	2999	1.8	25	0.9	25-40°C	500° C
н	28	68	1945	1.8	28.1	0.9	40°C	500° C
I	28	72	2231	1.8	36.8	1.2	40°C	500° C
L	42	88	2325	0.8	56.6	1.2	40-60°C	500° C
M	48	95	3397	1.8	35.1	1.5	25-40°C	500°C
N	58	98	2325	1.8	24.2	3	40-60°C	500°C





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Figure 3 - Titania nano-perforated thin film: (a) SEM-FEG top view and autocorrelation function in the inset; (b) 70° tilted SEM-FEG micrograph; (c) the GI-SAXS pattern and intensity profile in the blue line; (d) structural parameters of the array and (e) surface topography by AFM.

The SEM-FEG images display characteristic nano-perforations of about 20 nm in diameter (Fig. 3a). Several domains with a hexagonal-type compact structure and of a few hundred nanometers long-range ordering are found with different orientations. Figure 3b shows the SEM-FEG photo of the cross-section tilted at 70°. One can clearly identify the perforation network, and the good adhesion to the silicon substrate. The same surface has been characterized by X-ray diffraction and the corresponding G1SAXS 2D pattern is displayed in Fig. 3c. The organization of the perforations into a 2D hexagonal-like structure leads to the presence of the two characteristic diffraction rods indexed (90) and their harmonics. The elongated shape of the rods suggests that the film is very thin, and the perforations have a low aspect ratio. Their elongation in the vertical direction (normal to the surface) is evidence that a single layer of nano-perforations is present with a similar trend on the whole irradiated surface. The intensity profile in the  $Q_y$  direction, reported with the blue line, shows a d-spacing of 30 nm that corresponds to the (10) planes (Fig. 3d). This morphology is confirmed by atomic force microscopy (AFM), as in Fig. 3e.

Spectroscopic ellipsometry can also be used to determine the thickness of the layer as a function of the process conditions and to follow the evolution of the thickness upon thermal treatment by *in situ* ellipsometric analysis. The combination of all these techniques gives access to a complete structural characterization of the INPs, throughout the determination of the following values:

• D	Average diameter
• <i>b</i>	Center to center distance
• <i>W</i>	Wall thickness; $w = b - D$
• <i>d</i> (10)	$d(10) = \sqrt{3} / 2b$
• h	Thickness

The adjustment of these structural characteristics is achieved through a precise tuning of the solution chemical composition and of the conditions of liquid solution processing. In what follows, we will discuss the influence of each of the following critical parameters (M<sup>n+</sup> stands for the sum of all inorganic cations used as precursors):

• <i>B</i>	Units of butadiene in the PB chain
• <i>EO</i>	Units of ethylene oxide in the PEO chain
• <i>с</i> = [EO] / <i>vol</i> <sub>ЕtOH</sub>	Molar concentration of EO in ethanol
<ul> <li><i>m</i> = [M<sup>n+</sup>] / [EO]</li> </ul>	Molar ratio between the metal salt and the PEO
• $C_i = [M^{n+}] / VOI_{EtOH} = c \times m$	Molar concentration of the inorganic salt in ethanol
• e = [H <sub>2</sub> O] / [EtOH]	Molar ratio water/ethanol; 0.11 for TiO <sub>2</sub> ; 0.17 for ZrO <sub>2</sub>





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### 2.2 Influence of the block copolymer chain lengths

The easiest and more effective way to tune the size of the holes and their center-to-center distance is to choose the suitable structuring agent as shown in Fig. 4.



Figure 4 - Correlation between the PB-PEO chain and the structural parameters D and W of the ZrO<sub>2</sub> nano-perforated layers: (a) Plots of the average diameter versus chain length of butadiene; (b) Plots of the wall thickness versus the chain length of ethylene oxide; (c-f) SEM micrographs of ZrO<sub>2</sub> obtained from typical block-copolymer micelles with different chain lengths.

Several ZrO<sub>2</sub> INPs have been prepared from PB-PEO block copolymer micelles having a wide range of lengths of both PB and PEO chains. For all the simples, the ratio *m* (the molar ratio between the metal salt and the PEO) was fixed constant at 1.5. Figure 4a shows the correlation between the unit number of butadiene (*b*) and the average perforation size *D*. Similarly, the wall thickness (w = b - D) versus the length of the ethylene-oxide chain (EO) is plotted in the graph of Fig. 4b. The plots in Fig. 4 are evidence of a fairly good linear relation between the PB chain and the average final diameter and the PEO chain with the wall thickness, respectively. INPs prepared using different PB-PEOs are shown in the SEM images in Figs. 4(c-f). As expected, longer PB-PEO chains lead to larger micelles, and therefore to larger perforations. In this way, the center to center distance *b* of the INPs can be easily adjusted between 15 and 100 nm.

#### 2.3. Influence of the inorganic precursor to block copolymer ratio

Another parameter that has been taken into account is the molar ratio *m* between the metallic precursor and the ethylene oxide in the template. Evidence of the latter consideration is reported in Fig. 5.



Figure 5 - (a) AFM topography of TiO<sub>2</sub> nano-ring arrays; (b) depth profile versus distance from the ring center; (c) evolution of the depth values at distances ranging from 0 to 120 nm from the center for various m values ( $m = Ti^{4+} / EO$ ).





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For this investigation, a highly diluted solution of c = 12 mM was used to deposit dispersed hybrid micelles instead of a continuous network. Under these conditions, and fixing m = 2, arrays of TiO<sub>2</sub> nano-rings were obtained. The AFM topography of the surface bearing discrete single rings is displayed in Fig. 5a, while the depth profile from the ring center to the outer part is plotted in Fig. 5b. Three regions can be identified: Region 1 is the internal hole of the ring (average diameter of 60 nm) which corresponds to the PB core of the initial micelle. Region 2 is the thicker corona, referring to the polar EO part of the micelle. Assuming that the coordination of  $M^{++}$  by the EO groups is highly favorable, most cations are prevalently located in Region 2 for m < 1. In the case of Fig. 5, the molar ratio Ti<sup>4+</sup> / EO is equal to 2 (m = 2). There is an excess of cations that cannot be coordinated and is free in solution and found in the outer part of the ring after deposition in Region 3.

Other ring systems have been obtained starting from solutions having different *m* ratios from 1 to 8. For each system, we considered 20 rings and the depth profile (from the center to the outer part of the ring) was accessed by AFM for each of them. The average depth value was plotted for each system versus the distance from the center of the ring in Fig. 5c.

As expected, this results in an increase of the thickness of the rings for higher values of m. The latter consideration is more evident in Region 3 where, for m = 8, the outer part of the ring has almost the same depth as that of the corona. Additionally, for higher m, the corona is broader, also suggesting a reduction of the perforation diameter (error bars are related to the sharpness of the AFM tip). The influence of the parameter m on INPs prepared from more concentrated solutions for which a continuous network can be described is shown in Fig. 6.

Three films were obtained from three starting solutions having  $Ti^{4+}$  / EO molar ratios equal to 1.8, 4.0 and 10. Solutions with higher *m* (and thus richer in  $Ti^{4+}$ ) have been diluted to keep the same inorganic content (see Table 2, preparation d - f). SEM photos of the samples are reported in Figs. 6(a-c). Samples obtained by solutions having *m* = 10 exhibit perforations assembled in pseudo-squared arrays, which indicates the formation of a bi-layer system. The micrographs have been image-analyzed and the resultant values of *D*, *b* and % area covered are reported in table (h) in Fig 6.



Figure 6 - Nano-perforated layers obtained from solutions having *m* equal to 1.8, 4 and 10. SEM photos (a), (b), (c) and GI-SAXS patterns (d), (e), (f), respectively; (g) plot of diffraction intensity versus  $Q_y$ ; Table (h) gathering structural parameters obtained from image analysis.





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As expected, the area covered by TiO<sub>2</sub>, and the center-to-center distance, both increase when increasing the ratio m, which consequently leads to a lower density of perforation and smaller perforation size. The periodicity of the three layers has been accessed by GI-SAXS and the corresponding 2D patterns are shown in Figs. 6(d-f). The plots of the diffraction intensity versus  $Q_y$  for the three INPs are shown in Fig. 6g. The (10) diffraction rods shift to lower  $Q_y$  values for increasing m ratios, confirming the microscopy analyses.

### 2.4 Solution conditioning to improve micellar homogeneity

As described in Fig. 2, step (b) consists of heating the solution containing the block-copolymer at 70°C for 3 hours until complete dissolution. Cooling triggers the self-assembly of BCP into micelles through a progressive decrease of solubility. The rate of cooling has an influence on the rate of micellization and therefore, on the distribution in size of the micelles and consequently on the final perforation homogeneity. A qualitative indication of such a kinetically driven effect is shown in Fig. 7.



Figure 7 - (a) Schematic diagram of the cooling down and ageing steps; (b) perforation size distribution for the two samples; ZrO<sub>2</sub> layers on Si after fast cooling down (i) and after slow cooling down and ageing (ii).

Two identical initial BCP solutions (free inorganic precursors) were heated to 70°C for one hour. The first (i) was rapidly cooled to 20°C at a rate of 5°C/min. The second (ii) was taken back to room temperature at a rate of 1°C/min. Inorganic precursors were then added to both solutions just before INP formation. The SEM photos of the resulting INPs are shown in Figs. 7(i) and (ii) with the respective autocorrelation functions in the insets.

A broad size distribution of the perforations and poor organization resulted from the rapid cooling process. On the other hand, the film obtained from slow cooling exhibited a narrower perforation size distribution (Fig 7b), which led to a higher degree of hexagonal organization. The SEM photo in Fig. 7(ii) highlights with dashed lines the presence of quasi-perfectly organized domains having sizes of 400-500 nm.

Due to the length of co-polymer molecules and of the related entropic factor, a slow micellization is needed to achieve thermodynamic homogeneous distribution through the slow dynamic exchange. This is further confirmed by the fact that, before adding the precursor, a several-day long aging of the micellar solution led to a narrower size distribution. This is probably one of the main important criteria to follow to improve the degree of local organization and the long range ordering of the patterns.

The assembly takes place during evaporation and consists of the arrangement of the micelles that are considered to be rigid spheres. The homogeneity in the size of these spheres is a necessary condition to obtain highly organized patterns such as in the case of colloidal lithography.<sup>11</sup> Other self-assembled systems such as pure block copolymer thin films can be annealed after





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deposition at high temperature or in a saturated solvent atmosphere in order to increase the chain mobility and improve longrange order arrays.<sup>12</sup> This is not the case for most sol-gel systems since after evaporation of the solvents, cross-linking of the inorganic network takes place, causing a consequent loss of mobility.

### 2.5 Mastering dip-coating processing conditions for INPs

Sol-gel layers can be obtained by liquid deposition processes such as spin coating, dip coating, drop casting, etc. Even though these techniques are well known and easy to apply, the deposition and eventually the self-assembly of the preformed micelles is a complex multi-step mechanism that involves homogeneous wetting of the substrate, evaporation of the volatile species and dynamic evolution of the physico-chemical characteristics (*e.g.*, concentration, viscosity, solvent polarity, temperature). The combined effects of all evaporation-governing parameters can be controlled and contribute to the quality of the layer in terms of thickness, nano-ordering and long-range homogeneity.

Dip coating is, without doubt, the technique that allows the highest degree of control during evaporation and can be applied to large surfaces without wasting the mother solution.<sup>13</sup> Good control of withdrawal speed during the process is necessary to prepare perfectly homogenous or controlled graded films.<sup>14,15</sup>

The process thus plays a key role in the formation of good quality INPs, since they are formed by a single monolayer of micelles and the quantity of material applied must be carefully modulated. A higher film thickness leads to multilayers of micelles and thus to a mesoporous film (if not collapsed after thermal treatment). A lower amount of materials applied to the substrate will result in an incomplete covering of the surface with the formation of islands of nano-rings as shown in the AFM micrograph of Figs. 5a and 8c.



Figure 8 - Final thicknesses versus withdrawal speed for a PB-PEO titania system: (a) The influence of concentration of the inorganic part and (b) the influence of the evaporation temperature. AFM micrographs showing (c) low coverage of the substrate (nano-rings) and (d) a monolayer of nano-perforations.

Figure 8a shows the plot of the final thickness versus withdrawal rate at 25°C of a TiO<sub>2</sub> system for three different inorganic molar concentrations *C*<sub>i</sub> (designated low, medium and high) with the ratio Ti<sup>4+</sup> / [EO]; m = 2. The typical tendencies attributed to the capillarity and draining regimes are highlighted for low and high withdrawal speeds respectively.<sup>13</sup> As expected, the more concentrated solutions lead to thicker final films. For the intermediate speed, a minimum value of thickness is found for each concentration, referred to as the critical speed  $U_{c}$ , equal to 0.7 mm/sec in the three cases. For the preparation of good quality perforated layers, the final thickness must range between 7 and 15 nm.

INPs can be obtained from the medium concentration over a wide range of speeds, corresponding to the mixed regime. If the more concentrated "high" solution is used, multilayers of micelles are always obtained, even dipping at

the critical speed  $U_c$ . Dip coating in dry air at high temperature often results in a better quality of the patterns, since a higher evaporation rate prevents dewetting and leads to more homogeneous layers. The evaporation temperature in the chamber was thus investigated in detail.





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Figure 8b shows the plot of the final thickness versus the withdrawal speed for the medium concentrated solution deposited at different temperatures inside the chamber (25, 30 and 50°C). As reported in previous studies,<sup>13</sup> the temperature in the chamber affects the final thickness only for low withdrawal speeds, because the capillary deposition is governed by the evaporation rate of the solution in the meniscus region. On the other hand, in the draining regime, the evaporation rate does not significantly influence the final thickness.

An increase of the evaporation rate produces an increase of the minimal thickness and a shift of the corresponding critical speed  $U_c$  to higher values. From the same "medium" concentrated solution, good quality mesoporous films can be obtained at lower withdrawal speeds, as shown in Fig. 9. The TiO<sub>2</sub> layer obtained in the capillarity regime, U = 0.1 mm/sec at 60°C, is 90 nm thick and is mesoporous with a 3D ordered organization of pores.

Other treatments within the self-assembled inorganic nanopatterned INPs made by sol-gel dip coating include studies not covered here.

3. Applications in Nanotechnology

### 3.1 Wetting



Figure 9 - SEM image of the surface of a PB-PEO templated titania film, obtained in the capillarity regime and after thermal treatment at 500°C.

 $TiO_2$  INPs on oxidized silicon substrates<sup>9</sup> or on thin gold layer surfaces<sup>21</sup> were used as heterogeneous nano-structured surfaces for fundamental wetting investigations. Due to the different chemical affinities of the substrates and the INP materials, the discrete SiO<sub>2</sub> or gold patches found at the bottom of the perforation, and the thin continuous TiO<sub>2</sub> network surrounding them, could be selectively grafted with hydrophobic perfluorinated chemical agents, using suitable silane or phosphonate coupling agents (Fig. 10a). Non-grafted SiO<sub>2</sub> and TiO<sub>2</sub> surfaces remained hydrophilic, while gold is intrinsically hydrophilic.

Static and water dynamic contact angles were then measured for different perforation dimensions and for the four possible combinations: hydrophobic / hydrophobic, hydrophobic, hydrophobic, hydrophobic, hydrophobic / hydrophobic / hydrophilic and hydrophilic / hydrophilic. The results were then compared to predictions made using the various available models. Three different types of wetting were observed depending on the contrast conformation and the volume of the sessile drop applied to the patterned surface. For hydrophilic INP systems, full wetting of the surface was observed regardless of the contact angle of the perforation bottom surface. When small volumes of water were used, static and advancing contact angles between 100° and 120° were measured on hydrophobic INP systems regardless of the contact angle of the perforation bottom surface (Fig. 10b).

In both cases, the hydrophilic properties of the continuous network seem to govern the wetting behavior. For hydrophobic INPs, the contact angles match what is expected from the model for which a nano-bubble of vapor is trapped within each perforation. When the volume of water is high, the contact angles are lower and could be described by a combination equation. Large hysteresis between advancing and receding angles are observed for perforations larger than 20 nm due to the pinning effect allowed by the hydrophilic patches homogeneously dispersed onto the hydrophilic surface as schematically shown in Fig. 10a.



Figure 10 - (a) Schematic diagram of a heterogeneous hydrophobic layer with hydrophilic patches; static water sessile drop on (b) hydrophilic and (c) hydrophobic INPs.





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#### 3.2 Photocatalytic surfaces

In all types of photovoltaic devices, the need for a sustainable optical antireflective coating on top of the glass cover is a crucial issue to avoid the loss of photons due to reflection. The low index required for these layers is usually achieved by a precise combination of silica and voids (porosity), with domains that must remain small enough to prevent scattering. However, it is known that small pores tend to easily absorb pollutants, such as VOCs which increase the coating refractive index and consequently reduce its optical performance. These must then be continuously eliminated, which could be easily done by combining the TiO<sub>2</sub> photocatalyst already used in self-cleaning windows<sup>22</sup> with the porous layer.<sup>23</sup> However, such a combination

would be required to dramatically increase the porosity of the film to compensate for the high refractive index of TiO2, which would significantly decrease the mechanical stability of the laver. In order to overcome this issue, TiO<sub>2</sub> INPs have been deposited on top of a sol-gel water repellent mesoporous silica film as shown in Fig. 11a.24 The anti-reflective properties of the optical bilayer are only slightly affected by the presence of the INPs because of its extremely low thickness (10 nm) and the presence of the perforations that reduce its refractive index down to 1.8. During the liquid deposition process, titania molecular intermediates do not infiltrate the pores of the underlying silica layer because of their stabilization in the hydrophilic complexing shell of the block-copolymer micelles that are much larger than the pores. This hard TiO<sub>2</sub> INP top layer acts as a protective barrier toward mechanical aggressions and also brings high water wetting (antifogging) and photocatalytic properties into play. Indeed, the system shows an excellent capability of decomposing those organic species that were not only adsorbed on the surface but also absorbed in the antireflective (AR) layer pores as shown in the plot of Fig.11b.

It has been demonstrated that this decomposition takes place mainly through the diffusion of the pollutants towards the surface.<sup>25</sup> The bilayer multifunctional systems are easy to produce on a large scale at low cost and exhibit high mechanical and chemical durability. They are thus serious candidates to be used as antireflective, self -cleaning coatings for photovoltaic cells.

#### 4. Applications in nanofabrication

#### 4.1 Nanomasks for pattern transfer



Figure 11 - (a) SEM image and profile scheme of the anti-reflective, water repellent layer covered with self-cleaning TiO<sub>2</sub> INPs; (b) evolution of the refractive index versus time during the UV-decomposition of a pollutant for the anti-reflective layer with and without the INP photoactive layer.

The development of bottom-up methods to prepare large nano-patterned surfaces is stimulated by requirements in large-area electronics, photovoltaic displays or integrated smart systems. While top-down lithographic approaches yield extremely well resolved periodical feature arrays with dimensions as small as 20 nm, they remain slow, costly and have low throughput and are thus not directly appropriate for industrial production on large surfaces. Bottom-up approaches are capable of self-assembling organic<sup>34</sup> and inorganic materials<sup>35</sup> of much smaller dimensions using liquid deposition, but they suffer from poor long range order and the presence of localized points and extended defects. They can thus be used as a cheap alternative or an intermediate step in conventional nanofabrication protocols. Self-assembled nanosphere arrays<sup>36</sup> or block copolymer nanostencils<sup>37</sup> have been used in combination with reactive ion etching (RIE) for transferring 20-50 nm features with hexagonal or square organization on Si wafers, but their implementation on an industrial scale is not straightforward. Another alternative is to use the robust and simple method of preparing sol-gel derived INPs as self-assembled reactive nanomasks (RNMs)<sup>38</sup> for lithographic transfer through dry etching, as shown in Fig. 12.





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The distinctive feature of the latter RNMs is that they can react with the etching plasma to yield a highly stable, and thus highly selective stencil. The present INP RNM is composed of CaxTi(1-x)O(2-x), so that Ca2+ can react with the fluoride species of the plasma to yield CaF2, while the titanium species are etched away. The formal calcium titanate INP is thus replaced by calcium fluoride, a solid compound that is extremely stable under the present etching conditions without changing the initial lateral morphology. Using this approach and depending on the perforation size and the Ca2+ concentration of the initial mask, transfer of ordered arrays of Si vertical pillars or wells, having diameters down to 20 nm and heights, or depths, of 200 nm could be achieved. This novel concept combines simple self-assembly with RIE to achieve features up to 1:25 selectivity and aspect ratios up to 8. These novel RMNs are homogeneous, robust and they can be applied on a surface size limited only by the capacity of the RIE device. In addition, the complete process (mask fabrication + dry etching) can be performed in only 15 minutes. This versatile approach is thus likely to be a promising candidate



Figure 12 - Schematic diagram of the pattern transfer (left) and corresponding SEM images (right) of the INP initial nanomask and of the etched surface.

for the industrial large surface production of electronic and optical components.

### 4.2 Nanomask for LBL growth of photomagnetic nanodots

Molecular materials that exhibit bistability in their physical properties as a function of external stimuli such as light or electric fields, offer appealing perspectives for the realization of molecular-scale electronic devices.<sup>39</sup> In most cases, these functional materials need to be integrated as nanodomains within planar devices in specific locations and/or under controller dispersion. TiO<sub>2</sub> INPs have been used here as self-assembled heterogeneous substrates to selectively guide the growth of photomagnetic bistable CoFe nano-objects<sup>40</sup> within the nano-perforations.<sup>41,42</sup> The selective and controlled growth was achieved through INP functionalization followed by molecular layer-by-layer (LBL) deposition.



Figure 13 - TiO<sub>2</sub> INPs bearing (a) PBA and (b) FePt nanoparticles.

The INPs were first prepared on Au substrates with thicknesses around 10 nm and a perforation diameter of 60 nm. The titanium oxide network was then simply passivated with phenyl hydrophobic groups, while Au nano-patches were activated with carboxylic acid groups. Both selective functionalizations were done using phosphonate and mercaptopropyl coupling agents, respectively. The carboxylic acid functions play the role of active nucleating centers in initiating the PBA growth by LBL from the perforation bottoms. Only the grafted system was then immersed in successive aqueous solutions containing

each of the PBA precursors [hexaaquacobalt (II), hexacyanoferrate (III) and Rb(I)]. Washing in water was performed between each immersion. The thickness of the PBA multilaver can be adjusted by tuning the number of cycles, and the chemical composition of the PBA can be varied at will by the choice of the precursors. It is important to note that the formation of the nanodomains at the position of the perforations is achieved only if the pre-functionalization of both TiO<sub>2</sub> and Au is done (Fig 13a).





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As expected for nanosized particles, the collective magnetic bistability associated with the long-range magnetic order is lost, whereas the molecular electronic bistability associated with the electron transfer persists. The periodically organized nano-perforations filled with photomagnetic PBA can be seen as data bits, which could *a priori*, be optically addressed separately.

## 4.3 Nanomask for salt-assisted magnetic nanodot deposition

As for the PBA, nanometer-scale assemblies of permanent magnets on surfaces would constitute magnetic data storage or spintronic devices. One of the most promising materials for magnetic applications is FePt alloy in the face-centered tetragonal phase, since it is known to exhibit large magnetocrystalline anisotropy and high coercivity at room temperature. The major challenges that must be faced for achieving such complex systems are the preparation of hard magnetic FePt nanoparticles with permanent residual magnetization and their positioning on the surface by a controlled and versatile process. In this context magnetic nanocomposite surfaces composed of hard magnetic FePt nanoparticles into TiO<sub>2</sub> INPs were prepared by controlled chemical solution deposition of hexa-aqua-iron (II) hexachloroplatinate  $Fe(H_2O_6)$  (PtC<sub>16</sub>) salt into the INP perforations, followed by its direct transformation into the FePt phase by thermal annealing at 400°C in a reductive atmosphere (Fig. 13b).<sup>43</sup> This strategy exploits the dip-coating process that is highly suitable for homogeneously impregnating porosity as a result of the progressive evaporation conditions, the dip-coating process enables exact control of the amount of material that can be applied onto the substrate.<sup>13</sup> The magnetic properties of these systems have been investigated. The H-M curve shows typical hysteresis loops at 300°K. The TiO<sub>2</sub> / FePt system reveals a coercivity that indicates the presence of hard magnetic nanoparticles, confirming the effectiveness of the transformation from salt to the phase locally in the nano-perforations.

### 4.4 Nanomasks for magnetically percolated perpendicular recording

The demand for higher storage capacities is one of the driving forces in the development of innovative magnetic materials and several novel concepts for magnetic recording are being explored to achieve areal densities above 1 tbit / in<sup>2,45</sup> One of the proposed approaches is based on percolated perpendicular media (PPM), which consists of an exchange coupled magnetic film with a dense distribution of defects, which serve as pinning sites for magnetic domain walls.<sup>46</sup> Several experimental realizations of PPM have already been reported through codeposition of the magnetic material and nonmagnetic oxides,<sup>47</sup> magnetic films on anodized alumina templates,<sup>48</sup> and the deposition of hard magnetic CoPt films on nanoperforated ZrO<sub>2</sub> has also been proposed.<sup>50,51</sup> Two ZrO<sub>2</sub> nano-perforated surfaces with an average perforation of 55 nm and a period of about 90 nm for the first one, and with an average perforation diameter of 15 nm and average period of 30 nm for the second one, were used. In these systems (Fig 14).



Figure 14 - (a) Schematic illustration of the deposition process and recording of ZrO<sub>2</sub> /CoPt magnetic nanocomposites; (b) HR-TEM cross section of the ZrO<sub>2</sub> /CoPt system; (c) MFM images of the system highlighting one single magnetic domain stabilized by "pinning"; (d) MFM image of the ZrO<sub>2</sub> /CoPt nanocomposite with 17 nm large perforations after magnetic recording test.





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The nano-perforations act as pinning sites for the magnetic domain walls, while the exchange coupling between the magnetic material inside the nano-perforations and the continuous film outside can be used for tuning the pinning strength. A 4.4 nm-thick Pt seed layer was deposited onto the substrates, followed by six repetitions of a 0.25-nm Co / 0.65-nm Pt bilayer and a 2-nm Pt cover layer using a DC-magnetron sputtering technique as shown in Fig. 14b.

The recording performance of these two samples was investigated by scanning magneto-resistive microscopy using conventional hard disk read / write heads having a magnetic write width and magnetic read width of about 110 nm and 70 nm, respectively.<sup>52</sup> The size of the magnetic domains that can be written by a recording head is limited by the spacing between pinning sites induced by the nano-perforated INP template surface. Due to the period of 90 nm on the sample with the larger perforations, the minimum bit pitch is expected to be on the order of 200 nm. In this case, domains written with a smaller bit pitch merge together as observed experimentally. Figure 14d shows the read back image for various bit periodicities written on the sample with smaller perforations. On the sample with a period of 30 nm, the individual domains can be clearly separated even at a bit pitch as low 90 nm, close in dimension to that of the head read/write characteristics. Based on the signature of the pinning controlled domain wall movement for percolated media, a zero field energy barrier is determined by fluctuation field measurements and is elucidated by micromagnetic calculations using the nudged elastic band (NEB) method. This value is sufficiently large to qualify the material as promising percolated media.<sup>53</sup> It is proposed that further optimization of the magnetic layer stack, including the use of a soft magnetic underlayer of a hard scratch-resistant overcoat and lubricant might still increase the recording performance of this type of PPM.

### 4.5 Nanomasks for controlled solid dewetting of semiconductor nanodots

Self-organized nanoparticles for which the quantum confinement effect provides an additional engineering dimension to tune the emission wavelength, are of particular interest for applications in optoelectronics or nanocrystalline memory devices.<sup>54</sup> The electron-hole recombination induced photoluminescence (PL), nano-crystal dots is dependent on the quantum confinement states and occurs in the near IR infrared and in the visible region.<sup>55</sup> It is known that dot size affects the bandgap energy, and that the PL spectrum can be predicted using theoretical models.<sup>55</sup> Here, germanium dots have been formed by a dewetting process that occurred during an *in situ* thermal annealing at 450°C of an amorphous Ge layer deposited by molecular beam epitaxy on a thin nano-perforated TiO<sub>2</sub> layer prepared on SiO<sub>2</sub>/Si.<sup>56-58</sup> Three different TiO<sub>2</sub> nano-perforated thin layers having perforation sizes between 10-50 nm, were used to modulate the dimensions of the nanodots during solid dewetting. The dot size measured by AFM revealed that particles were in the range of 10-35 nm, depending on the sample. Larger particles were found in the harder perforations and thus a larger periodic distance of the TiO<sub>2</sub> pattern substrates, suggesting that the variation of surface free energy, related to the presence of the heterogeneous nano-perforated TiO<sub>2</sub> layer on the Si wafer is sufficient to govern the nucleation growth and dispersion of crystalline Ge nanoparticles from thermal annealing of an initial amorphous continuous layer.



The PL measurements performed on such self-assembled systems are shown in Fig. 15. An analysis of the PL response with respect to theoretical predictions of the bandgap versus dot size allowed an assessment of the size dependence of the PL quantum efficiency in the Ge dots. Good gualitative agreement was obtained between the PL derived dot size distributions and those from AFM. Further work showed a nonlinear increase in the PL efficiency with decreasing dot diameter, suggesting that dot PL spectra used in conjunction with the theory provided a promising method of evaluating Ge dot size distributions.<sup>59</sup> The latter approach

Figure 15 - Photoluminescence spectra recorded at 5 K with a 20 mW excitation laser (458 nm) for two different populations of Ge nanodots on TiO<sub>2</sub> INPs having two different average diameters (20.7 and 18.4 nm); Inset: schematic diagram of the Ge nanodots formed by dewetting on TiO<sub>2</sub> INPs.





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confirms that oxide nanoperforated surfaces with controlled pattern dimensions and periodicity can be used to control the size of metallic Ge nanodots formed by solid dewetting. This method could then be further applied to other interesting dot/substrate systems that require controlled distribution of nanoparticles onto a specific surface.

### 5. Conclusions

However, compatibility is but one facet of sol-gel derived biomedical applications. Sol-gel derived bioceramics have a great potential for application as a coating on metallic substrates, providing a high degree of biocompatibility and promoting a rapid heating response with minimal averse biological events. Since sol-gel processes are carried out at such low temperatures, they can also allow the inclusion of biomolecules, therapeutic agents including drugs, growth factors and proteins. The sol-gel method (Fig. 16) should be simple stable, cost-effective, and scalable for facilitating future industrial production and clinical translocation.

The latter examples showed that INPs obtained by the self-assembly of a single layer of block copolymer micelles in the presence of suitable inorganic sol-gel precursors during controlled dip-coating have potential interest in many fields of nanotechnology and nanofabrication. This is related to the versatility in adjusting the INP chemical composition together with the perforation dimensions and separation distance to the chemical-mechanical and thermal stability of the material, and to the ease of preparing very large surfaces at low cost. Despite the already very promising results, it is with no doubt that such INP systems will become more and more appealing, and that other types of composition and combination will soon see the light of day.



Figure 16 - Schematic diagram of steps and processes used to obtain sol-gel coatings.

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*Note*: References 1-8 are supplementary. References 9-59 are cited in the paper.

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#### About the author



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