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Synergetic combination of top-down and bottom-up lithography processes for large scale nanostructures applied to photonics

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Abstract

The scope of this thesis is to adopt a hybrid approach through the synergetic combination of bottomup and top-down lithography methods to fabricate nanostructures with interesting structural and optical properties. This multidisciplinary approach is a vast fruitful field where many combinations are promising but remains unexplored so far. By taking interest in, and bringing together, both materials chemistry and clean-room nanofabrication techniques, this work tries to find practical solutions to tackle some of the current challenges in nanofabrication. In details, we focus on the study of selected lithography techniques (in particular nanoimprint) and demonstrate the possibility to increase the fabrication throughput and obtain nanostructures on a centimeter scale. The nanofabricated structures are then mainly used as Mie resonators for their optical properties and their ability to modify incoming light. Demonstrators of several millimeters are produced and are shown to exhibit interesting optical properties; emphasizing the feasibility of our approach.

Résumé

Le but de cette thèse est d'adopter une approche hybride par la combinaison des méthodes de lithographie ascendantes et descendantes pour la fabrication de nanostructures avec des propriétés structurales et optiques d'intérêt. Cette approche multidisciplinaire est un domaine vaste ou les combinaisons prometteuses sont nombreuses mais restent inexplorées jusqu'à présent. Ces travaux vont s'intéresser aussi bien à la chimie des matériaux qu'aux techniques de nanofabrication de salle blanche afin d'apporter des solutions pratiques aux problèmes actuels rencontrés en nanofabrication. Plus précisément, nous nous intéressons à l'étude de certaines techniques de lithographies (en particulier à la nano-impression) et démontrons la possibilité d'améliorer la cadence de fabrication en obtenant des nanostructures sur une échelle de plusieurs centimètres carrés. Les nanostructures fabriquées sont principalement utilisées comme résonateurs de Mie pour leurs propriétés optiques et leur capacité à modifier la lumière incidente. Des démonstrateurs de plusieurs millimètres carrés sont réalisés et montrent des propriétés optiques intéressantes soulignant la viabilité de notre approche.

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General Introduction

Nano and micro structuration of materials is a blooming field of research where the properties can be very different from the one found in the bulk materials with for instance specific catalytic activity, enhanced surface effects, quantum confinement or exotic photonic properties. Devices incorporating nanostructures are now numerous and used in a wide variety of fields such as microelectronics, sensing, photonics or microfluidics to name just a few.

To transform a flat surface into a textured one, diverse micro-nanofabrication processes can be used. The various techniques can be divided in two categories: top-down or bottom-up. In the **top-down approach**, nanostructures are fabricated from bulk materials and are then templated for instance by lithography. This enables the design of complex architectures but with the downside of a relatively low throughput and limits in term of resolution. The large majority of the nanofabrication techniques (in term of industrial use) falls into this category. In the **bottom-up approach**, nanostructures are formed from the assembly of molecular building blocks. This allows to obtain architectures with very few limitations in term of scale or resolution but limited to simple designs. These two approaches are fundamentally different and combinations remain unfortunately in their infancy.

The requirements of ever smaller structural dimensions are pushing the actual lithography techniques to their limits. For instance, the size of transistors produced in industry is currently below 20 nm and is expected to reach 10 nm in the next couple of years. An important part of the R&D effort is thus focusing on fulfilling such requirements to obtain smaller features on larger surfaces at a cost compatible with industrial needs. In this context, the combination of both top-down and bottom-up approaches in a synergetic way is a fruitful field promising to bring new technological breakthroughs.

It is in this global context that unfold this thesis. Its goal is to integrate new materials into existing nanofabrication techniques. By bringing a new angle of view and combining both structuration approaches, we will propose sensible improvements to various lithography processes for/with sol-gel coatings. In details, we will focus on the study of selected lithography techniques (Nano Imprint Lithography, Focused Ion Beam Lithography, Directed Self-Assembly by dewetting) and demonstrate the possibility to increase the fabrication throughput and obtain nanostructures on a millimeter and even centimeter scale. The improvements obtained in the domain of nanofabrication techniques will then be applied to the emerging field of photonics for light management which is still confined into R&D labs due to its complex up-scaling needed for industrial production. In particular, the sol-gel nanofabricated structures composed of arrays of nano-sized pillars will demonstrate Mie resonances and will be used for their ability to interact with incoming light. Demonstrators of several millimeters are produced and are shown to exhibit interesting optical properties; emphasizing the feasibility of our approach.

This thesis is divided in four chapters. **Chapter I** is dedicated to the description of state-of-the-art nanofabrication techniques and allows to present and understand the principles of the various processes used throughout this thesis. Starting from a general introduction of sol-gel chemistry, chemical liquid deposition of nanostructured coatings is described. In particular, the deposition of ultra-thin sol-gel micelle-templated coatings, extensively used in this thesis, is highlighted. The various lithography techniques are then reviewed – with their advantages and limitations - keeping a specific focus on the direct patterning of sol-gel coatings.

The next three chapters present the results obtained during this thesis by the synergetic combination of selected lithography processes and tailored materials with chosen composition and nanostructure.

Chapter II aims to the up-scaling of surface structuration. A new addition to chemical liquid deposition process called angular dip-coating is first introduced as a way to increase the flexibility of the process and allowing to coat on a single face. To fabricate masters for Nano Imprint Lithography, two techniques are developed. First, direct lithography by Focused Ion Beam is applied to porous sol-gel layers resulting in a considerable gain in term of throughput. Then, large scale solid state dewetting of thick semiconductor layers is presented and explained.

Chapter III is dedicated to the improvements made to Soft Nano Imprint Lithography (Soft-NIL) applied to sol-gel coatings and its applications. After a description of the recent advances made to the Soft-NIL technique, the effect of Relative Humidity will first be detailed as a way to optimize the process, using water as a fluidizing agent. The Micro Transfer Printing technique applied to sol-gel coatings is then introduced with a focus on understanding the mechanism at stake and its potential. Two examples demonstrating the flexibility of soft-NIL and the feasibility of its up-scaling are then discussed. Finally, the last part of this chapter is dedicated to the applications of sol-gel nanoimprinted structures for photonics. The Mie theory is first presented and Mie resonances are then studied experimentally in our dielectric structures through two examples. After a brief work on sol-gel spherical TiO₂ nanoparticles, Mie resonances are studied in nanoimprinted titania surfaces bearing arrays of nanopillars. A detailed study on such pillars will show the interest of Mie resonances for light management and present the so-called "black" titania. As a conclusion, a large scale demonstrator will be presented.

Finally, **Chapter IV** presents a novel nanofabrication technique through templated solid state dewetting on sol-gel textured surfaces. This original self-assembly behavior of thin layers (*i.e.* dewetting) will first be controlled with the use of micelle-templated ultra-thin sol-gel coatings. An indepth study will highlight the dewetting mechanism of thin germanium layers on such sol-gel patterned surfaces. The micelle-templated sol-gel coatings will then be applied to direct the dewetting of gold layers. Finally, sol-gel nanoimprinted surfaces will be shown to be efficient systems to control the dewetting of thick semiconductor layers.

Finally, conclusions and perspectives of this work are presented.

An appendix, gathering the various techniques used and the transcriptions of the various publications and patents produced during this thesis, is given at the end of this manuscript.



Chapter I: State of the art

In this chapter we provide a review of the recent advances in the various nanofabrication techniques. Such methods regroup conventional lithographic approaches and also new emergent techniques such as self-assembly. As our goal is to combine various routes in a synergetic way, a special focus on solgel materials will be given. In the first part, nanofabrication routes belonging to materials chemistry and in particular sol-gel science will be described with a specific highlight on soft templating and inorganic nanopatterns. The second part of this chapter will be dedicated to lithography techniques with a special emphasis on the use of sol-gel resists. Routes belonging to the "standard" clean room technologies widely used in industrial processes will first be introduced. Then, new nanofabrication, will be addressed. The advantages and limitations of these techniques will be compared. A subsection will be devoted to direct self-assembly of thin semiconductor layers by solid state dewetting.

I. Nanofabrication by sol-gel route

First, the general principles of sol-gel chemistry will be introduced, then chemical liquid deposition techniques will be described and in particular dip-coating, as it allows the maximum degree of control over the entire process of thin film deposition. Finally, the mechanism of self-assembly in sol-gel thin films will be presented.

I.1. Sol-gel chemistry

I.1.a. Generalities

A **sol** can be defined as a colloidal suspension, which means that it contains a dispersed solid phase small enough (below 10 μ m) to be stable in solution. In the sol-gel process, two main reactions are usually considered: **hydrolysis** and **condensation**. The precursors are metal or metalloid elements surrounded by various ligands. Common precursors are inorganic salts MX_n and organometallic compounds M(OR)_n, where the R group represents a proton or another organic ligand (alkyl, aryl), M the metal or metalloid (Si, Ti, Al, Zr ...) and X a chloride, nitride or acetate group. The first reaction of the precursor with water is called **hydrolysis**, a hydroxyl ion is exchanged as in the following reaction:

$$M(OR)_n + H_2O \rightarrow M(OR)_{n-1}OH + ROH$$

Depending on the conditions (charge of the metal or metalloid, coordination number, pH, water concentration ...), hydrolysis may carry on, replacing all ligands by hydroxyl group, or stop at a partially hydrolyzed state: $M(OR)_{n-x}(OH)_x$.

Two partially or totally hydrolyzed molecules can then react together in a condensation reaction:

$$M(OR)_n OH + M(OR)_n OH \rightarrow (OR)_n M - M(OR)_n + H_2 O$$

$$M(OR)_n OR' + M(OR)_n OH \rightarrow (OR)_n M - M(OR)_n + R'OH$$

This reaction usually starts before the hydrolysis is completed and frees a molecule such as water. Most of all, with time and successive condensation, the molecules grow bigger; an **oligomer** then an **inorganic polymer** are formed:

$$M(OR)_n(OH)_m \Rightarrow MO_x + ROH + H_2O$$

A partial-charged model, developed by Livage et al^{1,2}, allows to quantify the pH-charge relationship. Depending on the charge and pH, three domains can be defined corresponding to the prevalence of the aquo (M- OH_2), hydroxo (M-OH) and oxo (M=O) ligands respectively (Figure 1). The kinetic of hydrolysis and condensation reactions is highly dependent on the pH as it modifies the charge of the molecule. In particular, it is generally necessary to be in the hydroxo domain to have condensation reactions. Finally, hydrolysis and condensation reactions are accelerated when the solvent is evaporating or when precursors are in close proximity: typically during the drying of thin films.



*Figure 1 : Charge – pH diagram showing the areas of dominance of the aquo, hydroxo and oxo ions*³.

If a monomer has four ligands, MR₂(OH)₂, such that 2 are reactive (here hydroxyl groups) and 2 are non-reactive (R groups such as methyl groups), it will be able to condensate and polymerize only into linear chains or rings. Whereas if the functionality is higher (f>2), monomers will be able to condensate into a 3D network. In similar conditions, the higher the functionality the fastest the condensation kinetic. For instance, methyltriethoxysilane (MTEOS) has a lower reactivity than tetraethoxysilane (TEOS). With advancing condensation, oligomers will grow, extend into a macroscopic 3D network (increasing the viscosity) and percolate throughout the entire solution to yield a gel. This continuous solid network has some elasticity (given by the flexibility of its structure) and contains a continuous liquid phase. Gelation can be fastened by rapid evaporation of the solvent, typically when making a thin film obtained by liquid deposition techniques.

Gels are usually made of many small clusters that will gradually attach to the solid network. Moreover, monomers can still be present in the sol or embedded in the gel network. Bonds formation do not stop after gelation; during aging, the network will evolve in term of structure and properties towards further condensation. During this step, the gel is at equilibrium with its environment and can swell/shrink by adsorbing solvents.

Shrinkage usually happens spontaneously in gels, through *syneresis*. Indeed, as liquid evaporates from the gel, capillary pressure build up in the gel pores causing shrinkage of the gel network. This shrinkage will in turn draw reactive functions closer for continuous condensation and "squeeze out" the liquid from the drying gel. Heating a gel will lead to the removal of solvents and organic molecules, leading

to a full condensation and densification of the gel through **sintering**. This latter phenomenon is characterized by a reduction of the surface energy through the collapse of pores attributed to viscous flow and diffusion in amorphous and crystalline materials respectively.

I.1.b. Silicates systems

In the specific case of silicates, hydrolysis and condensation steps can be catalyzed in acid or basic conditions (Figure 2a). Under acidic conditions, the hydrolysis is faster than the condensation and the formation of long polymeric silica chains will be favored. On the other hand, in basic catalysis, condensation is faster than hydrolysis and the formation of spherical SiO₂ nanoparticles will be favored through a conventional nucleation/growth mechanism followed by Ostwald ripening. The colloidal system can eventually evolve in a percolated interconnected network. This last phenomenon is governed by surface charge interaction and can be controlled by the pH of the solution or the ionic strength (Figure 2b). The most used silicate precursor is tetraethylorthosilane, TEOS, $(Si(OC_2H_5)_4) - as$ the reaction with water, to create hydroxyl intermediate, is easily controlled through the dilution, pH or water content of the solution.



Figure 2 : a) Kinetic of hydrolysis (H), condensation (C) and dissolution (D) as a function of the pH for a system with TEOS as a precursor and a given hydrolysis ratio⁴. b) Polymerization route of sol-gel silica. In acidic solution small particles aggregates into a 3D network forming a gel. In basic condition, particles grow in size while decreasing in number by Ostwald ripening.

I.1.c. Non silicates systems

In this thesis, transition metal oxides (such as TiO_2 , ZrO_2) but also triels (such as Al_2O_3) will be used and in particular TiO_2 . The oxidation number is generally +IV for transition metals and +III for triels. Those systems are generally more reactive than silicates due to their elevated coordination number (>4) and their high electrophilicity. When dissolved in water, metal cations are solvated by water molecules and rapidly hydrolyzed to various extent. Increase in water acidity or in the charge density of the metal cation usually facilitates hydrolysis whereas it is inhibited when the number of hydroxo or larger ligands coordinating the metal increases. Those complex interactions described by Bradley *et al* ⁵ are even harder to quantify for non-aqueous systems. For instance in a mixture of water and ethanol, the exact composition of Ti^{IV} hydrolyzed intermediates will depend on the chemical equilibrium between free and coordinated nucleophilic molecules (H₂O, OH⁻, Cl⁻, CH₂CH₃O⁻ ...) and can be written as:

 $\left[Ti(0)_{x}(OH)_{y}(OH_{2})_{v}Cl_{u}(OCH_{2}CH_{3})_{w}\right]^{z+}$

The particularity of transition metals (compared to silicates) is that they are often stable in various coordination degrees so they can expand their coordination via nucleophilic association mechanisms: olation, oxolation or alcoxolation (step b in Figure 3). This will form oligomers and will facilitate condensation by subsequent nucleophilic substitution reactions (steps c) and (d) in Figure 3):



Figure 3 : Mechanism of possible reactions, namely alcoxolation, oxolation and olation, of transition metals complexes with coordination of the metallic center via nucleophilic association (b) followed by substitution (c then d). Reproduced from ref⁴.

The quantity of water and the pH of the solution are highlighted as being key factors determining the condensation kinetic and the formation of titanium complexes as studied by Crepaldi *et al* in mesoporous titania thin films⁶. In very acidic conditions, promoted when chlorine precursors are used, small positively charged Ti-oxoclusters can be stable in the sol and condensation can be hindered. It is this approach that will be used here to stabilize TiO_2 solutions. Such solutions will be deposited by Chemical Liquid Deposition to form films. Another characteristic of those systems is that they have a high degree of shrinkage after thermal treatment due to the high volume of organic molecules stabilized in their coordination sphere. It is for this reason that small, volatile precursors are usually preferred such as chloride salts (TiCl₄ in the case of titania) to reduce the film shrinkage¹.

Another way to stabilize solutions is to add chelating agents able to bind the metallic center such as chelating molecules (acetylacetone, diethanolamine ...) or polymers. For instance, poly(ethylene oxide) (PEO)-based polymer can weakly chelate Ti^{IV} species by stabilizing them in the outer shell of the forming micelles. It is important to keep in mind that the addition of large stabilizing molecules, bound to the metallic centers and that will be removed during annealing, provokes a great increase of shrinkage. On the contrary, weakly bound molecules such as structuring polymers will not increase the shrinkage as it is not involved in condensation. This will be discussed more in details later on in Chapter III.

I.2. Chemical Liquid Deposition

I.2.a. Generalities

Chemical Liquid Deposition techniques are among the many processes able to deposit a thin film (typically from few nanometers to few micrometers) of material in a controlled way. A liquid precursor solution, such as an inorganic sol (containing inorganic sol-gel precursors), a colloidal suspension of nanoparticles or an organic polymer solution, is typically used to coat a given substrate. Since the first patent describing a method to deposit a sol-gel layer from Schott Glaswerke Co. in 1939, many different Chemical Liquid Deposition (CLD) methods have been developed to elaborate sol-gel coatings with increasing complexity, with higher throughput, and with more and more control over the homogeneity and structure through the fine-tuning of the chemical and processing conditions ^{4,7–} ¹⁰.They are thus today regarded as reliable processes, complementary to dry deposition techniques, because they combine excellent control over the layer inner structure and composition while keeping high manufacturing rapidity and cost efficiency.

The main phenomenon responsible for the evolution of films is **evaporation** due to the large surface of exchange between the layer and the atmosphere but not the only one as it can come with other effects such as *water uptake*, viscous flow, capillarity, coalescence or other kind of instabilities. Chemical Liquid Deposition techniques can be separated in various successive steps (Figure 4): (i) a stable solution optimized for a given deposition technique is formulated (ii) the sol is deposited by the chosen technique and evolves to a gel by evaporation in controlled conditions (iii) the gel is in equilibrium with the atmosphere and can be further modified, for instance by lithography; (iv) the gel finally undergo a treatment for stabilization.

Here our goal is to fabricate **nanostructured surfaces**, to do so with liquid deposition techniques, two ways are possible: 1) the nanostructures are made by **direct self-assembly**. In this case structuring agents present in the initial solution will self-assemble and yield the desired structure during evaporation. No additional modification of the film is necessary and final stabilization can be performed directly after evaporation. This route will be explained in details in the next sub-section. 2) **Additional lithography** process is used to structure and functionalize a deposited thin film. This takes place in step (iii) when the gel is in equilibrium with the atmosphere and can still be modified. A promising lithography technique: Nano Imprint Lithography (NIL), applied to sol-gel systems will be discussed in details in Chapter III.



*Figure 4 : The different steps involved in Chemical Liquid Deposition techniques (here applied to dip-coating). Reproduced from Handbook of sol-gel*⁸.

Amongst the various existing liquid deposition techniques, the most used are spin-coating and dipcoating as they have many advantages. In particular, dip-coating offers the highest degree of control over the deposition process with fine control over the deposition speed, the temperature and the environment during deposition. In this thesis, all film deposition were performed by dip-coating, for this reason only this technique will be explained in details.

I.2.b. Fundamentals of dip-coating

Dip-coating is one of the most convenient methods used in laboratory and industry to deposit a solid layer onto a surface with a controlled thickness from a chemical solution. Here the substrate is immersed in the solution and vertically withdrawn at a controlled speed, leading to the deposition of a thin layer. This technique gives a very high degree of accuracy over the deposition parameters (withdrawal speed, temperature, relative solvent vapor pressure) which is of paramount importance to precisely control the inner layer structure for instance for organized porous layers. Moreover, it is waste-free since the solution can be retrieved after the substrate is withdrawn.

The model usually proposed to predict the thickness of a homogeneous fluid layers obtained by dipcoating is from Landau and Levich. It is based on the equilibrium between the adhesion of the fluid on the substrate and the gravity-induced viscous drag for a Newtonian and non- evaporating fluid ¹¹. It is given in equation (1), where h_0 , μ , γ_{LV} , ρ , and u are the film final thickness, the fluid viscosity, the fluid surface tension, the fluid density, and the withdrawal speed, respectively.

(1)
$$h_0 = \frac{0.94\mu^{2/3}}{\gamma_{LV}^{1/6}(\rho g)^{1/2}}u^{2/3} = Du^{2/3}$$

This equation predicts that the equilibrium thickness depends on the fluid physical-chemical characteristics and is proportional to the withdrawal speed at the power of 2/3. Some works were then

conducted to improve this model, taking for example in account the influence of evaporation existing for sol-gel systems ^{12–17}. In any case, these models are barely verified with sol-gel complex systems that undergo fluid evolution through evaporation, and this especially in extreme conditions (high evaporation rate, high solution concentration, highly reactive species...) and for extreme withdrawal speeds (ultra-low or ultra-fast speeds). Faustini et al. used an experimental approach to investigate the variation of sol-gel coating thickness applied at speeds ranging from 0.01 to 20 mm.s^{-1 18}. This semi-empirical model (given in equation (2)) allows to predict the final film thickness h as a function of the withdrawal speed u.

(2)
$$h = k \left(\frac{E}{L.u} + D.u^{\frac{2}{3}}\right)$$

Where *k* is the material proportional constant (proportional to the inorganic molar concentration in solution and the volume fraction of inorganic material in the final film), *E* the evaporation rate (dependent on the relative vapor pressure), *L* the substrate width, *D* the fluids physical constant (see equation 1) and *u* the withdrawal speed. At high withdrawal speed ($u > 0.5 \text{ mm.sec}^{-1}$), in the **Draining Regime**, the amount of solvent evaporated at the liquid meniscus is negligible and the film formation follows the model proposed by Landau and Levich in 1942¹¹. The thickness increases with higher withdrawal speed (see Figure 5). At low withdrawal speeds ($u < 0.1 \text{ mm.sec}^{-1}$), in the so-called **Capillary Regime**, solvent evaporation takes place at the liquid meniscus, which is continuously fed through capillary rise from the solution. In this case, no dragging is involved, and the film thickness is directly related to the evaporation rate *E*. In capillary regime, the thickness is seen to increase with decreasing withdrawal speed, really thick film (up to more than 1 µm) can be obtained. At intermediate speeds, in the Mixed Regime, both contributions are balanced. The speed range of this intermediate domain strongly depends on both solution composition and processing conditions such as temperature. The same behavior is also true for less complex systems such as polymeric solutions ¹¹.



Figure 5 : Plot of the thickness versus withdrawal speed (log-log scale) for a thin film deposited by Dip-Coating (sol-gel film in this example). Inside the graph: scheme of the meniscus region for (a) capillary

regime at low withdrawal speed and for (b) draining regime at fast withdrawal speeds. Reproduced from ⁸.

I.2.c. Recent advances in dip-coating

Recent works have managed to tackle some of the remaining issues inherent to dip-coating giving more accuracy and more flexibility to this technique. Programming of the withdrawal speed, with an appropriate acceleration of the speed, have been shown to produce gradient of thickness ¹⁹ (Figure 6a). Unidirectional gradients can be very useful for assessing the influence of the thickness on a single substrate or when gradient properties need to be applied on a support. Furthermore, one of the main drawbacks of dip-coating, compared to other liquid deposition techniques, is the large quantity of solution necessary to fill the dip-coating tank. This issue was recently cleverly addressed by Ceratti et al ²⁰ with biphasic dip-coating (Figure 6b). By using a perfluoroalcane to fill the majority of the tank, they demonstrated the deposition of films on large surfaces from a very small amount of solution. Finally, it is well known that conditions need to be precisely controlled during liquid deposition in term of withdrawal speed, temperature and relative humidity to obtain homogeneous and reproducible films. Recently, Bindini et al²¹ highlighted the role of the atmosphere during dip-coating and its impact on the final film characteristics (Figure 6c). Variations in the evaporation rate of the solvent during deposition give rise to gradients of solvent relative pressure in the chamber and is strongly dependent on the geometry of the dip-coating tank and chamber. Those variations, if controlled, can be used to create huge thickness gradient profiles.



Figure 6 : Recent advances in dip-coating understanding. a) Functional gradients made by acceleration of withdrawal speed during deposition. 1D photonic crystals (Bragg mirrors) have been implemented by stacking alternate layers featuring different thickness resulting in different light transmission and reflection (see optical image) ¹⁹. b) Biphasic dip-coating for a minimal volume of solution ²⁰. c) High degree of control of the atmosphere (solvent vapor relative pressure) for engineering huge thickness gradients ²¹.

Another important drawback of dip-coating is that it doesn't allow to deposit only one side of the substrate. This problem was addressed during the present thesis and the solution will be explained in Chapter II.

I.3. Mechanism of self-assembly in sol-gel thin films

In this part, the various types of structuring agents will first be presented. The organization of the porosity in inorganic films during chemical liquid deposition through the so-called Evaporation Induced

Self-Assembly will be described. Finally, the formation of inorganic nanopatterns made from the selfassembly of a single layer of micelles will be explained.

I.3.a. Structuring agents

Structuring agents showing the tendency to self-assemble are of great interest in the synthesis of inorganic porous materials. They can be divided in two main categories: hard templates such as PS spheres and soft templates such as amphiphilic molecules. Soft templates are usually amphiphilic molecules or macromolecules containing a hydrophobic region (for instance an alkyl chain) and a hydrophilic region (for instance an ionic or polar group) covalently bound together. First applied to inorganic materials templating by Mobil Oil researchers for the synthesis of mesoporous silica²², soft templating is based on the supramolecular assembly of organic species.

Such molecules start to self-assemble when their concentration in solution is higher than the Critical Micellar Concentration ([C] >> CMC). Spherical micelles self-assemble and are at equilibrium with monomeric species. In a polar solvent, micelles are composed of a hydrophobic core (from the hydrophobic chains) and a hydrophilic shell. If the concentration is far higher than the critical micellar concentration, and depending on the temperature and polarity of the solvent, micelles can minimize their surface energy through the formation of a liquid crystal phases. Various geometries can be obtained such as cylinders, lamellar structures or bicontinuous phases featuring a degree of long-range ordering (Figure 7).



*Figure 7 : Examples of micellar structures: A) sphere, B) cylinder, C) planar bilayer, D) reverse micelles (i.e. in apolar solvents), E) bicontinuous phase, F) liposomes. Reproduced from ref*²³.

Two main categories of soft-structuring agents can be defined: ionic and non-ionic. **Ionic** macromolecules presenting ammonium groups such as CTAB (Cetyltrimethylammonium Bromide, $[(C_{16}H_{33})N(CH_3)_3]Br)$ are among the first and most widely used. Small pores in the range of 1.5 to 2 nm are obtained. The small dimension of these micelles leads to narrow inorganic walls (space between two micelles) and relatively low mechanical stability. Moreover, such molecules are usually toxic for the environment. **Non-ionic** macromolecules have been firstly used for the synthesis of mesoporous silica in 1995 by Pinnavaia *et al.* using neutral primary amine micelles ²⁴. Block copolymers, macromolecules with at least two blocks presenting different chemical functions, represent a large part of those non-ionic macromolecules. Commercially, amphiphilic tri-blocks such as Pluronic type $([PEO]_x-[PO]_y-[PEO]_x)$ and di-blocks so called Brij $(CH_3(CH_2)_x-[PEO]_y-OH)$ are widely used and present

several advantages with respect to ionic templates: 1) they are non-toxic for the environment and for health; 2) the porous structures are more robust due to the large dimension of the macromolecules leading to larger micelles and thicker walls; 3) it is possible to obtain pores ranging in size from few nanometers to several tens of nanometers by using high molecular weight block copolymers; 4) the mesophase morphology can be tailored by changing the copolymer nature (chemistry, length of each block) or the polarity of the solvent. The hydrophilic ethylene oxide group (-EO) is of particular interest as it can stabilize inorganic precursors by strong coordination chelating bonds between oxygen doublets and the vacant d-orbital of the metallic atoms. Widely known block copolymers, which are used in this thesis, are Pluronic F127 (PEO106PPO70PEO106), Pluronic P123 (PEO20PPO70PEO20) or smaller diblock copolymers like Brij58 (C16H33-PEO20) ^{25,26} with hydrophilic PEO (polyethylene oxide) and hydrophobic PPO (polypropylene oxide). They lead to pores of 3 to 7 nm in diameter. To obtain even larger micelles (with diameter ranging from 10 to 50 nm), larger block copolymers such as PB-b-PEO or PS-b-PEO with blocks of more than few thousands units are usually exploited ²⁷ with polybutadiene (PB) or polystyrene (PS) hydrophobic blocks.

I.3.b. Thin film templating by Evaporation Induced Self-Assembly

As it can be deduced from its appellation, in Evaporation Induced Self-Assembly (EISA), the porosity is formed via self-assembly of the surfactants into micelles during evaporation before their elimination by a final thermal treatment. The concept of **Evaporation Induced Self-Assembly** (EISA) of surfactants was first described by the works of Ogawa *et al*²⁸, Brinker and coworkers²⁹ in the nineties for sol-gel systems following the pioneering work of Mobil on surfactant-templated materials²². It was shown that the mechanism at stake is much more complex than a thermodynamically driven organization of the micelles followed by the stiffening of the surrounding sol-gel network. In the EISA approach, the structuring agent and the inorganic moieties are present in the same formulation. The conditions (precursor stoichiometry, pH, ageing time, solvent) are adjusted in order to have a homogeneous and stable formulation. In the case of thin films, the formulation is then deposited through Chemical Liquid Deposition techniques such as dip-coating (see previous chapter).

The self-assembly of the organic moieties occurs during the evaporation of the volatile solvents (solvent such as ethanol but also water or HCl). During the evaporation, the concentration in partiallycondensed inorganic precursors and organic molecules progressively increases until it reaches the micellar critical concentration. After this limit, micelles start to form, surrounded by inorganic precursors.



Figure 8 : a) Schematic representation of the different steps involved during Evaporation Induced Self Assembly during dip-coating. Reproduced from ³⁰. b) TEM (top) and SEM (bottom) images of a porous film made through the EISA approach. Reproduced from ³¹.

The mechanism of EISA was described in details by Grosso *et al* using in-situ SAXS³⁰, and revealed the critical role of evaporation conditions (relative pressure and temperature) on the final nanostructures. EISA involves four steps that can be more or less intertwined during the coating and drying process (see Figure 8a):

- 1) fast evaporation of solvents
- 2) creation of an equilibrium between water content in the film and atmospheric relative humidity
- 3) Formation and stabilization of the hybrid mesophase (interactions between organic micelles and surrounding inorganic network) while at the equilibrium with the atmosphere
- 4) Consolidation of the inorganic network by condensation

Steps 1 and 4 are kinetically governed whereas steps 2 and 3 are thermodynamically driven. The two first steps need to be as fast as possible to limit phase segregation between the different components displaying different solubility (cations or hydrophobic silane aggregation). This will allow to obtain a homogeneous film limiting the extent of the inorganic condensation, which is important for obtaining a flexible network with a certain mobility. Step 3 is the **Tunable Steady State** (TSS), the gel is still flexible and in equilibrium with the atmosphere. A modification of the atmosphere composition, mainly in term of relative humidity, will modify the mesophase organization. This step can be very fast or slow (from few seconds to several hours) depending on the system (initial conditions) and on the relative humidity. In step 4, the film is consolidated by condensation of the inorganic precursors. This is generally done by thermal treatment but it can also be performed by other means such as ammonia vapor treatment³² or UV treatment ³³. In the case of consolidation by a thermal treatment, the organic micelles can be removed from the inorganic network by going over their degradation temperature which leads to organized, open porosity (Figure 8). This complex phenomenon of Evaporation Induced Self Assembly has been specifically studied for various systems such as SiO₂/CTAB ^{30,34}, SiO₂/Pluronics ³⁵, TiO₂/Pluronics ³⁶.

I.3.c. Inorganic NanoPatterns (INPs)

In the case of larger structuring agents, the length of the hydrophobic block drastically reduces the CMC leading to the point that, generally, micelles are already formed in the formulation. During deposition, the mechanism follows an EISA-like assembly: spherical micelles are already formed in solution and will self-organize into closely packed arrays over large scales during the tunable steady state (see Figure 9 in the case of a monolayer of micelles). An important advantage of such block-copolymers is their high thermal stability, up to 400°C for polybutadiene blocks. Complete condensation and stabilization of the inorganic network is possible before the decomposition of the organic template preventing pore collapse. Moreover, they can stabilize systems that have the tendency to crystallize at low temperature such as mesoporous SnO₂³⁷ and preventing the growth of large crystallites as demonstrated for mesoporous γ -Al₂O₃ with crystallites of 5 nm at temperature up to 900°C³⁸.



Figure 9: Deposition of a single layer of micelles by dip-coating leading to a bi-dimensional perforated layer after annealing (in this example, titania is used as the sol-gel matrix).

If the solution concentration in non-volatile species is high, thick films with multilayers of micelles will be deposited, embedded into an inorganic matrix (Figure 10a). By accurately controlling the inorganic precursor to block copolymer ratio, their concentration and the deposition speed, a narrow range exists for which it is possible to deposit one single layer of micelles on a substrate (Figure 10b). If less matter is deposited, isolated non-organized micelles will be observed³⁹ (see Figure 10c). After heat treatment at elevated temperature (T > 400°C), the organic template is removed from the perforations. Simultaneously, crystallization of the inorganic matrix will lead to a reduction of curvatures in the system by diffusive sintering. In amorphous systems with low shrinkage (i.e. SiO_2), after annealing, a monolayer of closed pores is obtained whereas for crystalline systems with high shrinkage, pores will open and lead to perforations (Figure 10d). Moreover, as the crystallites grow larger with increasing temperature, the surface roughness and the number of defects (grain boundaries, crystal defects ...) is reduced (Figure 10e).



Figure 10 : **a**) SEM image of a porous titania film resulting from the deposition of a multilayer of micelles ³³. **b**) AFM and SEM images of a single layer of micelles in TiO₂ leading to perforations referred to as inorganic nanopatterns (INPs) ²⁷. **c**) AFM image showing partially covered TiO₂ perforations³⁹. **d**) SEM images of TiO₂ nanopatterns after thermal treatment at 300 °C, 400 °C, 500 °C and 600 °C for 5mins. The progressive opening of the perforations can be seen. **e**) AFM images of the TiO₂ nanopatterns after annealing at 500 °C (top) and 650 °C (bottom), the increase of the grain size is visible.

In the latter case, this monolayer – referred to as **inorganic nanopatterns** (INPs) - will then bear perforations in place of the micelles with a bi-dimensional inorganic network on the surface (Figure 9 & Figure 10b). Through the perforations, the surface of the substrate is directly accessible giving an interesting chemical heterogeneity between the perforated layer and the bottom of the perforations.

Self-assembly of block copolymers has been used to homogeneously deposit perforated monolayers of various size (from 10 to 70 nm in diameter) and with various spacing (wall thickness) between perforations (from 10 to 60 nm) simply by using block-copolymers with different chain length ⁴⁰. Many sol-gel systems have been investigated for instance SiO₂, TiO₂, ZrO₂, Al₂O₃, SnO₂ or RuO₂. Different block copolymers can be used such as P(E-co-Bu)-b-PEO, PS-b-PEO, PB-b-PEO, PB-b-PEO, PS-b-PLA, PS-b-P4VP giving similar results ^{27,37,41-43}. Influence of the inorganic to organic ratio, of solution conditioning and of dip-coating parameters for optimized perforated layer has been studied for PB-b-PEO block copolymers by Faustini *et al* ⁴⁰.

Compared to other nanopatterning methods, self-assembly is easy to scale up and, in particular, INPs have the advantage of being cheap and reproducible without the use of specialized equipment. Such inorganic perforations have been used for many applications: in lithography processes with micropatterning of INPs with X-ray lithography⁴⁴ and as Reactive Ion Etching nanomasks ⁴⁵; for their high surface area (*i.e.* as nanoelectrode arrays⁴⁶, for hybrid LEDs⁴⁷, to narrow size distribution of Ge dots⁴⁸ and photocatalytic surfaces⁴⁹); for their chemical heterogeneity (*i.e.* for wetting studies ³⁹, for local deposition of photo-switchable prussian blue analogues⁵⁰, for the selective deposition of photomagnetic nanodots⁵¹).



Figure 11: 1) Micropatterning by X-ray lithography. TiO_2 INPs are used as a positive resist sensitive to X-ray exposure. The SEM image shows an exposed layer after revelation where hexagonal non-exposed zones where stripped with the appropriate chemical etching ⁴⁴.2) INPs used as a mask for the deposition of magnetic nanodomains⁵¹. 3) Taking advantage of the selective heterogeneity of INPs for selective functionalization and/or subsequent local chemical reaction with a) precipitation of Prussian Blue Analogs⁵⁰ b) deposition of gold nanoparticles by galvanic displacement.

II. Nanofabrication by Top-Down techniques

II.1. Nanofabrication by lithography

In lithography, the very large majority of the resists in use are organic. Indeed, using polymeric resists has many advantages as the solutions and films are stable in time and their properties can be easily tailored with temperature (their fluidity is dependent on the temperature and varies sharply around their glass transition temperature) making their lithography quite straight-forward ^{52–54}.

Applying lithography approaches to metal oxides is highly attracting since robust and thermally stable patterned surfaces with adjusted mechanical, chemical, and optical properties can be directly produced. Indeed, in a conventional oxide patterning process, many steps are required: a polymeric resist is patterned and used to selectively deposit a hard mask that will in turn be used to selectively etch and pattern the underlying oxide. In contrast, direct oxide patterning is straightforward: the oxide is directly patterned by lithography to give the desired motifs. Thus, patterning of sol-gel materials was quickly developed to replace polymeric resist in many applications requiring patterned inorganic oxides such as microelectronics or optics. Most of the sol-gel resists used industrially are still inorganic-organic hybrids due to easier processing and compatibility with existent lithography processes developed for polymeric resists. For instance, Hydrogen silsesquioxane (HSQ) is one of the most widely used silica-based resist⁵⁵. Based on a caged-like structure, it provides a better mechanical and chemical resistance than polymers while keeping rheological properties close to its polymeric counterparts. However, such resists are limited to only few sol-gel materials.

The present part will detail the main industrial lithography techniques with a focus on research works applied to the patterning of inorganic sol-gel resins with the use of a minimal ratio of organic precursor, if any.

Lithography techniques can be divided in 3 main categories:

> Lithography involving exposure through a mask: Photolithography

- Lithography by moulding/imprinting: Soft-lithography
- > Direct writing with a focused beam: Direct lithography

Industrially, the large majority of the lithography processes rely on **photolithography**: a film of resist (photosensitive material that will undergo a chemical reaction once exposed to light) is deposited onto a substrate and exposed to high energy photons (UV, Deep UV) through an opaque mask that delimitates the final patterned areas (see Figure 12). This process can be coupled with complex optical systems: by using projection lenses with a specifically designed mask, the size of the patterned areas is decreased, increasing the process resolution. Photolithography is currently used with excimer lasers ($\lambda = 193$ nm for Deep UV) and state-of-the-art optics to pattern features under 20 nm at a very high technological cost. Since smaller resolution is directly related to shorter illumination wavelength, extreme-UV lithography ($\lambda = 13.5$ nm) is now being considered, among other techniques, in order to reach new technological targets.

Nevertheless, the resolution of this technique is intrinsically limited by the wavelength used due to diffraction at the mask edges. To obtain ever smaller patterns, photolithography light sources already moved from UV to deep UV wavelength. To go even beyond such resolution, X-rays have to be used but this presents many limitations as the system used is complex and expensive: no suitable refractive material can be used in this wavelength range. Therefore in the optical system, lenses are replaced by shaped multilayers mirrors. The mask itself is composed of reflective multilayers. For this reason, very small patterns are usually performed by E-beam lithography.

Most of the resins used in photolithography are polymer-based but intensive research focuses on photocurable oxides or hybrid organic-inorganic resins to directly obtain inorganic patterns. In general, the presence of a catalyst is required to trigger the condensation reaction of the sol-gel material, creating a contrast between exposed and unexposed areas, necessary to selectively remove the undesired areas⁵⁶. Another approach is to use acrylate-chelated precursors that will cross-link and initiate condensation as it has been conclusively demonstrated for many metal oxides^{57,58}.





In **Soft lithography** processes, an elastomeric stamp with patterned structures is used to mould a material and generate structures. This non-photolithographic strategy has been extensively developed by the team of Whitesides *et al* in the late nineties⁵⁹. Polydimethylsiloxane (PDMS) stamps are generally used, fabricated from an initial master. From a single master, generally made by an expensive and low throughput technique - such as Electron-Beam Lithography on a silicon wafer - it is possible to

easily fabricate many unexpensive PDMS molds bearing the same features. Moreover, each mould can be used dozen of times and in continuous processes such as roll-to-roll. Soft-lithography englobes different techniques depending if the mould is used in a stamping process or as a template to fill. In **Nano Imprint Lithography (NIL)**, a film is embossed with a mould, imprinting its features after its release (Figure 13). This technique has seen extensive research and showed very promising results with sub-25nm resolution obtained already in 1995 by Chou *et al.*⁶⁰ in PMMA resins and, more recently, sub-10nm resolution on dense patterns in sol-gel resists^{61,62}. The evolution from NIL towards **Soft Nano Imprint Lithography (Soft-NIL)** applied on sol-gel materials will be described in details in Chapter III. Usually after imprinting, a thin residual layer is present between the substrate and the sol-gel structures (Figure 13b) and necessitates an additional etching step to be removed. Physico-chemical etching with high anisotropy such as **Reactive Ion Etching** (RIE) is often preferred to wet isotropic etching to avoid a reduction of the dimensions of the imprinted structures.

Many variations of Soft-NIL have been developed with different advantages and limitations. In Micromolding in capillaries (MIMIC), the patterned surface of the stamp is placed down onto the substrate having a network of connected micro channels with open ends through which the precursor solution flows in the channels and fills them by capillary action ^{63,64}. The permeability of the stamp to gases then permits the evaporation of the solvent in the capillary patterns, allowing the drying of the resist solution. The stamp is then peeled off, leaving the molded microstructures on the surface of the substrate. In addition to being time consuming due to the slow capillary flow in the microchannels, all features cannot be reproduced since some, such as isolated cavities for instance, may not be accessible to the solution by capillarity. To obtain connected or isolated features, other techniques can be applied. Microcontact printing is a technique in which only the raised features of a stamp are "inked" and then contacted with a substrate for selective deposition. The ink is transferred from stamp to substrate only in the area of contact ^{65,66}. This technique is mainly used with biomolecules that are positioned on the stamp surface and subsequently transferred to a substrate producing a selfassembled monolayer (SAM). In microtransfer molding (μ -TM), the mold is first filled by a sol-gel solution before being applied onto the substrate, transferring the patterns⁶⁷. To avoid incomplete filling, the material is often applied in excess and must be removed from the raised areas of the stamp, either by scraping with a blade or with a stream of nitrogen. This technique has been successfully used on silica based sol-gel materials to transfer high aspect ratio patterns⁶⁸. Recently, disposable watersoluble PVA molds have been shown to yield really high aspect ratio structures without residual layer on sol-gel⁶⁹.

These non-photolithographic approaches relying on imprinting are usually cheaper than photolithography or direct lithography. They can be used with most precursors since the process does not rely on photoactive monomeric groups and it does not require expensive optical systems and light sources. Moreover, according to the International Technology Roadmap for Semiconductors (ITRS)⁵³, soft-lithography is considered as a realistic candidate to reach the next technological target with sub-25nm patterns. In addition, the higher throughput and scalability is a huge advantage compared to direct lithography.



Figure 13 : a) Schematic representation of soft-lithography. b) SEM image of a squared array of TiO_2 squares made by soft-NIL.

Finally, **direct lithography** consists in the **direct writing** of features without a mask (see Figure 14). The most exploited technique is the Electron Beam Lithography (EBL) where a focused beam of electrons is used to locally condense an E-beam reactive resin into a pattern. Even if most resists are polymeric, sol-gel resists have been developed for instance silica-based HSQ⁵⁵ available industrially but also $TiO_2^{70,71}$ or alumina ^{72,73}. Alternatives to the direct writing of a sol-gel resist exists for instance by casting a sol-gel solution onto a pre-patterned EBL polymeric resist in order to fill its features and obtain its negative⁷⁴.

Following a similar strategy, Focused Ion Beam (FIB) uses a beam of accelerated ions to mill into a substrate the desired features. The unique advantage of this technique is that it can be applied to most materials (i.e. silicon but also any sol-gel material as long as it is conductive or thin enough to avoid accumulation of charges). No specific resin or reactive functions is needed compared to EBL or other non-direct lithography techniques. Moreover, this flexible technique can be applied to etch side by side various patterns at different depths and allows fast prototyping for research purposes. In addition, recent advances allowed to tackle one of its main drawback which is its low throughput: by etching on porous substrates we will show that it is possible to increase drastically the etching time (see Chapter II).



Figure 14 : a) Schematic representation of EBL/FIB lithography. b) E-beam patterning of mesoporous TiO₂ thin film by filling of patterned E-beam resist and subsequent lift-off, adapted from ⁷⁴

II.2. Nanofabrication by self-assembly

II.2.a. Directed self-assembly

Nanofabrication by self-assembly is being developed as an alternative for classical lithography routes as it allows very high resolution (down to the size of the structuring agent) and is applicable to large surfaces ^{75,76}. In nanofabrication, diblock polymers with two highly incompatible blocks are generally used (e.g. polystyrene-block-polymethylmetacrylate, PS-b-PMMA). Self-assembly occurs naturally from the microphase segregation between the two blocks and is triggered by giving mobility to the system through heating or by solvent exposure. Different phases can form as presented before for micellar structures (see Figure 7).

To avoid disorder and defects and obtain the organization of one single self-assembled domain on large scales, chemical or topographical structuration of the substrate is first performed in order to obtain a **directed self-assembly**. The latter approach is generally preferred and called graphoepitaxy. It combines block copolymer self-assembly with a pre-patterning lithography step that can be performed by any of the lithography processes seen above. For instance, block copolymers can be deposited in a defined spatial space (*i.e.* between two lines) to obtain perfectly organized lines, cylinders or spheres^{76–78}. It has also be cleverly coupled with nanoimprint lithography to obtain self-organized structures within the imprinted features during the nanoimprint step ⁷⁹. The assembly of block copolymers into domains is generally followed by the specific dissolution of one block while the other block acts as a resist to replicate the polymeric features into the substrate (see Figure 15). Another widely used approach, limited to micron size structures, takes advantage of the self-assembly of polystyrene spheres to obtain a mask through which the substrate can be selectively etched ^{80,81}.



Figure 15 : a) Schematic representation of the directed self-assembly of a block copolymer (PS-PMMA) layer into well-organized lines followed by selective removal of the PMMA block and etching of the substrate (here the sol-gel layer) by using the PS block as a mask. b) SEM image of the resulting lines made by self-assembly, before and after transfer into the substrate by reactive ion etching. Adapted from ⁷⁸.

II.2.b. Highlight on Solid State Dewetting

Another way to obtain self-assembled micro or nanostructures on a surface is by **solid state dewetting**. This is of particular interest as it is directly applicable to the fabrication of arrays of metallic or semiconductor 3D nanocrystals without additional lithographic step. Dewetting characterizes the

instability of a film (liquid, metal, polymers ...) when it is so thin that surface tension dominates such that the film breaks into isolated islands (Figure 16a).



Figure 16: (a) Image of water droplets on a surface. (b) Schematic representation of a drop in equilibrium with the projection of the various surface energy density γ at the interface and θ the contact angle.

Thermodynamically, dewetting is driven by the minimization of the surface energy between the film and the substrate, the film and surrounding atmosphere, and the substrate and the surrounding atmosphere. The equilibrium of a drop on a solid surface is given by the Young equation for a contact angle θ (Figure 16b):

$$\gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos\theta$$

where γ_{sv} , γ_{fs} , γ_{fv} are the substrate-vapor, film-substrate, film-vapor interfacial energy density respectively. If the condition $\gamma_{sv} \geq \gamma_{fs} + \gamma_{fv} cos\theta$ is respected the film will wet the surface $(\theta = 0)$ otherwise the film is unstable and will tend to decrease its surface energy by breaking into islands. The formation of isolated islands is much more favorable for a thin film as it displays a high surface to volume ratio. It is for this reason that for solids, dewetting occurs at temperatures lower than the corresponding melting point, the thin film thus dewets while being in the solid state.

This phenomenon is based on surface diffusion limited kinetics: variations in the surface curvature drive mass transport and lead to further evolution of the surface. The kinetical aspect of dewetting was well explained in the case of semiconductors by Danielson *et al.*⁸²; it can be described by Mullins equation ⁸³:

$$V_n \propto \nabla^2 \kappa(s)$$

where V_n is the dewetting speed of an atom, ∇^2 the laplacian operator, and $\kappa(s)$ the mean surface curvature. Thus, the dewetting speed of an atom on the film surface is increased with higher chemical potential which is linked to surface curvature. In other words, if the curvature of the surface increases, diffusion will take place more rapidly, promoting dewetting.

In the case of dewetting on a flat substrate (Figure 17b), the curvature of the dewetting film will have a strong impact on the local speed of diffusion, this is the origin of the dewetting front with breaking of the film into fingers then into islands (Figure 17c & d)⁸². Diffusion is promoted when the system is placed under vacuum (*e.g.* in the ultra-high vacuum of an epitaxy chamber) and heated. The final outcome in term of size and arrangement of the islands will be highly dependent on the initial film thickness, the substrate surface energy and inhomogeneity (chemical and physical) of the surface. Sites of higher energy such as defects (holes, pits, grain boundaries) or slight thickness variations are usually

the starting points of dewetting (see Figure 17b). Spontaneous dewetting will thus lead to the formation of islands randomly arranged on the surface as defects are randomly located.



Figure 17 : a) Schematic representation of the diffusion speed depending on the curvature of the film for a flat substrate. b) Optical Dark field microscope image of a spontaneously dewetted silicon on insulator (SOI) substrates (11 nm of silicon on silicon oxide). Dewetting is seen to start only at specific location. Reproduced from ⁸⁴. c) SEM image of a partially dewetted SOI film. The thin film breaks down into elongated fingers before forming isolated Si droplets. The dewetting front can be seen at the top left of the image. d) The different steps of an advancing dewetting front: I) critical void formation, II) void edge thickening, III) void edge breakdown, IV) void finger formation and growth, and V) island formation⁸².

Templated dewetting

In order to control the final outcome of dewetting, defects can be artificially introduced. Such defects can be chemical, structural or topographical defects. Generally, structural and topographical defects are preferred as the conditions for solid state dewetting (high temperature, vacuum) are not favorable to chemical functionalization. To control the final geometry, two strategies can be used: either prepatterning the thin to-be-dewetted layer or pre-patterning the substrate before deposition of the thin layer (Figure 18a). In the first case, the mechanism will be similar to the one described above with a control over the location of the defects in the thin layer and thus over the organization and size distribution of the final islands. In the second case, when the surface of the substrate is not flat and for the deposition of a conformal thin film, the speed of dewetting will similarly increase with the surface curvature. For this reason, the morphology of the surface needs to be taken into account as it will locally modify the diffusion speed. By templated dewetting, narrower size distribution and control

over the location of the islands can be obtained as can be seen in optical dark field microscope imaging in Figure 18b.



Figure 18 : a) Schematic representation of the diffusion speed in the case of directed dewetting. (top) the thin layer is pre-patterned creating localized defects: the starting points of dewetting. (bottom) the substrate is pre-patterned modifying the surface curvature and the dewetting speed which will trigger and direct dewetting on the patterned areas. b) Dark field image of E-beam assisted dewetting. The sample silicon layer (11 nm) was pre-patterned with parallel lines. In A, the interspace is 4 μ m while it is 1 μ m in the central part (C). More homogeneous color is observed in accordance with a sharper size distribution compared to spontaneous dewetting (B). Reproduced from ⁸⁴.

Templated dewetting has been shown to be applicable on large scales by using self-assembly or other high throughput techniques to pre-pattern the surface. For instance, electrochemically self-organised surfaces (AI, Ti or Ta) ^{85,86} have been used to organize dewetting. Indeed, any means used for standard nanofabrication, such as organized nanoperforated layers ^{48,87}, direct lithography or nanoimprint lithography^{88,89} or silicon etching⁹⁰, can be used as long as the introduced topography has a periodicity which is shorter than the scale of the natural instability. In other words, if the thin layer naturally breaks down in islands separated by 1 μ m, the periodicity of the patterned surface will need to be inferior to 1 μ m.

However, all the above mentioned examples focus on the dewetting on metals (Au, Pt ...). Indeed, dewetting of semiconductor materials (i.e. Si or Ge) is much more complex than in the case of metals (i.e. Au or Pt) with a lower diffusion requiring very high dewetting temperatures and defect-free ultrahigh vacuum chamber (epitaxy chamber). It is mainly because of those extreme requirements that only little research has been done on this topic. Moreover, metals are key elements in many industrial applications such as electric contacts in microelectronic or as catalyst in the growth of nanowires by VLS (Vapor Liquid Solid)^{52,91}. On the other hand, dewetting of semiconductors have seen little attention in the past decades, nevertheless interest is growing as organized 3D crystals of semiconductors are now foreseen to overcome the limitations of conventional non-volatile memories. In addition, such nanostructures have recently attracted much interest as they display quantum size effects that can open the way to new applications in optoelectronics ⁹² and nanoelectronics ⁹³. Organized 3D island of Ge on Si are of particular interest as this system is fully compatible with the microelectronic industry.

In the case of the templated dewetting of semi-conductors, only direct lithography techniques have been studied with pre-patterning of the semiconductor layer by FIB^{84,94–96} or by E-beam ⁹⁷ (see Figure 18b). In particular, it has recently been shown that it is possible to deterministically predict the final geometry of very complex dewetted structures by careful design of the initial "defects" (see Figure 19) ^{97,98}. This is really interesting as it is directly applied to the dewetting of semiconductor thin films and such complexity would be challenging to achieve by other means. However, using those direct lithography techniques as pre-patterning steps makes the overall process expensive and inherently restricted to small surfaces.



*Figure 19 : (a) SEM image of an E-beam patterned silicon thin film after solid state dewetting. Many repetitions of the same pattern can be seen with very good homogeneity. (b) Dark field optical microscope images giving some example of the complexity of the obtained structures*⁹⁷.

In summary, dewetting can be performed on a scale of centimeters to yield homogeneously dispersed structures. However, if control is needed over the organization or size of the dewetted islands, a prepatterning step is necessary. It is the combination of those two steps (pre-patterning and dewetting) that make the strength of this process with very high resolution over the dimensions and organization of the final structures but the pre-patterning step can also limit the scalability and cost (for instance with direct lithography). In the case of solid state dewetting of semiconductors, research mainly focused on direct lithography as the pre-patterning step leaving the field unexplored for directed dewetting using large scale nanofabrication techniques. Such techniques will be shown in Chapter IV as a way to efficiently control the organization and dimension of the final semiconductor dewetted structures by using self-assembled inorganic nanopatterns and sol-gel nanoimprinted surfaces.

III. Conclusion

In this chapter, concepts of sol-gel chemistry were briefly introduced. We described chemical liquid deposition techniques and in particular dip-coating and its advances. The concept of self-assembly of macromolecules during deposition in sol-gel films was exposed. In particular, a specific focus was given on the deposition of porous ultra-thin sol-gel films. This approach was used to obtain inorganic nanopatterns that will be used in this present thesis to direct dewetting.

The state of the art of nanofabrication techniques have been presented with their various advantages and drawbacks. Lithography techniques are widely used in industry and allow to shape a given material directly or indirectly. Those techniques were described with a specific focus on directly patternable sol-gel layers. Self-assembly and in particular Solid State Dewetting is also presented as it can be exploited to nanostructure semiconductor thin films on large scales with a high degree of control especially when coupled with another lithography technique.

In the next chapter, advances on large surface structuration will be discussed by improvement of thin film deposition techniques with angle dip-coating or with new original approaches for master fabrication.

	Technique	Advantages	Limitations
Photolithography	UV, Deep-UV	Mature technology	Diffraction-limited resolution
		High throughput, large surfaces	Few UV-sensitive oxides
Soft lithography	Nanoimprint lithography	High resolution (< 10 nm)	Costly fabrication of the
		High throughput, large surfaces	master
		Reusable molds	Appearance of defects after
			several use
			Residual layer
	MIMIC	Easy implementation	Limited to inter-connected
			patterns
			Slow capillary filling
	Microcontact printing	Easy implementation	Limited to monolayers
	Microtransfer molding	Large aspect ratio	Sacrificial mold
		High resolution	
		Possible to avoid residual layer	
Direct writing	Electron Beam Lithography	High resolution (< 5 nm)	Low throughput
		No mask or mold	Expensive
	Focused Ion Beam	High resolution (< 5 nm)	Low throughput
		Direct etching of the desired	Expensive
		material	
Self-assembly	Directed self-assembly	High resolution (< 5 nm) and	Limitation in the pattern
		self-organization	geometry
		Large surfaces	
	Solid State Dewetting	High resolution (< 5 nm)	Need of a pre-patterning step
		Large surfaces	
		Directly applicable to	
		semiconductors	
Chapter II: Large surface structuration

This chapter will be dedicated to the efforts towards the scaling up of surface structuration with submicrometric and organized patterns. For structuring large surfaces, the first challenge is often to homogeneously deposit a uniform coating. Spin-coating is the process of choice for research purposes but it remains difficult to upscale it over 8-inch wafers and it cannot be used for the industrial production of heavy structures such as solar cells. Dip-coating has overtaken spin-coating in the industry but has the major drawback to deposit a coating on both sides of the substrate. In this focus, angle dip-coating will first be presented as a solution to obtain homogeneous coatings on very large scales and only on one side of the substrate.

Once a coating is deposited, a subsequent micro/nano-structuration of the coating is often required to confer tailored properties (*i.e.* anti-reflective, light trapping, water repellent ...). For this purpose, large scale techniques have been developed and are now mature such as Nano-imprint Lithography among others. However a remaining bottleneck in such soft lithography techniques is the fabrication of the original master, often made by time-consuming and expensive techniques (i.e. E-beam, FIB). In this respect, a synergetic approach involving direct lithography and sol-gel porous layers will be presented. By using porous sol-gel layers as substrates for focused ion beam, the milling rate can be greatly enhanced. Finally, spontaneous dewetting of ultra-thick semiconductor films will be described as a way to obtain complex masters on a very large scale.

I. Angle dip-coating

As explained in the previous chapter, dip-coating is a really robust chemical liquid deposition technique as it allows the highest degree of control over the entire process (withdrawal speed, temperature & relative solvent vapor pressure in the deposition chamber). This is especially important when soft templates are used to create inorganic nanopatterns as the self-assembly is highly sensitive to small variations in withdrawal speed and atmosphere composition during deposition. Dip-coating is thus a technique of choice to deposit in a reproducible manner such highly organized thin films.

However, there are still drawbacks remaining when using dip-coating on large scales. One of its main drawback is that all faces of the substrate are coated. This drawback will be addressed in the following part with the development of angular dip-coating. It will be demonstrated that in those conditions, a wider range of thickness can be obtained with the same solution composition when compared to vertical geometry. In addition, dipping at a very low angle enables the deposition of only one face (the lower side), at relatively high throughput, and with a minimal amount of solution, addressing thus important issues associated with mass production. This experimental investigation will be related to predictions of models developed for dip-coating, modified for angle dip-coating. This work led to a publication⁹⁹.

I.1. Theory of angle dip-coating

The Landau-Levich equation and the semi-empirical model developed by Faustini et al have shown to be efficient to predict the thickness for a given withdrawal speed for complex sol-gel systems. The equation combining draining and capillary regime, developed in Chapter I, is the following:

(1)
$$h_0 = k \left(\frac{E}{Lu} + Du^{2/3}\right)$$

Where h_0 , *k*, *E*, *L*, *D* and *u* are the final film thickness, the material proportional constant (proportional to solution inorganic molar concentration and the volume fraction of inorganic material in the final film), the evaporation rate (dependent on the relative vapor pressure), the substrate width, the fluids physical constant (as defined in equation (1)), and the withdrawal speed, respectively.

However this relation is valid as long as the dipping geometry is vertical, this is to say when the angle between the solution surface and the substrate surface is fixed at 90°, which corresponds to most of the practical cases. For a planar substrate, changing this angle would result in a different thickness on the upper and the lower sides of the substrate due to the difference in the draining contribution that applies on both sides (see scheme in Figure 20b). Here, upper and lower sides designate the side facing up and the side facing down of a substrate and should not be mistaken with the top and bottom edges of the substrates (see scheme in Figure 20a). If well adjusted, deposition in such an Angle-Dependence Dip-Coating (ADDC) configuration can been exploited to produce optical filters by taking advantage of the thickness difference on both faces of the optical support^{100,101}. As expected and experimentally demonstrated in these latter works, for tilting angles ranging from 90 to 30 degrees with respect to the liquid surface, the film is always thicker on the upper side. This effect and the associated mathematical prediction of the thickness (equation (2)) were reported by J.A. Tallmadge in 1971 for the pure viscous-drag regime¹⁰².

(2)
$$h_0 = \frac{0.94 \,\mu^{2/3} \,U^{2/3}}{\sigma^{1/6} \,(\rho g)^{1/2} \,(1 + \cos \theta)^{1/2}}$$

In this equation, U is the speed of meniscus motion (corresponding to the speed of the withdrawal substrate in the direction of its length), μ the fluid viscosity, ρ the fluid density, h_0 is the thickness of the film on the lower side of the substrate and θ is the angle between the substrate and the surface of the liquid reservoir as shown in Figure 20b. By replacing U with the vertical component of the speed u and combining equations (1) and (2), one obtains the global relation (3) that links the film final thickness to the dipping angle and to the vertical withdrawal speed for both regimes of deposition (note that equations (2) and (3) account only for the lower side of the substrate and not for the upper side).

(3)
$$h_0 = \frac{kE(\sin\theta)}{Lu} + \frac{kDu^{2/3}}{(\sin\theta)^{2/3}(1+\cos\theta)^{1/2}}$$

In vertical geometry and for a non-null evaporation rate ($E \neq 0$), which corresponds to most of the cases, the plot log h_0 vs log u exhibits a typical V shape with a minimal thickness existing at an intermediate speed, where both regime contribute to the film formation. If E = 0, the first term of

equation (3) becomes null and the plot $log h_0 vs log u$ becomes a linear tendency allowing in theory to elaborate extremely thin films at extremely low speed, where the draining regime would dominate without perturbation induced by the capillary regime. However, such conditions are difficult to be achieved in practice due to the difficulty to saturate the vapor in the atmosphere of the drying chamber and to maintain this situation constant all along the substrate length and the duration of the deposition.



Figure 20: a) Scheme of successive steps applied to perform the coating at low angles. b) Schemes representing the (projected) gravity-force applied on the lower side of the substrate and the relation between the speed of the meniscus motion U and the vertical translation speed u applied to the substrate. c) Schemes of the configuration used to dip-coat a single glass slide substrate at various tilting angles.

The following work will try to experimentally verify equation (3) by dip-coating sol-gel solutions at various angles down to quasi-horizontal geometry ($\theta = 2$ degrees), where the gravity-induced viscous draining and the evaporation rate are minimized, especially for the lower side of the substrate.

Experimental procedure

The sol-gel solutions used to perform the investigation were prepared from the following molar ratios in precursors: (see Table 1)

TEOS	MTEOS	TiCl₄	H ₂ O	EtOH	HCI	F127
0.5	0.5	/	3	40	0.0042	0.006
/	/	1	12	100	/	/

Table 1 : Molar ratios of the precursors and solvents used in this chapter.

TEOS, MTEOS and F127 stand for TetraEthylOrthoSilicate, MethylTriEtOxySilane and F127 Polyethylene oxide-Polypropylene oxide triblock Pluronic copolymer, respectively. The solutions were aged for 3 days at room temperature before use. In the first formulation, F127 is used to enhance the wetting property of the solution. In addition, the added quantity is large enough to form micelles and play the role of a template for pore generation⁷. Besides, by using 50% of MTEOS, the xerogel is expected to show more flexibility too as MTEOS exhibits one non-reactive methyl group. This property is necessary to avoid cracks in thick films induced by the tensile stress during drying. The reservoir containing the solution during dipping was a circular beaker with a diameter of 11 cm and a height of 14 cm, filled with the solution up to 6 cm. The top of the beaker was covered with an aluminum foil to maintain the

partial vapor pressure in volatile species from the solution as high as possible and prevent extensive evaporation. Microscope glass slide substrates were thoroughly rinsed with acetone and ethanol before being blow dry and attached to one extremity of a flexible stem using vacuum, while the other extremity of the stem was attached to the translation stage of the dip-coater (see scheme in Figure 20a) which displays high accuracy over the entire withdrawal speed range (e.g. u between 0.0005 and 10 mm.s⁻¹ in the present case). The stem was lowered into the beaker through the aluminum foil through an opening. The dipping angle was adjusted by simply bending the stem and was carefully measured using the reflection of a laser on the top surface of the substrate. After withdrawing the substrate from the solution at a constant vertical speed u, the cover was removed and the substrate was elevated above the beaker top edge to insure a fast and homogeneous drying of the coating. Only the coating deposited on the lower side of the substrate was investigated. The wet coating present on the upper side was cleaned up with a solvent imbibed tissue straight after deposition. This configuration was used to investigate all angles in the laboratory but this will not be suitable for mass production. In practical cases, when dipping at extremely low angles, only the lower side of a plane substrate is coated. To do so, the angle must be low enough such that only the lower side is wetted. Otherwise, one would require a specific set-up to hold the substrate and prevent solution to wet the upper side. To complete the present study, a 2 mm thick 130 x 160 mm² glass substrate was coated with a TiO_2 thin film using a simple flat reservoir with no cover (see Table 1 for details about the formulation). The dipping angle and the vertical withdrawal speed were fixed around 1 degree and 0.001 mm.s⁻¹, respectively. Eventually, all coatings were cured at 450 °C for 10 min under IR lamps and their refractive index and thickness were measured by spectroscopic ellipsometry (Woollam M2000V) using a Cauchy model for dielectric films.

I.2. Experimental study of dip-coating at low angle

In what follows the coatings were homogeneous in thickness and in refractive index all over the deposited surface as confirmed by a systemic analysis by ellipsometry on various parts of the sample. The refractive index was measured to be n_{600nm} = 1.20 ± 0.02 in all coatings whatever the dipping angle confirming that silica films are porous ($n_{dense SiO2, 600nm}$ =1.45). The variation of final thickness with the vertical speed *u* for dipping angles, ranging from 90 to 2 degrees is measured and plotted in log-log in Figure 21. For clarity purpose, Figure 2b shows only the curves for 90, 30 and 2 degrees on a wider range of vertical speeds.

First of all, it is clear from Figure 21b that dipping at low angles provides an extension of the range of possible thickness with the same initial solution. To be more precise, at 90 degrees one can elaborate homogeneous films with thicknesses ranging from 53 nm to 530 nm, while with the same solution at 2 degrees, this range extends between 10 nm and 850 nm.

Despite the effort made to reduce the evaporation rate in the beaker, the typical V shape of the curve is observed for high dipping angles, suggesting that the capillary regime can still dominate the formation of the film at low speeds. Nevertheless, as the tilting angle decreases, the slope of the curve in the capillary regime decreases. For **the lower speeds** (e.g. $0.01 < u < 0.1 \text{ mm.s}^{-1}$ at 90 degrees / 0.001 $< u < 0.01 \text{ mm.s}^{-1}$ at 30 degrees), with the progressive decrease of the tilting angle, the contribution of the capillary regime progressively diminishes until it is totally canceled at very low angles. This phenomenon can likely be attributed to the reduction of the evaporation rate on the lower side of the coating since the substrate is kept closer to the liquid surface during withdrawal at low angles. A more detailed investigation of the effect of dipping angle on the capillary regime will be presented below.



Figure 21: a) Log-log plots of the thickness h_0 versus vertical withdrawal speed u for different dipping angles (θ) ranging from 90 to 2 degrees. b) Similar diagram showing only plots for 90, 30 and 2 degrees clearly demonstrating the differences in the tendency. For both diagrams, dashed curves are added as guides for the eyes.

If we now focus on **intermediate speeds** (e.g. $0.2 < u < 3 \text{ mm.s}^{-1}$ at 90 degrees / $0.01 < u < 1 \text{ mm.s}^{-1}$ at 2 degrees) corresponding to the right side of the curve; the tendency for all dipping angles is linear with a slope corresponding to *u* at the power 2/3 as described by the Landau-Levich model. This confirms that viscous-drag is the only effect that governs the film formation in this range of speeds. For **higher speeds**, thicknesses diverge from the viscous-drag regime model as already described for the conventional vertical geometry (see Chapter I). Indeed, such a deviation is attributed to the fact that, in these extreme conditions, the thickness of the deposited solution is too high such that the gravity-induced viscous drag cannot be counterbalanced by the adhesion of the layer to the surface¹⁰³. The solution layer is thus thinning more than what can be predicted from equation (3).

Coming back to the intermediate speeds, the linear Landau-Levich tendencies for speeds above 0.1 mm.s⁻¹ are quasi overlapping for dipping angles of 90, 75 and 60 degrees, before progressively shifting toward thicker layer from 45 degrees and below. This effect was expected as a result of the diminution of the gravity contribution with the angle, also predicted from equation (3), and shown in Figure 20b). Indeed, viscous flow induced by gravity is responsible for the thinning of the liquid film and, in the case of angular dip, this viscous flow is proportional to the sin θ . In other words, at very low dipping angle (low θ), draining will be considerably reduced leading to thicker films. Besides, the linear tendency extends to much lower speeds for lower dipping angles. This is because at lower speeds the capillary contribution cannot be neglected anymore when close to vertical geometry (θ = 90 degrees). However, in the case of low dipping angles, the evaporation rate is reduced which in turn diminishes the capillary regime contribution.

Variations from the theoretical model predicted in equation (3)

A more convenient way to address and visualize the shift in the draining regime when going to lower angles is to plot the experimental thickness h_{exp} versus the dipping angle for different vertical speeds, taken in the pure Landau-Levich regime (e.g. 0.2; 1 and 5 mm.s⁻¹). In Figure 22a, such experimental results are plotted and compared to the theoretical thickness h_{theory} calculated from the theoretical equation (3) in evaporation-free (*E=0*) ideal conditions (the left part of the equation corresponding to the capillary contribution is equal to zero). Calculation of h_{theory} was made using $kD=1.8.10^{-4} \text{ mm}^{1/3}\text{s}^{2/3}$,

a value deduced from the linear regression of data obtained in the vertical geometry (θ = 90 degrees). We logically assume that the dynamic viscosity, the surface tension and the density of the fluids are equivalent for all dipping angles. In view of Figure 22a, one can observe that experimental points follow quite well the theoretical data for large dipping angle but they become dramatically lower than the theoretical predictions when dipping angles are below 30 degrees. This effect is amplified for faster withdrawal speeds. To assess the deviation from the theoretical value, the ratio between the experimental and the theoretical thicknesses h_{exp}/h_{theory} can be plotted. Figure 22b displays such a diagram. As expected the deviation is quite low for angles above 30 degrees then it increases as the dipping angle diminishes. At 2 degrees, close to the horizontal configuration, the deviation from the theory is very high, reaching 40% for 0.2 mm.s⁻¹ and 80% for 5 mm.s⁻¹



Figure 22 : a) Plots of the thickness h_0 versus tilting angles (dipping angle) for vertical withdrawal speeds u of 0.2, 1 and 5 mm.s⁻¹. Dashed lines correspond to calculated theoretical curves from equation (3). b) Plots of h/h_t (corresponding to h_{exp}/h_{theory}) versus tilting angles for vertical withdrawal speeds u of 0.2, 1 and 5 mm.s⁻¹(dashed lines are given as guides for the eyes). In both diagrams, the theoretical thickness is calculated for evaporation-free (E=0) ideal conditions.

According to equation (3), theoretical calculation of the film thickness at an angle of 0° should result in a film of infinite thickness which of course is practically impossible. It seems that it exists a film thickness limit above which the method provides the same thickness, whatever the applied dipping angle and the withdrawal speed. This explains why the experimental data deviate from the theory for low dipping angles and high withdrawal speed. This is related to the physical-chemical characteristics of the fluids that does not allow film thicknesses (or mass per unit surface submitted to the gravity force) above a certain limit. When the substrate is withdrawn from the solution, an equilibrium exists between the adhesion forces existing at the interface with the substrate which is transmitted away from the surface through the molecules composing the fluid in relation with the viscosity. Those forces have a finite value which result in a finite film thickness. On the other side, at extremely low speeds and in evaporation-free conditions, a lower limit of the thickness also exists, that must be close to the definition of a Langmuir film, composed of a single layer of non-volatile molecules that directly interact with the surface. This explains why the experimental data deviate from the theory for low dipping angles and low withdrawal speed.

In order to complete the investigation, the critical speed u_c and the critical thickness h_c were measured graphically. Those values correspond to the speed and thickness obtained at the minimum of the curve as displayed in Figure 23a (see circles). Only coatings deposited at angles above 30 degrees are considered since at lower angles as the capillary contribution becomes negligible, no minimum is found. These points can also be obtained by resolving the derivative of equation (3) in the conditions dh/du = 0^{18} . At this critical point, the contribution to the final thickness of the draining regime is equal

to the contribution of the capillary regime. Moreover, the variation of the draining contribution for angles above 30 degrees can be considered as negligible (curves overlap in the Laudau-Levich regime). Figure 24b and c show the evolution of u_c and h_c as a function of the cosine of the dipping angle. From those figures, u_c and h_c decrease with the dipping angle and exhibit a linear dependence with the cosine of the angle. This is consistent with the fact that in the specific conditions when u_c and h_c are deduced, and for angles above 30 degrees, the draining contribution is constant and the only variable is the evaporation rate E (note that the evaporation rate is the main variable in kE/L, k being the material proportional constant and L the substrate constant width).



Figure 23 : a) Log-log plots of the thickness h_0 versus vertical withdrawal speed u for dipping angles (θ) ranging from 90 to 30 degrees. The circles correspond to the critical speed u_c and thickness h_c where both capillary and draining regimes have equivalent contribution. b) Plot of critical speed u_c vs cos θ ; c) Plot of critical thickness h_c vs cos θ . Dashed curves are added as guides for the eyes.

Finally, the *KE/L* constant associated to the evaporation rate driving the capillary regime, was deduced by fitting the experimental points with equation (3) and assuming again that $kD=1.8 \times 10^{-4} mm^{1/3}s^{2/3}$. Figure 24 can be exploited to deduce the evaporation rate variation of the wet coating (present on the lower part of the substrate during deposition) depending on the applied dipping angle. It is clear from this last plot that for angles below 30 degrees ($\cos\theta < 0.87$), the evaporation is quasi inexistent (E \approx 0) and the film formation follows perfectly the tendency described by the equation (3) of Landau-Levich modified by Tallmadge for angle dependence (linear tendency in log-log plot).



Figure 24: Plot of evaporation rate constant kE/L vs $cos\theta$. The dashed curve is added as guide for the eyes.

I.3. Example of application

In order to confirm the robustness of the low-angle dipping method, a TiO₂-based coating was applied only on the lower side of a 2 mm thick, 130 x 160 mm², glass substrate (see details in the experimental section). In general and in the present case, at very low dipping angle and depending on the dimensions of the substrate, only the lower side is immerged in the solution. Ellipsometry investigations reveal that a homogeneous thickness of about 20 nm was deposited all over the substrate. The quality of the deposition in this low dipping angle conditions is illustrated by Figure 25 where the coated glass substrate on the left appears homogeneous and clearly more reflective, as a result of the presence of 20 nm of high refractive index TiO₂ ($n_{dense TiO₂, 600 nm$ =2.25), than a non-coated glass on the right. As in all dip-coating configurations, a drop is formed at the bottom of the substrates at the final stage of the withdrawal, when both substrate and solution separate. This drop can be technically eliminated by bridging the lower part of the substrate and the solution with a drain.



Figure 25 : Picture of glass substrates coated with 20nm of TiO_2 at a dipping angle of 1° (left) and noncoated (right) for comparison.

I.4. Conclusion

It was demonstrated that dip-coating a flat substrate at very low angle, close to the horizontal position, can be exploited to deposit sol-gel solutions exclusively on the lower side with an excellent control over the thickness. This configuration avoids perturbations associated to evaporation and is compatible with large surfaces and high throughput. It also presents the advantage of coating only one side of a flat substrate. We also demonstrate that a wider range of thickness can be obtained with a single solution at low angles when compared to the conventional vertical configuration, limited in both low and high speeds by the physico-chemical characteristics of the initial solution. Finally, we show that the Landau-Levich model, modified by Tallmadge for angle dependence, is verified for intermediate conditions.

Summary

- By dipping at low angles, a larger thickness range is possible for a given formulation (*i.e.* from 10 to 850 nm at 2 degrees instead of 53 to 530 nm in vertical configuration).
- > A theoretical model for angle dip is proposed and studied
- From the semi-empirical equation developed here, it is possible to predict the experimental thickness
- > Dip-coating of a single face of a substrate at very low angle is demonstrated
- > Deposition technique compatible with large scale production (solar panels)

II. Fast Focused Ion Beam lithography on porous sol-gel layers

Focused Ion Beam is a powerful direct lithography technique with high resolution but very low throughput (see Chapter I). FIB lithography is usually performed on silicon wafers as they are standard microelectronics substrates: it is mainly used for prototyping and failure analysis. In the current thesis, this technique is used to design complex masters for nano-imprint lithography (NIL). By applying FIB on porous layers, it will be demonstrated that the speed of milling can be dastrically increased compared to standard silicon substrates (Figure 26).



Figure 26 : a) Scheme representing the focused ion beam milling of a silicon substrate to design a motif that will then be used as a master for NIL. b,c) Scheme representing the depth reached by FIB milling of the substrate surface for a given ion dose in the case of a silicon substrate and a porous sol-gel layer respectively.

Experimental procedure

The sol-gel solutions used to perform the investigation were prepared from the molar ratio described in Table 2:

TEOS	MTEOS	TiCl₄	H ₂ O	EtOH	HCI	F127
0.5	0.5	/	3	40	0.0042	2.10 ⁻⁴ - 6.10 ⁻³
/	/	1	7	40	/	2.10 ⁻⁴ - 6.10 ⁻³

Table 2 : Molar ratios of the precursors and solvents used in this chapter.

The quantity of F127 (Polyethylene oxide-Polypropylene oxide triblock Pluronic copolymer) is varied from 2.10^{-4} to obtain dense films to 6.10^{-3} for highly porous films. The range of porosity investigated in this study is obtained by changing the F127 quantity between those two values. The solutions are stirred for 24 h at room temperature before deposition by dip-coating at 23 °C and a relative humidity of 20%. Straight after deposition, the films are annealed at 450 °C for 30 mins under IR lamps and their refractive index and thickness are measured by spectroscopic ellipsometry (see Appendix).

A Focused Ion Beam (FIB) with a Liquid Metal Alloy Ion Source (LMAIS-FIB) is used with an AuSi source. The FIB column uses a Wien filter in order to get only one specific ion specie, Au⁺ in our case, chosen for its abundance compared to Au²⁺ and high sputtering rate. As FIB is generally used to etch a surface, the milling speed can practically be defined as the time necessary to etch a given pattern. However this value depends on many different parameters such as the acceleration voltage and the probe current (quantity of ion per second reaching the substrate). Here an acceleration voltage of 30 kV and a probe current of 130 pA is used. A convenient way to assess the milling rate is to measure an excavated volume (μ m³) for a given absolute ion dose (pC) thus in μ m³/nC. Two milling rates are used

in this study: the **standard milling rate** is a measurement of the etched volume for a given dose whereas the **differential milling rate** takes into account only the etched volume in between two successive measurements. The latter is used to obtain the milling rate when the evolution of the etched volume with the ion dose is not linear. In the case of a linear evolution, the standard and differential milling rates are equal. As the etched area varies along the study, and for the sake of comparison, the ion dose per surface (pC/cm²) will be used in graphs and discussions instead of the absolute ion dose (pC). In any case, all the ion doses used in this study are considered sufficient to induce etching of the layer. Phenomena valid for very low doses, such as swelling and amorphisation of the layer (in the case of Si) will be neglected.

II.1. Study of the mechanism of FIB milling of porous layers

To study the influence of the layer porosity, different silica and titania layers were deposited on silicon substrates with porosity ranging from 0% to 73%. Volumic shrinkage upon annealing being higher for TiO₂ than for SiO₂, highly porous TiO₂ is more challenging to achieve. This is the reason why titania films with porosity above 60% could not be easily achieved. $1.5 \times 1.5 \mu m^2$ squares were etched on various substrates using a fixed dose of $3 \times 10^9 \, pC/cm^2$. The excavated volume was deduced from AFM analyses and normalized to the dose in order to obtain the milling rate. Figure 27 shows the evolution of the milling rate with the layer porosity with a relative milling rate of 1 corresponding to dense silicon (0.38 $\mu m^3/nC$). No significant difference is reported between dense silicon, dense SiO₂ and dense TiO₂. Interestingly, the milling speed is seen to increase exponentially with the porosity. For instance, a speed of $1.41 \, \mu m^3/nC$ is found for a SiO₂ layer with 42% porosity whereas it goes up to $5.86 \, \mu m^3/nC$ for a 73% porous SiO₂ layer which is an increase by a factor 15 compared to silicon. The lower pulverization for TiO₂ films can be explained by the fact that the molar mass of silicon is lower than the one of titanium. Since our goal is to increase the milling rate as much as possible, only SiO₂ films will be studied thereon.



Figure 27 : Evolution of the milling rate for SiO_2 and TiO_2 layers with various percentage of porosity normalized to the milling rate of silicon. Dotted lines are added as guides for the eyes.

If we now look at the excavated volume as a function of the dose – by etching a 1 μ m thick, 48% porous SiO₂ layer – its evolution can be approximated by three successive linear regimes with a progressive decrease of the milling speed (Figure 28a). Very fast milling is found in regime I for very low doses. It quickly evolves towards a second regime with a slower milling rate constant over a wide range of doses.

The critical dose (D_c), marking the transition between regime I and regime II, can be graphically deduced: $D_c = 4 \times 10^8 \text{ pC/cm}^2$. Finally, a third regime is reached for very high doses corresponding to etched depths of more than 1 µm.

Another, more convenient, way to visualize the different regimes is to plot the differential milling rate as a function of the dose (Figure 28b). This value corresponds to the milling rate between two data points (slope of the curve between two successive data points in Figure 28a) and does not take into account the relative contribution of the previous regimes. The differential milling rates are extracted graphically and summarized in Table 3. In the first regime, the pulverization goes up to $4.0 \pm 0.3 \,\mu\text{m}^3/\text{nC}$ while it decreases to $1.0 \pm 0.25 \,\mu\text{m}^3/\text{nC}$ in the second regime and to $0.36 \pm 0.05 \,\mu\text{m}^3/\text{nC}$ in regime III. Regime III actually corresponds to the etching of the silicon substrate – when the porous layer has been entirely etched - as confirmed by AFM and by subsequent ellipsometry analysis. In any case, as long as the pulverization involves the porous layer (regime I & II), the milling rate remains faster than for dense layers ($0.38 \,\mu\text{m}^3/\text{nC}$ for silicon).



Figure 28 : a) Milling rate and b) differential milling rate as a function of the dose. The layer used in this experiment is porous SiO_2 with a thickness of 1 µm and a porosity of 48%. Three different regimes can be determined.

Regime	Dose range (pC/cm ²)	Differential milling rate (µm ³ /nC)
I	< 5 x 10 ⁸	4.0 ± 0.3
П	5 x 10 ⁸ - 5 x 10 ¹⁰	1.0 ± 0.25
III	> 5 x 10 ¹⁰	0.36 ± 0.05

Table 3 : Summary of the three regimes with corresponding differential milling rate and the dose range in which each regime is valid.

Environmental Ellipsometric Porosimetry

To get some insight into the mechanism and understand the nature of regime I and II, the characteristics of the films were systematically analyzed by ellipsometry. To do so, large squares of 400 x 400 μ m² were etched in a 1 μ m thick porous silica layer (66% porosity) in order to get a homogeneous area for the ellipsometer beam (Figure 29). The ellipsometry beam was manually aligned using a home-made set-up with a CCD camera mounted onto an optical microscope. This system allows to obtain sufficient resolution to align correctly the beam onto the impacted areas. Whatever the dose, the layer could be divided into a top "impacted" layer and a bottom "non-impacted" layer (with the same refractive index than far from the etched zones). Experimentally, the film was fitted with a bi-layer Cauchy model with fixed refractive index for the bottom layer (n = 1.17+0.01/ λ^2) and a varying thickness (as the thickness decreases with increasing dose). The refractive index and the thickness of the top layer were also fitted. For all doses, the thickness of the top impacted layer was found to be h_c = 50 ± 10 nm. The model assumption of a sharp change between impacted zones, non-impacted zones and pure dielectric layers is a good approximation (Mean Square Error, MSE < 20) for doses corresponding to regime I. The remaining layer thickness of the etched area (thickness of the impacted layer) was systematically compared with AFM data of the etching depth.



Figure 29 : Scheme representing the etched porous layer analyzed by ellipsometry using an alignment system composed of an optical microscopic lens and a CCD camera. The etched areas were large squares of 400 x 400 μ m² in order to perform ellipsometry analysis. The layer etched by FIB can be divided into two sub-layers: one top "impacted" layer of thickness h_c = 50 ± 10 nm and one bottom "non-impacted" layer having the same characteristics than the initial porous layer.

First, the evolution of porosity of the top "impacted" layer is studied and deduced from its refractive index using a Bruggeman Effective Medium Approximation (BEMA) (see Appendix). Results are displayed in Figure 30a. For small doses, corresponding to regime I, the porosity of the top layer is seen to decrease rapidly with increasing etching dose and reach 0% for a critical dose of $D_c=2.7 \times 10^8 \text{ pC/cm}^2$ which corresponds to the transition between regime I and regime II. For this dose and for all

measurements corresponding to regime II, the top densified layer was found to have a refractive index above the one of dense silica ($n_{dense SiO2} \sim 1.5$) and a poor fit as detailed below.

SEM images of the five doses corresponding to regime I are displayed in Figure 30b (equivalent to the data points in Figure 30a). Before milling, the small pores corresponding to the F127 porosity are visible at the surface (pore diameter around 7 nm). In the second image, after the lowest ion dose, the morphology of the pores is drastically different. The pore average diameter increases to about 30 nm probably resulting from a reorganization of the initial porosity. With an increasing etching dose, the pores gradually collapse to yield a smooth surface. This densification is consistent with the increase of the layer refractive index. Moreover, for the highest dose (D_c , 2.7 x 10⁸ pC/cm²), some nanoparticles are visible at the surface. These gold nanoparticles are likely originating from the implantation of gold atoms into the layer (since Au⁺ is used as the incident ion) followed by nucleation and growth. In addition, the presence of gold nanoparticles would explain that the refractive index for the highest dose was found to be superior to the one of dense silica. We will see latter that these nanoparticles induce a clear plasmonic band in the k distribution of the layer optical constants.



Figure 30 : **a)** Evolution of the porosity as a function of the dose measured by ellipsometry. The critical dose D_c corresponds to the dose for which the porosity reaches 0%. **b)** SEM images of the substrate surface taken at different doses corresponding to the five data points on the curve a). **c)** Adsorption-desorption isotherms and **d)** corresponding pore size distributions for a non-impacted film and an impacted film after a dose of $2.7 \times 10^8 \text{ pC/cm}^2$ and a reference taken far from the impacted areas. After etching with a dose corresponding to regime II, the porosity is seen to entirely collapse.

To analyze the pore size distribution, Environmental Ellipsometric Porosimetry (EEP) was performed using isopropanol (see Appendix for the explanation of EEP). Figure 30c shows the results for a non-

impacted layer and an impacted film with a dose of $2.7 \times 10^8 \text{ pC/cm}^2$ and a reference taken on the porous layer far from the areas impacted by the ion beam. In the case of a non-impacted layer, the isotherm is typical of mesoporous films. The pore volume was determined to be of about 59% with an average pore diameter of 7 ± 2 nm as expected from F127-templated films (Figure 30d). This is in good agreement with measurements far from the etched areas (porosity 66%, pore diameter of 7.2 ± 2 nm) confirming that the bottom layer is indeed untouched by the ion beam. As the EEP treatment was done on a multilayer system, this adds a degree of complexity to the calculations and is probably the cause of the slight deviation between the reference and the non-impacted layer. EEP analysis of the impacted film shows no solvent adsorption confirming the collapse of the porosity and its densification.

Confirmation of gold implantation

To confirm the nature of the nanoparticles observed on the samples surface, TEM analysis was performed on the impacted areas for a high dose (regime II, $3 \times 10^9 \text{ pC/cm}^2$). Figure 31a shows the TEM cross-section of the film. The darker zone at the surface corresponds to the top densified layer. The thickness of this layer is measured to be of about 50 nm which is consistent with the ellipsometry model used before (h_c = 50 ± 10 nm). The impacted layer is seen to extend to the sides of the etched area due to beam tails (the energetic distribution of the beam can be defined by a Gaussian). EDX analysis confirms the presence of gold implanted in the dense region on a depth up to 60 nm with a maximum of 20% of gold in the layer (Figure 31b). Further away from the impacted zone, the stoichiometry of the silicon oxide is retrieved (67% oxygen, 33% silicon) confirming that after a depth of 60 nm, the layer is mainly unchanged.



Figure 31 : a) TEM cross-section of the etched area, the impacted layer close to the surface has been densified after FIB etching. The arrow indicates the position where the EDX profile was taken. b) EDX analysis profile following the arrow in a), gold implantation is visible up to 50nm in the layer. c) Ellipsometry analysis showing the refractive index n (full lines) and absorbance k (dotted lines) of a non-impacted and an impacted layer.

Furthermore, after milling, the refractive index of the impacted layer is seen to shift from a standard Cauchy model for dielectrics to a more complex model with light absorption at near-UV frequencies.

It is for this reason that a poor fit was obtained for doses corresponding to regime II when using a purely dielectric model. In Figure 31c, the refractive index n and absorbance k are plotted for a non-impacted layer and a layer etched with the same dose of that studied in TEM (zone II, $3 \times 10^9 \text{ pC/cm}^2$). Before etching, the refractive index is n = $1.17+0.01/\lambda^2$ with k = 0 (Cauchy model for dielectrics) whereas the refractive index varies strongly with the wavelength and goes up to 2.5 at 600 nm for an impacted layer (n_{dense SiO2} ~ 1.5). A large absorption centered at 420 nm is visible for the impacted layer which is attributed to the plasmonic resonances caused by the presence of gold nanoparticles.

Proposed mechanism

A possible mechanism is schematized in Figure 32. Regime I thus corresponds to the densification of the top 50 nm of the film from a porous non-impacted layer to a dense layer, the milling rate is extremely fast as the porosity collapses. Gold atoms are implanted forming small nanoparticles and further densifying the layer. In regime II (reached after a dose $D = 5 \times 10^8 \text{ pC/cm}^2$), a steady state is reached with an equilibrium between etching and pore collapsing. The milling speed is lower than in the case of the first regime but superior to the milling speed of the bulk material. The top densified layer remains at a critical thickness of $h_c = 50$ nm, its density is constant and higher than the one of dense silica due to gold implantation. Its thickness is determined by the depth of interactions between the incident ions and the layer. Interactions can be divided in several categories as there is a cascade of collisions during the interaction of incident ions with the substrate such as the heating and the creation of defects in the layer, the displacement of the layer atoms in the matrix or their sputtering, or the implantation of the incident ions. The study of all those interactions is very complex and out of the scope of the current thesis. Nevertheless, the depth of implantation can be approximated by simulations such as SRIM (Stopping Range of Ion in Matter) simulations¹⁰⁴ (Figure 33). In the case of gold ions at 30 keV (similarly to the experimental conditions) in dense SiO₂, the simulation gives an implantation range maximal at 22 nm with a wide sphere of interactions of about 20 nm around the maximum. This value is in good agreement with the measured critical thickness of 50 nm which corresponds to a maximum of interaction at a depth of 25 nm with a large size distribution. The thickness of the densified layer might thus change with the ion energy or the type of ions (Ga, Si, Au ...). Finally, regime III begins when the densified layer reaches the substrate. In this case, the ion beam interacts only with dense materials and the milling rate falls back to the value corresponding to the substrate which, in our case, is the value for silicon.



Figure 32: Possible mechanism for the etching of porous layers by Focused Ion Beam. In regime I, a thin layer at the surface is impacted and progressively densified. In regime II, a steady state is reached, the

milling speed decreases. The dense impacted layer thickness (h_c) remains at ~50 nm. Its density is higher than the one of dense silica due to gold implantation. In regime III, only the densified layer is left, the milling speed diminishes towards the speed on a dense layer.



Figure 33 : SRIM simulation of the ion implantation depth with increasing energy (5, 10, 20, 30 keV) for Au^{+} in dense SiO₂¹⁰⁴.

II.2. Application as soft-NIL masters

To put this in the context of master fabrication, the overall speed of the process will be highly dependent on the requested depth. Indeed, for shallow motifs, only regime I will be used which relate into a huge increase of the etching rate. For deeper motifs, the time spent in regime II can be a preponderant portion of the overall etching time decreasing the total etching speed. Nevertheless, in this regime, the etching rate is still more than twofold the one of silicon, the total etching time will thus still be greatly reduced.

Samples etched by Focused Ion Beam will be used in this thesis as masters to make PDMS stamps for soft-nano imprint lithography. FIB gives a good resolution (theoretically down to 5 nm) and allows to etch side by side different patterns with various depth and shape. Experimentally, we use a LMAIS-FIB with Au⁺ at a probe current of 35 pA and an acceleration of 30 kV to fabricate masters with a maximal resolution of about 70 nm for large and deep etched patterns. Lower probe current is equivalent to slower etching rate but better resolution. To better understand the advantages of using a porous layer for master fabrication, the etching parameters for an array of squared pillars will be detailed. To yield squared pillars, a network of lines was etched in the substrate. To etch lines on a 20 x 20 μ m² surface with a pitch of 1 μ m and a depth of 500nm (yielding a network of squares after etching, see Figure 34), 33 mins are necessary on a silicon substrate. By using a SiO₂ layer with a porosity of 73% this value goes down to 3 min. This allows to etch larger surfaces in shorter times. For instance in the same time necessary to etch a 20 x 20 μ m² zone in silicon, a 60 x 70 μ m² can be etched on 73% porous SiO₂.



Figure 34 : (right) SEM image of a pattern of lines (yielding squared pillars) etched by FIB on a porous layer with a pitch of 1 μ m and a measured depth of 500 nm. (left) Chart representing the time necessary to etch the motif on the left on an area of 20 x 20 μ m².

The implantation of gold in the layer can be a problem for a number of applications, in particular in microelectronics, but not for master fabrication. Moreover, even if the porous layer could be mechanically weak, the top densified layer at the surface strengthens the structure. In addition, the PDMS precursor infiltrates the layer porosity, hardening the network. In the case of a 73% porous layer, the refractive index is seen to increase strongly after PDMS casting and demolding (n_{600nm} = 1.17 before casting and n_{600nm} = 1.40 after the mold removal). This confirms the possibility to use FIB on porous layers to make robust masters for Soft-NIL. Such masters were used to produce dozens of moulds without any evidence of lower mechanical resistance than standard silicon masters. Those masters will be used in Chapter III for soft-NIL on sol-gel layers for applications in photonics.

Summary

- > FIB on porous layers give a higher milling speed up to a factor 20
- > A mechanism with three successive regimes was ascribed
- ➢ In regime I: A densification of the porous layer occurs by pores collapsing and gold implantation. A very high milling speed is found.
- In regime II: A steady state is reached with a stable densified layer of 50 nm in the case of Au⁺. The milling speed is constant and faster than for dense substrates.
- In regime III: the porous layer has been completely etched, only dense material is left. The milling speed decreases to the one corresponding to the substrate.
- > Porous layers structured by FIB proved to be robust masters for Soft-NIL

III. Dewetting of thick layers of Si/Ge for randomly dispersed islands

Dewetting of semiconductors is well-studied experimentally and theoretically for ultra-thin layers with thickness of less than 20 nm ^{82,83,96,105,106}. On the other hand, instability and dewetting of thicker layers has never been reported so far even at high temperature and under ultra-high vacuum. Here, we demonstrate that thick layers of silicon-germanium alloys can be dewetted in certain annealing conditions. The resulting dewetted structures will be used as masters in soft-NIL (see Chapter III) and templated dewetting of thick semiconductor layers will be presented in Chapter IV by combining this process with nanoimprinted surfaces.

The main part of the experiments presented here were performed by Mr. Mohammed Bouabdelaoui as a close collaboration with our team and in particular with Dr. Marco Abbarchi, my role was mainly focused on using such dewetted surfaces as masters for soft-NIL.

Experimentally, silicon on insulator layers (Si substrate/ 25 nm SiO₂ / 14 nm Si layer) are used after being thoroughly cleaned by successive immersion in concentrated HF (30%) and concentrated HNO₃ (70%) in order to remove the first few nanometers of silicon and to minimize surface defects. Straight after chemical treatment, substrates are placed under ultra-high vacuum and a layer of Si_{0.7}Ge_{0.3} of a given thickness is deposited by molecular beam epitaxy. SiGe alloys are preferred for the study instead of pure silicon in order to facilitate dewetting. Indeed, germanium has a lower melting temperature than silicon, its diffusion will thus be higher. During deposition, substrates are maintained at a temperature T_{dep} . After deposition, substrates are annealed at 800 °C for 4 hours in order to promote diffusion and to trigger dewetting. Such conditions are summarized in Table 4.

	Thickness deposited	Temperature of deposition (T _{dep})	Dewetting conditions	Dewetting?
а	50 nm	500°C	800°C, 4h	Yes
b1	200 nm	500°C	800°C, 4h	No
b ₂	200 nm	700°C	800°C, 4h	Yes

Table 4 : Summary of the conditions used for dewetting Si_{0.7}Ge_{0.3} layers of various thickness.

First, a "standard" dewetting is performed on a thin layer of Si_{0.7}Ge_{0.3} (deposition of 50 nm of Si_{0.7}Ge_{0.3} at 500°C, annealing at 800°C for 4 hours). In those conditions, the thin film dewets to form isolated islands as schematized in Figure 35a driven by the minimization of its surface energy. The mechanism of dewetting starting with the formation of void localized at a defect and its evolution towards elongated fingers and finally to isolated islands is described in Chapter I⁸². The same procedure is followed for thicker films: deposition of 200 nm of Si_{0.7}Ge_{0.3} at 500°C followed by annealing at 800°C for 4 hours (Figure 35b₁). In those conditions, dewetting does not occur. The layer is stable as the energy barrier is too high for dewetting to start (lower surface to volume energy). AFM characterization shows that the deposited film has a very low roughness (Root Mean Square roughness (RMS) = 0.37 nm) which is consistent with a conformal deposition. After annealing, the roughness increases (RMS = 14.3 nm) but the layer remains stable. In contrast, if the deposition of 200 nm of Si_{0.7}Ge_{0.3} is performed at 700 °C, the layer is seen to dewet (Figure 35b₂). Just after deposition, the roughness is very high (RMS = 35.5 nm) with pits up to 140 nm depth. This large thickness fluctuation will promote diffusion and will be sufficient to drive the layer towards a fully dewetted system with isolated islands (see SEM and AFM images in Figure 35b₂). The final structures are homogeneous all over the sample on a scale of several centimeters.



Figure 35 : Comparison of dewetting for a) ultra-thin layers of SiGe (h < 50 nm) and b) thick layers of SiGe (h >> 50 nm). Annealing is performed at 800°C. For thick layers, the system remains stable if the deposition temperature (T_{dep}) is under 500°C (b_1) while it dewets for a deposition at 700°C (b_2). AFM and SEM images corresponds to a 50 nm Si_{0.7}Ge_{0.3} layer and 200 nm Si_{0.7}Ge_{0.3} layer in case a) and b) respectively.

Interestingly, in the first steps of dewetting of thick layers, matter arranges into a fully interconnected network that will eventually break up and form isolated islands as the dewetting proceeds. This network is not seen in the case of ultra-thin semiconductor layers and is very similar to polymer phase segregation and hyperuniform spinodal structures¹⁰⁷. By increasing the temperature or dewetting time, it is possible to map this evolution from a continuous network to isolated islands (see Figure 36).

Various parameters can be modified to tailor such systems. By changing the layer thickness, the size and density of the resulting objects will vary with larger, more spaced islands for thicker layers. By changing the layer composition (Si_xGe_{1-x}) , the shape of the islands can be modified with higher aspect ratios (higher height to diameter ratio) for higher Ge proportion¹⁰⁸.

Importantly, in the case of connected networks or isolated islands, the dewetted structures are randomly dispersed over the surface with no ordering at short or long range. As a consequence, they do not display any light diffraction properties (*i.e.* constructive interferences). In term of applications, such dewetted layers will be used as masters to imprint random 3D structures on large scales (Chapter III) and could find application in optical coatings or for microfluidics. For instance, connected networks with a height of few hundred nanometers could give anti reflective coatings with interesting mechanical properties. Moreover, dewetting of thick semiconductor layers will be directed with precise organization of the islands by dewetting such layers on nanoimprinted substrates (see Chapter IV).



Figure 36 : SEM images presenting the evolution of a 150 nm thick $Si_{0.7}Ge_{0.3}$ layer with advancing dewetting deposited at 700 °C and dewetted at 800 °C for 4 h. The layer first breaks into connected islands before evolving towards isolated objects. The evolution of the islands morphology is followed from the center (connected network) to the side of the substrate (isolated islands) due to temperature gradient (higher temperature on the sides).

In summary, we demonstrated that thick layers can be destabilized as long as they display a sufficient roughness before dewetting. To do so, coatings are deposited at temperatures over 500 °C. During dewetting, an intermediate state with an interconnected network was observed, yielding isolated islands after extended annealing. Homogeneity of the structures is visible on a scale of several centimeters. Dewetted structures do not diffract light as they are randomly arranged. Such layers will be used as masters and replicated in sol-gel materials (Chapter III).

Summary

- > Possible to dewet thick layers (h > 50nm) of semiconductors on very large scale
- Deposition of SiGe needs to be perform at high temperature (T>500°C) to obtain coatings with high roughness in order to trigger dewetting
- Interconnected networks were found corresponding to a transitional dewetting stage

IV. Conclusion

In this chapter, techniques to fabricate nanostructures on larger surfaces were developed. First, angular dip-coating was shown to allow the deposition of a wider range of thicknesses from a single formulation just by varying the withdrawal speed. In particular, by dipping at a very low angle, single-face deposition was demonstrated. Direct lithography by focused ion beam was proven to be far more effective on porous layers prepared by sol-gel chemistry than on conventional silicon substrates. The milling rate was found to increase with the value of the layer porosity up to a factor 20 compared to dense layers. This allowed quick prototyping of soft-NIL masters that will be used in Chapter III. Finally, random dewetting of thick layers was proven to be possible by increasing the deposition temperature. Homogeneous interconnected networks or isolated islands were obtained on 2 x 2 cm². Resulting structures showed no organization at short or long range, interesting for optical applications as non-diffractive coatings. Directed dewetting of thick layers will be presented in Chapter IV while randomly dewetted structures will be used in Soft-NIL in Chapter III.

Chapter III: Nanofabrication by Soft Nano Imprint Lithography (Soft-NIL)

I. Principle of Soft-NIL on sol-gel materials

The first work on nanoimprint lithography (NIL) was developed by Stephen Chou *and al.* in the 1990s when its team reported 25 nm patterns, initially etched in a silicon mould, transferred in a polymeric resist ¹⁰⁹. His experiment was performed by strongly pressing (P=50-100 bars) while heating at 100 °C to deform and shape the thermoplastic polymer. This study opened the way to lithography at the sub-100nm scale. Imprinting of sol-gel resists was first demonstrated by Lukosz *and al.* in the 1980s at high pressure (P=280-500 bars) through the appellation of hot embossing ¹¹⁰. Even if the pressure used to imprint the sol-gel resist was rapidly reduced, it still represented one of the major drawback of this technique. Indeed, silicon substrates used in microelectronics can easily break if the applied pressure is not perfectly homogeneously. Moreover, the use of hard and brittle moulds (mostly silicon or fused silica) presented several downsides: (i) resist often sticks to the mould surface due to its high surface energy (ii) long range deformation can easily break the mould (iii) solvent and air bubbles cannot escape once trapped under the mould (iv) rigid moulds cannot accommodate any curvature or defects. Due to all those limitations, costly hard moulds could be used only a very limited number of times.

The emergence of **Soft Nano Imprint Lithography**, first developed by Whitesides *et al.* in the 1990s, tackled all those problems by the introduction of polydimethylsiloxane (PDMS) elastomeric moulds⁵⁹. Soft moulds have a low surface energy (y^{PDMS} = 21 mJ.m⁻² compared to y^{Si} = 52 mJ.m⁻²), are permeable to solvent vapors and can deform to follow the features of the substrate (Figure 37). In addition of being inexpensive, each PDMS mould can be used dozen of times. Soft-NIL allowed to drastically reduce the pressure (P < 5 bars) and temperature applied to emboss the resist layer. With the huge improvements made in the past decades, Soft-NIL is currently performed at ambient pressure and room temperature and is now reaching sub-10nm resolution^{61,62} on sol-gel resists when performed with optimized PDMS moulds as detailed below.



*Figure 37 : a) Chemical formula of linear polydimethylsiloxane (PDMS). b) Pattern imprinted over a dust particle demonstrating the flexibility of the mold (from ref*⁶¹*)*

I.1. High resolution PDMS stamps

To fabricate a mould, a prepolymer - generally composed of vinyl functionalized linear di-methylsiloxane (Fig. 10(a)) and a silicon-hydride functionalized linear di-methyl-siloxane – is mixed with a catalyst – generally a platinum compound - and poured onto a patterned surface. The crosslinking reaction, called hydrosilylation, is catalysed by platinum and involves the addition of Si-H bonds across unsaturated bonds:



The transition of the prepolymer from a viscous liquid to a solid elastomer takes usually several hours at room temperature. It is generally accelerated by heating at a mild temperature for instance 70 °C. The hydrosilylation crosslinking route is generally preferred as no by-products are formed and it offers a comfortable working window before extended crosslinking.

Once fully crosslinked, the resulting mould is easily demoulded from the master thanks to its elasticity (Figure 38a & b). The mould perfectly replicates the initial master features (relative shrinkage between master and mould can be neglected) and can be used dozens of times. In addition, many moulds can be fabricated from a single master. However, with extensive use, defects will start to appear on the master mainly due to local adhesion of PDMS during mould release (Figure 38c). It is for this reason that the surface of the master (for instance made from silicon) is functionalized (e.g. with fluoroalkylsilanes) to decrease the surface energy and reduce the interactions with the PDMS chains.



Figure 38: a) Schematic representation of the mould preparation. The precursor is poured onto the hydrophobized surface of the master and cured before demoulding. b) Picture of a silicon master and its negative replica into a flexible mould. c) SEM image showing a defect on a silicon master after the preparation of many PDMS stamps.

When patterns with features smaller than 100 nm are needed, the excessive softness of PDMS can induce deformations of the mould shape. This phenomenon has been widely studied both theoretically and experimentally^{111–114}. As first demonstrated by Delamarche *et al* ¹¹¹, only a fraction of the structures accessible by nanofabrication in hard materials will give stable structures in PDMS stamps. If the aspect ratio (defined as h/2a, where h is the height of the motif and a the half-width, see Figure 39a) is too high, structures can collapse under their own weight (see Figure 39a). Moreover, during the stamping process, capillary forces can be strong enough to deform the stamp features and contact two neighbouring structures. This is the case for densely packed structures, long grating lines or tightly spaced pillars. These structures are prone to pairing due to their high surface to volume ratio (see Figure 39). Once collapsed it is very hard to restore the PDMS features. Different ways of restoring the structures have been explored such as washing with low surface tension solvents or with water containing surfactants but without much success^{111,115}.



Figure 39 : a) Scheme of possible mould failures from excessive softness¹¹². b) Experimental observation of pillars failure. Optical images of a master (left) and its replica in PDMS (right). The master displays circular cavities (diameter 2 μ m, pitch 3 μ m, depth 1 μ m) and the corresponding PDMS mould has pillars of the same dimensions (diameter 2 μ m, pitch 3 μ m, depth 1 μ m). The pillars are seen to laterally collapse and pair with their neighbour forming agglomerates composed of several pillars.

The easiest way to prevent deformation of small patterns is to increase the rigidity of the PDMS material. Such PDMS called hard-PDMS (h-PDMS) have been first developed by Schmid et al in 2000¹¹⁶. Hard-PDMS uses branched siloxanes, shorter cross-linkers and a higher concentration of reactive groups compared to standard PDMS in order to increase the cross-linking density and the rigidity between the cross-linking points. The different concentration in reactants and their ratios have been extensively studied¹¹⁵ and commercial products are now available. Practically, PDMS hardness is estimated through its Young's modulus which is measured by indentation with a durometer shore A (35° truncated cone of 1.4 mm in diameter). For instance, Young's modulus of 20-30 MPa is typically expected for PDMS while it goes up to 60 to 70 MPa for h-PDMS. Of course, different materials than PDMS could also be used such as siloxane-composite¹¹⁷ or thermo-plastic polymers¹¹⁸ but they do not have the intrinsic advantages of PDMS. Similarly, using pure h-PDMS has limitations. First, a highmodulus polymer can increase the stress during the curing step, making it more difficult to separate from the master. Moreover, h-PDMS has a low degree of flexibility making it difficult for conformal contact on rough surfaces. The increase of rigidity would also lead to a poor accommodation to inhomogeneous stress during imprinting that might lead to plastic deformation or cracking of the stamp or of the substrate. In order to increase the rigidity and, at the same time, keep the advantages of low-modulus PDMS, hybrid stamps have been developed with a thin h-PDMS layer of few microns that contains the patterns and a thick layer of standard PDMS of about 0.5 mm (see Figure 40). In addition, to minimize in-plane deformation, for easier handling and automatization, this assembly (standard PDMS + hard PDMS) can then be backed by a thin glass plate as usually done for substrate conformal imprint lithography. Hard PDMS will be used in this thesis for soft-NIL of large scale structures for instance on the 1 mm² demonstrator presented at the end of this chapter.



*Figure 40 : Scheme of the hybrid PDMS mould with a thin stiff hard-PDMS layer bearing the patterns and a thick soft PDMS cushion layer. This assembly allows to establish conformal contact with high resolution. Reproduced from ref*¹¹⁹.

I.2. Context of Soft-NIL applied to sol-gel materials

Applying soft-NIL processes to directly imprint sol-gel metal oxides is highly interesting however it is quasi-unachievable due to two limitations: the impossibility to deform a brittle ceramic film and the difficulty to reach a plastic state at moderate temperature. A promising soft-NIL method on metal oxides exploits as-deposited sol-gel layers (xerogels). Xerogels are poorly cross-linked networks of solgel organometallic precursors or hydrolysed intermediates. Such gels remain flexible and will stiffen from advancing polycondensation during drying and ageing of the films and finally with thermal annealing to form the final metal oxides. The properties of xerogels can be exploited in soft-NIL at two conditions: (i) that imprinting takes place when the layer is under a gel-like form and (ii) the demoulding is made after sufficient solidification. Both these controls are challenging in sol-gel since the as-deposited layers undergo more or less fast cross-linking upon drying and mild thermal activation. These phenomena are generally accompanied by the release of water or solvent molecules that are trapped within the materials underneath the mould, affecting the replica morphology, density and shrinkage factor. For instance, TetraEthOxySilane (TEOS), a conventional silica precursor in sol-gel chemistry, can be used in Soft-NIL processes but it usually provides gels having a too rapid stiffening; the elapsed time between film deposition and Soft-NIL must then be very short. Alternatively, MethylTrieEthOxySilane (MTEOS) is used to decrease the condensation rate of the silica network⁴ due to the non-hydrolysable CH₃-Si bond. Eventually, the hybrid silica is converted into a purely inorganic structure after calcination and conversion of the CH₃^{120–122}. Non-silica metal oxides are also very interesting systems to pattern. However, only a few works addressing ZnO¹²³, ITO¹²⁴, PZT⁵⁴ or TiO₂¹²⁵ were reported, all underlining the high potential for micro and nano-fabrication but also the great difficulties intrinsic to the involved chemistries.

In the case of these transition metal oxides, one relies on sol-gel approaches and on the use of polymeric or organic stabilizing agents in order to adjust the rheology and the precursor reactivity and achieve a good resolution and a large geometrical aspect ratio of the final 3D structures. For instance, large molecules such as diethanolamine can be used to chelate the sol-gel precursor to limit its reactivity. Another approach involves sol-gel alkoxides modified by acrylate monomers, both being

polymerized during thermal or UV treatment ^{57,126}. However, the main drawback associated with this approach is the severe shrinkage due to the elimination of organic moieties during the annealing step (between 50 and $80\%_{vol}$) ^{121,126–129}. Alternatively, sol-gel formulations containing metal oxides nanoparticles (NPs) can be directly imprinted resulting in a reduced shrinkage ¹³⁰. However, the reported material has low density (refractive index of n_{600nm}=2 against 2.45 for dense TiO₂) resulting from the presence of pores associated with the packing of NPs. A compromise thus needs to be found between lower shrinkage and denser material. Of course, stabilising-agent free xerogels can be used which will allow for a reduced shrinkage factor. However, the very high viscosity of the intermediate xerogel will prevent efficient mass transfer within the sharp features of the mould. *In fine*, no increase in the aspect ratio will be found. In order to promote the filling of the mould features, a new technique called **Degassed Assisted Patterning**, taking advantage of the properties of PDMS to enhance its permittivity towards solvents, will be presented.

I.3. PDMS mould: Focus on Degassed Assisted Patterning

Historically, Degassed Assisted Patterning was used in microfluidics as a pump-free manipulation. First reported by Hosokawa *et al* in 2004 ¹³¹, it allowed to pre-store the pumping energy in the degassed PDMS in order to obtain a liquid flow in the PDMS channels during the experiment without the use of external pumping. Indeed, the solubility of a gas in PDMS follows Henry's law: the concentration of gas dissolved is proportional to the partial pressure of the gas around the mould. When a PDMS mould is degassed and brought back to the atmosphere, it equilibrates by absorbing air ¹³². In our case, we use the fact that the mould is not yet equilibrated with the atmosphere (this takes few minutes) to induce a micro-aspiration that pumps air and solvents through the mould (see Figure 41). The patterning process can thus be broken down in four steps: i) the mould is first pumped under vacuum (P < 10mbars) for 10 mins. ii) Straight after breaking the vacuum, the mould is deposited on as-prepared xerogels. iii) Air trapped in the mould cavities is easily pumped through the mould promoting the filling of the PDMS pattern cavities.



Figure 41 : Scheme presenting the Degassed Assisted patterning (DAP) process applied to the nano-impression of sol-gel layers.

Therefore, by using degassed PDMS moulds, a better filling of the cavities can be achieved. Nevertheless, this is only verified in the case that the imprinted xerogel displays a low enough viscosity to flow in and fill the cavities and that it does not undergo fast cross-linking, which still requires the use of fluidizing agents with the downside of a larger shrinkage.

II. Optimisation of the Soft-NIL process

To obtain metal oxides replica exhibiting optimised characteristics, it would require to use a minimal amount of fluidizing agent into the xerogel for an efficient mass transfer, as well as a limited shrinkage after thermal treatment. Ideally, this agent may induce fluidization of the xerogel when incorporated in a small volume fraction and may also be easily incorporated and removed from the xerogel when necessary during the imprinting process. All these criteria are met with water since (i) it is amongst the smallest molecules; (ii) its presence at the molecular level in the coordination and solvation spheres of the intermediate metallic complexes allows them to interact through weak flexible hydrogen bonds and prevents them to condense too rapidly by forming oxo or hydroxo bonds;³⁶ (iii) it can be easily absorbed or withdrawn from the hygroscopic xerogels through dynamic equilibrium with the environment, meaning that its volumic proportion in the xerogel can be controlled by the environmental relative humidity; (iv) it can be easily eliminated through pumping into the vacuumed moulds. The use of atmospheric water to adjust the fluidity during imprinting was already exploited for PEDOT:PSS polymeric resists to improve the quality of the replica.¹²⁹ However, applying this additional control during processing of sol-gel films, for which water is also a reactant for the condensation reaction, has never been reported to the best of our knowledge.

In this work, we explore the possibility of using water as a fluidizing agent by simply adjusting the humidity and temperature during the process without the use of any additional organic agents. This study has resulted into a publication¹³³ and a patent¹³⁴.

The following experiments were performed in close collaboration with Dr. Olivier Dalstein and Dr. Marco Faustini from Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP) from Pierre and Marie Curie University (UPMC) in Paris. The data presented here are the result of a joint work with equal contribution of Olivier Dalstein and myself.

In this part, the process used to perform Soft-NIL will be thoroughly described. The role of the environment and in particular of the relative humidity with respect to the final quality of the replica will be discussed. First, the quality and large scale homogeneity (several cm²) of the replica with respect to applied relative humidity, temperature and ageing time prior to imprinting is fully investigated for TiO₂. This study is then completed by similar, but more succinct, investigations for Al₂O₃, Hybrid and pure SiO₂, and Y-stabilized ZrO₂, to draw a more general picture of the study and confirm the mechanism proposed initially for the TiO₂ system. This will allow to highlight the particularity of each system and to show that this work can be transferred to any sol-gel oxide. Interestingly, we show that for each studied system, optimal results are obtained when the volume fraction of weakly bound water in the xerogel is around 30%.

II.1. Experimental procedure

Preparation of the moulds

Moulds were prepared from the following procedure: Si masters were prepared with different features and periodicities using FIB (Focused Ion Beam) or EBL (Electron Beam Lithography) on Si wafers. Their surfaces were first rendered hydrophobic by immersion for 10 min in a solution of 0.05M SiCl₂(CH₃)₂ in ethanol before being thoroughly rinsed with ethanol and acetone. PDMS reactants (90w% RTV141A; 10w% RTV141B from BLUESIL) were poured onto the master and cured at 70°C for 1h before unmoulding to ensure complete cross-linking ¹³⁵.

Preparation of sol-gel formulations

Sol-gel initial solutions were prepared from the reactants, solvents and polymers with respective molar ratios displayed in Table 5. TEOS stands for TetraEthylOrthoSilicate, MTEOS for MethylTriEtOxySilane, Pluronic[®] F127 for PEO₁₀₆PPO₇₀PEO₁₀₆ and CTAB for CetylTrimethylAmmonium Bromide [(C₁₆H₃₃)N(CH₃)₃]Br).

	Sol-gel precursors					Solvents			Polymers	
Material	TiCl ₄	Al(OiPr)₃	Zr(Cl) ₄	Y(NO ₃) ₃ ,2H ₂ O	TEOS	EtOH	H ₂ O	HCI	F127	СТАВ
TiO ₂	1	/	/	/	/	40	7	/	2.10 ⁻⁴	/
Al ₂ O ₃	/	1	/	/	/	29	4.8	1.4	/	4.10 ⁻³
Y-ZrO ₂	/	/	0.94	0.06	/	41	12	/	2.10 ⁻⁴	/
SiO ₂	/	/	/	/	1	40	10	0.01	/	1.10 ⁻²

Table 5 : Molar ratios of the precursors and solvents used in this chapter.

Al₂O₃ solution was filtered with a 0.45 μ m PTFE membrane before use. For hybrid silica solution, 2/5 (in mole) of TEOS was replaced by MTEOS. Solutions were stirred 24 hours at room temperature prior to use. CTAB and F127 are added in very low molar fractions in the present work to enhance the wetting property of the sol. The added quantity is in no case enough to play the role of micellar template for pore generation ⁷. CTAB is usually preferred since it does not change much the xerogel viscosity. When CTAB interacts too much with the inorganic molecular precursors, such as with Ti(IV) and Zr(IV), its surface energy reducing effect is less efficient and Pluronic types amphiphilic agents can be used, in spite of the associated viscosity increase. ^{30,136}

Deposition of sol-gel thin films

Xerogel films were prepared by dip-coating using an ACEdip equipment from SolGelWay. Depositions were made on glass or on Si (100) substrates at constant relative humidity of 20% and with controlled withdrawal speeds between 1 and 6 mm.s⁻¹ in order to adjust the final thickness. The relative humidity is chosen to give a reasonably long Tunable Steady-State (TSS, see Chapter I) while ensuring good film quality. Indeed, low RH (<10%) drastically decreases the duration of the TSS while high RH (>40%) gives longer TSS but lead to inhomogeneous coatings with large thickness fluctuations due to slow evaporation of water. Moreover, at high RH, partial dewetting can occur on the sides of the substrate and small defects (dust particles, scratch on the substrate's surface ...) produce large thickness inhomogeneity.

Soft-nanoimprinting in controlled environment

Imprinting of sol-gel films with PDMS mould involves the following steps illustrated in Figure 42. First, PDMS moulds are pumped under vacuum (P < 10mbars) for 10mins prior to nanoimprinting. Moulds are brought out during deposition of the sol-gel films by dip-coating and are quickly used before full equilibrium with the atmosphere. The elapsed time between taking the mould out of the vacuum and putting it in contact with the gel is less than 1 min. After dip-coating, the sol-gel films are quickly introduced in a custom-designed chamber allowing accurate control of the atmosphere composition

and temperature and brought into contact with the PDMS mould, without additional pressure (Figure 43).



Figure 42 : Schematic representation of the successive steps involved in the soft-NIL/sol-gel processing. The controlled environment was performed using a computer-piloted set of mass flow controllers delivering air at a constant flow and temperature, and at humidity adjusted between 2 and 98% with 2% error. The xerogel layer/substrate sample stands on a heating plate (not-shown) in the chamber to increase slightly the temperature if required.

A controlled flow of air or nitrogen with adjusted relative humidity, and/or relative vapour pressures of any volatile species, can be introduced into the chamber using mass-flow controllers sets (ACEflow from SolGelWay) (Figure 43b). To do so, dry air is flowed through a bubbler containing a solvent to give a saturated flow $(P/P_0=1)$ which is then mixed with dry air $(P/P_0=0)$ to obtain a given relative humidity.

The as-deposited sol-gel film is generally allowed to equilibrate for 1min at a given temperature and RH before nanoimprinting. The temperature of the xerogel layer could be increased from 22°C to 28°C using a heating element localized inside the chamber, while the atmosphere was maintained at 22°C using the constant humidity-controlled air flow. The temperature of the film was considered to be similar to the temperature of the heating element as the silicon substrate has a very good thermal conductivity. After 2 min, the samples were transferred in a 70°C stove for 1 min then in a 120°C stove for 1 min to consolidate the sol-gel films before peeling off the PDMS mould. Finally, if not stated otherwise, the sol-gel replicas were annealed at 450°C for 10 min for consolidation.



Figure 43 : Picture of the experimental set-up used for soft-nanoimprinting of sol-gel films. a) Soft-NIL environmental chamber with humidity sensor and heating stage on which the sample is placed. b) Humidity regulation system with mass flow controllers mixing dry air and wet air (after passing through a bubbler containing water) to obtain a value of relative humidity ranging from 5 to 95%.

II.2. Soft-NIL imprinting of TiO₂ xerogel: a case study

II.2.a. Focus on the effect of relative humidity

First, the relative mobility of TiO_2 xerogel with respect to the applied Relative Humidity (RH) during imprinting was assessed by measuring the height profile of final cured replica obtained with a mould bearing a single "large" square cavity with a height of 1 μ m (Figure 44). Due to the large lateral dimension of the cavity and the softness of the mould material, the latter tends to collapse at the

centre when applied on the xerogel (Figure 44a). The outer edge of the cavity, presenting a step, is analysed by AFM and exhibits a specific profile (Figure 44b). A constant thickness of 100 nm is measured, by ellipsometry, at the theoretical step position at RH = 40%, suggesting that the imprinting did not occur at such humidity likely because of a too low xerogel mobility. On the other hand, for humidity above 40%, the mass transfer has clearly occurred as revealed by the presence of a thickness step formed at the cavity edge.



Figure 44 : a) Scheme of the mould deformation at the step edge during imprinting b) Replica thickness profiles, plotted from the step edge for 40, 50 and 70% RH.

The thickness difference between each side of the step is around 200nm and roughly corresponds to the value expected if the mould surface on the left of the edge reaches the surface of the solid substrate (Figure 44b). As a result, most of the xerogel was displaced (from the left part to the right part) over a distance of at least 5 μ m according to the assumption that it corresponds to the displaced volume on the right side of the step. On the right side, the height of the motif line is maximal at the edge and decreases gradually to reach the initial value of 100 nm at 20 μ m from the edge. At 70% RH, a similar result is obtained with only a slightly higher motif at the edge. It suggests that above 40%RH, the fluidity of the xerogel is such that matter can be displaced from the edge of the cavity to over 20 μ m. Note that the heights at the edge do not reach the maximal value of 1 μ m imposed by the mould depth, which can be expected from the insufficient initial volume of xerogel (100 nm thick xerogel layer in the present case).

These results confirm the crucial role of humidity on the xerogel mobility, and state that no imprinting can occur below a certain critical RH. It is difficult to establish exactly the strain field dispersion responsible for the material reorganisation. A simulation would be necessary but this is out of the scope of the present work. However, it is reasonable to expect that most of the mass is expelled from the surroundings of the cavity and accumulate at the edges of the cavity, displacing the xerogel to form the observed converging profile. In such conditions, where mass transport can extend over length scale of several microns, imprinting motifs of sub-micron sizes may only be limited by the xerogel fluidity.



Figure 45 : Variation of thickness and refractive index of as-deposited TiO_2 xerogel films as a function of RH measured by environmental ellipsometry. Each point was measured independently (equilibrium took less than 1min). The dotted line is added as a guide for the eyes.

At high RH, the absorption of water in the xerogel is promoted, which is expected to reduce its viscosity. This reduction will, in turn, lead to higher mobility. This can be quantified by directly measuring the evolution of a xerogel layer thickness – percentage of swelling/shrinkage - upon RH variation. Figure 45 displays such a swelling curve for an as-deposited TiO_2 xerogel film (less than 5 min after deposition). The refractive index decreases with increasing relative humidity as water (n=1.33) is incorporated to the dry xerogel (n_{600nm} =1.63). The water uptake is not proportional to RH and tends to increase at higher humidity. This effect can be explained by the cumulative effect of the increasing xerogel hygroscopy with increasing water content and by a progressively weaker network offering less mechanical resistance to the absorption of water. At 40%RH, the xerogel is charged with around $8\%_{vol}$ of water and has been shown not flexible enough to be imprinted. At 50%RH, this uptake reaches 14% and allows imprinting. If RH is increased up to 80%, an uptake as high as 80% is observed. It is thus clear that a compromise is required. Indeed, on one hand, high RH must be used to allow efficient mass transfer while, on the other hand, low RH will reduce the potential shrinkage induced by the elimination of the absorbed water during annealing.

In the following experiment, morphology of TiO₂ replica, obtained at different relative humidity from 40% to 80%, from the same PDMS mould bearing micron-scale square arrays of square cavities (see Table 6 for exact dimensions) were investigated. The imprinting was performed 2 min after deposition in order to allow equilibration with the atmosphere without modifying too much the xerogel condensation degree. The time management is of particular importance and will be discussed in details later on in this article. The lateral dimension and height of the structures were measured both on the master and on the replica by AFM and SEM (Figure 46a) and Table 6) and were assumed to be identical between mould and master (negligible shrinkage applied during PDMS cross-linking). TiO₂ features exhibit the typical truncated square pyramids expected through imprinting from square cavities, as reported in previous studies.¹³⁷ No replication occurred below 50% relative humidity, while imprinting is efficient above 50% RH, confirming the results of Figure 44. Results are gathered in Figure 46 a) & b)

together with the surface roughness of the replica deduced from AFM images (Figure 46c). While, below 80% RH, replica show Root Mean Square Roughness (RMS) around 1 nm, those obtained at 80% RH present higher roughness (up to a factor of 4). Furthermore, AFM and Dark-Field optical images of such replicas revealed numerous cracks and topographic inhomogeneities (see Figure 46c & Figure 47).



Figure 46 : a) AFM maps and profiles of the square arrays of square truncated pyramids with a 1 μ m pitch imprinted at various relative humidity. b) Motif's height and roughness after thermal curing as a function of humidity. c) AFM maps of the film roughness on flat surfaces beneath the mould at different humidity.

	Mold	Replica 45%	Replica 50%	Replica 70%	Replica 80%
Patterns height (nm)	700 ± 20	20 ± 20	300 ± 20	430 ± 20	400 ± 40
Lateral dimension (nm)	700 ± 20	440 ± 20	440 ± 20	440 ± 20	460 ± 40
RMS (nm)	0.4	0.55	0.5	0.25	4.13

Table 6 : Dimensions of the imprinted structures deduced from AFM and SEM.

The lateral dimension does not change significantly with the relative humidity after thermal treatment. Thus, the increase in the pyramid's height must mainly be due to the xerogel better infiltration into the mould cavities. Therefore, a relative humidity of 70%, which corresponds to 30%_{vol} water content (Figure 45), allows for an optimal filling of the mould cavities.

In this experiment, even if the shrinkage is expected to be higher at 80% RH than at 50% RH because of the increased amount of water present in the xerogel; it has not been evidenced experimentally. Importantly, the degassed PDMS mould pumps all volatile species, including water, from the xerogel. This pumping is critical since it first eliminates trapped air from the cavities, inducing efficient xerogel filling and second, it eliminates absorbed water from the xerogel at the PDMS interface, promoting even further filling. While the filling proceeds, the xerogel viscosity progressively increases - with the decrease of water content - up to the threshold from which the viscosity becomes too high to allow further mass transfer. Furthermore, the augmentation of viscosity is also a result of the polycondensation of the xerogel, which kinetic depends on the temperature. It is thus important to apply conditions (e.g. RH and temperature) allowing the slowest possible polycondensation to permit optimal filling as it will be demonstrated.

When the water content is too high (e.g. reaching more than 50% increase of the gel volume above 70%RH), the filling of the cavities is efficient but the pumping does not allow the full extraction of the absorbed water molecules from the xerogel. The xerogel stabilizes thus into a less dense state than at moderate humidity with water remaining trapped inside. Upon consolidation at 120°C, trapped water gather into microdomains driven by the inorganic network polycondensation before pervaporating eventually through the PDMS mould microporosity. ¹³⁸ After unmoulding and during the final thermal annealing, the more fragile intermediate microporous TiO_2 network collapses on itself, revealing cracks, defects and high roughness. For such a reason, an optimal content in water exists – which seems to be around 30% in volume – leading to patterns with the highest aspect ratios and homogeneity.

Figure 47 shows optical microscope Dark Field images of $20*20 \,\mu\text{m}^2$ arrays, gathering each 400 square TiO₂ motifs imprinted at different humidity. Optical dark field imaging allows to collect the resonant scattered light from Mie modes formed within the pillars composing the arrays.¹³⁹ The spectral dispersion in the far field scattering is thus extremely sensitive to slight variations of motif size and shape. Similar visual appearance (colour and intensity) within each motif in dark field configuration accounts thus for its structural homogeneity. First, it is clear that arrays replicated at 80% RH exhibit bright additional scattering, especially outside the imprinted zones, associated to the formation of defects and cracks as mentioned above. At 45% RH, the scattering intensity of the motifs is very low compared to 50% RH and 70% RH as a result of its much lower motif height. It is clear that the 400 pillars present in each array feature negligible fluctuation of lateral dimensions and heights in the optimal range of humidity accounting for the low deviation determined by statistics on AFM (Table 6).



Figure 47 : Optical microscope dark field images of TiO2 replicas imprinted at 45%, 50%, 70% and 80% RH, replicated from a mould bearing arrays of 400 pillars featuring 440 nm width, 1000 nm pitch and 700 nm depth (left array) or 1100 nm depth (right array). All the images are collected in the same

conditions of illumination and detection to be directly compared. Strong scattering around the structures due to cracks can be seen at 80% RH. Scale bar is $10 \mu m$.

II.2.b. Focus on the effect of ageing time

Performing soft-NIL on sol-gel systems is thus very dependent on the relative humidity. Besides, it is known that as-prepared xerogel layers consolidate more or less rapidly through polycondensation with time and temperature. The xerogel may thus not be mobile enough to be imprinted after a certain time. In order to standardize soft-NIL processing on sol-gel resists, it is crucial to determine the imprintability time window for each metal oxide depending on the external temperature. First, one can use in situ environmental ellipsometry investigation on plain xerogel thin films to assess their transition from non-cohesive sol to cross-linked gels that dictates the imprintability of the material. This sol-gel transition, named gelation time, is a characteristic of any xerogel and varies only with the polycondensation kinetics. The measurement of this transition, first presented by Soler-Illia et al ¹³⁶ on mesoporous films, is done by monitoring the variations of the refractive index and the swelling amplitude of an as-prepared xerogel with time, both directly related to the network condensation degree. This investigation necessitates a cycling between low (25% RH) and high (65% RH) humidity as presented in Figure 48a. TiO₂ xerogel, and the other studied oxides, were cycled at different temperatures to measure their sol-gel transition and investigate the correlation between this transition and their ability to be easily imprinted. Figure 48b shows the variation of a TiO₂ xerogel refractive index (n) and thickness (t) at 30°C during humidity cycling. The global evolutions of t (decreasing with time) and n (increasing with time) suggest that the xerogel densifies as expected from the expulsion of water (syneresis) induced by the network progressive cross-linking and the progressive evaporation of HCl.



Figure 48 : a) Determination of TiO_2 xerogel gelation time corresponding to the inversion of the refractive index dependence to RH (top curve) at 30°C. The relative thickness shrinkage (bottom curve) with respect to RH cycling and ageing time is presented on the same graphic. b) Humidity ramp cycled in the ellipsometry chamber during the measurement. c) Schematic representation of the mechanism at stake when modifying the relative humidity before and after the gelation time for mesoporous films. Reproduced from ref ¹³⁶.

The explanation of the origin of the gelation time is the following (Figure 48c): during the first humidity cycles (from 0 to 70 min), the refractive index of the film decreases while the thickness increases at high humidity, and inversely at low humidity, indicating a swelling of the xerogel by water absorption (the refractive index of water is lower than that of the xerogel at any time). For both variables, the amplitude between high and low RH diminishes progressively, due to the xerogel progressive stiffening. At 70 min, a critical point (the gelation time) is reached where an inversion of the amplitude is observed only for the refractive index. The only possible explanation for such an inversion of the
refractive index amplitude involves a complete change of the network behaviour over water successive up-take and departure. After the gelling time, the network is stiffened enough so that it does not completely collapse, and micro-cavities of air are formed, upon water departure. Because air has a lower refractive index than water, the global measured refractive index of the porous xerogel is thus now inversed, being lower at low humidity than at high humidity where water adsorbs and condenses replacing the air from the pores. In summary, the gelling time (or point) corresponds to the xerogel state where the 3D framework can withstand the presence of empty micro-pores. In less stiff 3D frameworks, such as those present before 70 min, micro-pores tend to collapse, due to the strong Laplace pressure applying at their highly curved interface, which leads to the thickness decrease. The gelling point observed by this method is thus a good indication of the relative kinetics of xerogel layer condensation.

The determination of the gelation time vs temperature has been also investigated using the same experimental protocol but by modifying the temperature of the sample during the experiment using a Peltier modulus (Figure 49a). The corresponding plot of the gelation time vs temperature in Figure 49b) gives a good indication of the condensation kinetic dependence to the temperature for the present TiO₂ xerogel layer system. The gelation time is shown to decrease quasi-exponentially with respect to the temperature ($t_{gel} = A.e^{-\alpha T}$ where α =0.52°C⁻¹) with a fairly good correlation (R²=0.995), confirming that the imprintability window of TiO₂ xerogel must be much shorter at high temperature.



Figure 49 : a) Evolution and inversion of the refractive index during cycling for three different temperature b) Extracted gelation time for TiO_2 xerogel as a function of temperature in semi-log scale. The dotted line represents an exponential fit to the data.

The critical effect of time and temperature on the imprintability of sol-gel was verified on the same TiO₂ xerogel, using the same custom-designed chamber as described before and using a PDMS mould patterned with a diffraction grating composed of lines (dimensions: 190 ± 30 nm wide; 180 nm height; grating pitch 1 µm). Optical images of the diffraction grating replica are shown in Figure 50a). Keeping RH and T constant at 50% and 22°C, respectively, the diffraction intensity is better after 5' than after 6'30", to eventually disappear totally after 8', confirming the critical role of aging time. It is important to note that only the intensity is compared as the colour of the diffracted light is dependent on the measurement angle. The topography of the replicated gratings was evaluated using AFM as shown in Figure 50a). The dual peak deformation visible on the AFM profiles, is likely due to the visco-elastic properties of the xerogel and its interaction with the cavities during filling as explained elsewhere with polymeric resins.¹⁴⁰ Investigated imprinting conditions were: ageing times from 2 to 30 min,

temperatures fixed at 22°C or 28°C, and RH between 50% and 80%. Efficiencies of replication are summarized in diagrams Figure 50b) and Figure 50c) for 22°C and 28°C respectively. "Good quality" replica feature 40 nm tall lines and intense diffraction are represented by round points while "poor quality" replica show less than 20 nm tall lines and non-homogeneous or defects are represented by crosses.

At 50% RH, good replicas are prepared up to 5 min of ageing, while this period increases to 12 min and above 30 min for 60% and 70% RH, respectively. This shift originates from the lower condensation rate of the network when water is present in high quantity in the xerogel. The optimal viscoelastic property of the xerogel is thus maintained for longer periods at such intermediate humidity. In addition, the cross-linking is accompanied by water expulsion from the network which also participates to the mobility adjustment as revealed in Figure 50d). Indeed, just after deposition, applying 80% RH to the film induces the maximal 80% swelling after 3 min as already shown in Figure 3. Then, the film starts to shrink back, as a result of the network condensation, to reach around 25% residual swelling after 10min. Therefore, the optimal mobility of the as-prepared TiO₂ xerogel can also be achieved at high humidity but for longer periods of ageing. This decrease of the water content in the gel with aging, even at high humidity, explains why the gel maintained at 80%RH must be aged at least 15 min before yielding good replicas. This property is extremely important since it gives more time for potential intermediate operations before imprinting (*e.g.* system transfer, mould aligning, atmosphere adjustment...), which is a real issue in sol-gel processing.



Figure 50 : a) Optical images and AFM profiles showing the diffraction of the TiO₂ replicas imprinted at 22°C and 50% RH after 5, 6.5 and 8 minutes (respectively first, second and third panel from the top). AFM map of the diffraction grating imprinted after 5 minutes is shown in the bottom panel. Mould motifs are parallel lines (190 ± 30 nm wide, 180 nm height, 1 µm pitch). b), c) Imprintability diagrams obtained at 22°C and 28°C, respectively ("good" and "poor" replicas are represented by round points and crosses, respectively). d) Evolution of as-prepared TiO₂ xerogel swelling with time when exposed to RH = 80% (reference initial thickness is taken at RH < 10%).

To go further, we investigated the possibility to prepare replicas when the temperature is increased up to 28°C during ageing. Diagram c) of Figure 50 gathers the conditions leading to "good" and "poor" replicas (RH values correspond here to $100*P/P_0$, with P_0 the saturated vapour pressure at 28°C). As water uptake decreases and inorganic condensation rate increases with temperature, the conditions for which optimal conditions are present exists at much lower ageing times, as expected. Only high humidity allow to extend the imprintability time over 5 min. This emphasizes again the real dependence of sol-gel systems to external conditions for nano-imprinting, as already demonstrated for dip-coating ³⁰ but certainly also for other processes. Besides, not all sol-gel systems evolve with the same kinetics and TiO₂ xerogels from TiCl₄ sols are known to have a relatively slow condensation (due to very high acidity of the formulation) which is ideal for nano-imprinting.

II.2.c. Focus on the annealing-induced shrinkage and characterization of obtained TiO₂ films

As mentioned, soft-NIL process of transition metal oxides and in particular TiO_2 , is accompanied by a more or less significant degree of shrinkage. In the present study, shrinkage was measured for 2D (plain film) by ellipsometry and for 1D (lines) and 0D (square motifs) by AFM. These investigations are gathered in Figure 51. First transversal shrinkage of the plain 2D film, was assumed to be equivalent to the total volume shrinkage. It was measured by ellipsometry to be 50% between as-prepared (2 min/10% RH) and 120°C, and 70% after treatment at 450°C (see Figure 51a). Measuring the dimensions of the imprinted motifs before pre-treatment at 120°C, underneath the mould is impossible. Thus it is assumed that 1D and 0D motifs already shrank of 50%vol at 120°C, as for the plain xerogel layer. By taking this into account, the overall shrinkage (from as-prepared to 450°C) for 1D and 0D motifs can be extrapolated from the measurements at 120°C and 450°C. For 1D structures (lines motifs studied above), the shrinkage is greater for the height (43%) than for the width (25%). This can be explained by the fact that, on the one hand, vertical shrinkage induces less stress for the overall structure due to the substrate-structure interaction, and on another hand, shrinkage in the shorter dimension of the object is facilitated. For OD structures (studied previously), it is interesting to note that shrinkage is greater horizontally (37%) than vertically (27%) even if the inverse trend was expected in view of the previous observations for lines. This effect is yet not fully understood. More investigations, and in particular simulations, would be needed to assess and predict the anisotropic shrinkage depending on the morphology and orientation of the motifs with respect to the surface.

In the present conditions, where chloride salt precursors are used and controlled humidity is applied, the volume shrinkage is 20% lower than previous reports¹²⁸ and inherent to the precursor chemistry. In particular, the height shrinkage is twofold lower than in previous studies (only 27% against more than 56% previously¹²⁸) making it particularly interesting for high aspect ratio structures.



Figure 51 : Schematic representation of shrinkage in a) 2D, plain layer structure with the evolution of the thickness during annealing between 25°C and 450°C obtained from in situ ellipsometry; b) a 1D, line structure and c) a 0D, point structure. AFM 3D maps of studied structures after annealing at 120°C for 10 mins and after 450°C for 10 mins are also provided for lines and point structures.

 TiO_2 films were annealed at increasing temperature and their refractive index measured by ellipsometry (Figure 52a). The refractive index is seen to increase with higher annealing temperature for instance $n(\lambda) = 2.05 + 0.05/\lambda^2$ (with λ in μ m) for TiO₂ after annealing at 450°C. Annealing at higher temperature will further densify the material through sintering. In the case of titania, crystallisation into anatase phase starts as about 350°C and be complete around 450°C (depending on the temperature ramp, annealing history, defects and thickness of the film), if further heated the rutile phase becomes thermodynamically stable. From Environmental Ellipsometric Porosimetry (EEP) measurement, the pore volume and pore size distribution was assessed (Figure 52b). The adsorption curve shows a progressive increase of the quantity of adsorbed water up to a relative pressure of P/P0 = 0.4, suggesting that the pores are mainly micro and small mesopores with broad size distribution (diameter of 2.5 ± 1 nm). The plateau present above P/P0 = 0.5 reveals that no larger textural pores are present. The desorption curve almost overlaps the adsorption one (very small hysteresis). This isotherm is typical of a porosity composed of interstitial voids created between randomly packed small particles (as it is the case here with small Anatase particles). XRD measurement confirms the presence of anatase crystallites with the (101), (200) and (211) peaks as expected for such temperature (Figure 52c).



Figure 52 : a) Plot of the refractive index measured by ellipsometry for titania films annealed at various temperature. b) Adsorption and desorption curves recorded by ellipsometric porosimetry on TiO_2 film after annealing at 450°C as a function of the relative pressure of water with corresponding pore size distribution derived from the adsorption and desorption curves. c) XRD diffraction pattern (acquired in Bragg-Brentano geometry and indexed with PDF #00-021-1272).

II.3. Soft-NIL imprinting of various xerogels: (hybrid-) SiO₂, Al₂O₃ and Y-ZrO₂ xerogels compared to TiO₂.

Three other xerogel systems were selected and compared to TiO_2 . These materials are among the most used sol-gel materials and are known to present different affinity to water and different rates of condensation under xerogel form.

II.3.a. Study of Al₂O₃ and Y-ZrO₂

Aluminium oxide is highly interesting for a large number of applications in micro and nanofabrication and microelectronics. Several crystalline phases are stable to relatively high temperatures such as oxyhydroxides (γ -AlOOH, boehmite) and need further annealing to be converted to α - Al₂O₃ or γ -Al₂O₃ usually at temperatures above 1000°C. Al-based oxides resist are highly appealing because of their very good properties as etching masks for Reactive Ion Etching, an etching selectivity of 100:1 towards Silicon have been demonstrated ⁷³. Al₂O₃ has been shown to surpass SiO₂ as insulator for silicon photovoltaics ^{141,142}. Furthermore, crystalline α -Al₂O₃ (often referred as sapphire) is broadly used as substrate for the epitaxial growth of GaN for blue-LED technology and studies highlighted that light efficiency is improved by substrate patterning ¹⁴³. Y-ZrO₂ is extensively used as a coating for his mechanical stability and high thermal expansion coefficient (10.5x10⁻⁶/K) matching the one of many metals. As an N-type transition metal-oxide, it is used as an Electron Transport Layer in LEDs ⁴⁰. It is a promising candidate for high-K dielectric materials in capacitors 53 and it can also be used as a catalyst, as a pure phase or mixed with other sol-gel materials such as TiO₂ 144 .

To the best of our knowledge, Al₂O₃ and Y-ZrO₂ have never been used in soft-NIL before, those results present the first nanoimprint of such materials thanks to a control over the environment during imprinting. The swelling-dependence to humidity plots for as-prepared xerogel layers are shown in Figure 53a). They reveal that Y-ZrO₂ and Al₂O₃ have the ability to uptake water and swell in the ideal range of about 30%. Indeed they are much more hygroscopic than TiO₂ since they can swell up to 110% of their initial thickness at 70% RH. The corresponding gelation time of Al₂O₃ and Y-ZrO₂ as a function of temperature, obtained experimentally following the same procedure used for TiO₂, are given in Figure 53b).



Figure 53 : a) Water uptake of Y-ZrO₂, AI_2O_3 and TiO₂ xerogels with respect to relative humidity measured by in situ time-resolved ellipsometry. Dashed lines are displayed as guides for the eyes. b) Results of gelation time measurements at 25°C for the various studied xerogels.

 Al_2O_3 and Y-ZrO₂ have gelation times that extend over several hours, like TiO₂. This can be explained by the slow condensation rate of these non-silica systems due to acidic conditions and the higher coordination number. This is confirmed by successfully imprinting alumina after 5 mins at 28°C, 40% RH against 2 mins at 28°C, 70% RH for TiO₂.

Diffraction grating replicas were then produced from a mould patterned with diffraction gratings composed of lines with the following dimensions: 190 ± 30 nm wide; 180 nm height; grating pitch 1 μm. Optimal imprinting conditions, deduced from the gelation time and water uptake for each system, were applied. These conditions correspond to water uptake of 35% (RH = 50%; T = 25° C; t = 2 mins) for Y-ZrO₂ and of 25% (RH=35%; T = 28°C; t = 1 mins) for Al₂O₃. AFM height profiles are provided in Figure 54, together with the corresponding optical and XRD characterisations. AFM and optical images confirms that the imprinting is homogeneous over 5 x 5 mm for Y-ZrO₂ and Al₂O₃ and that good quality replicas can be obtained with different metal oxides when the conditions are adjusted such that water uptake in the as-prepared xerogel remains close to 30% in volume. The differences in AFM profile shape and relative gap between lines is due to the relative shrinkage of the materials. $Y-ZrO_2$ shows a rougher surface caused by the growth of larger crystallites during the annealing step. In XRD measurements, a shift of the diffraction peaks towards lower diffraction angle is seen for Y-ZrO₂ probably due to a slight deviation in composition compared to the reference pattern (PDF #00-030-1468). In the case of Al_2O_3 , replica were further heated at 1000°C for 2 h (8°C/min). However, even in GIXRD geometry, no diffraction peak can be detected for the expected γ -Al₂O₃ phase: the measured pattern exhibits only a peak centered at 56° corresponding to the Si substrate (311) Bragg reflection (in Bragg diffraction conditions for such GIXRD geometry) and a broad signal around 20° probably due to amorphous SiO₂ contribution. The absence of γ -Al₂O₃ diffraction lines may be due to the presence of too small nano-crystallized domains providing a too small diffraction domains to be detected with the present X-ray equipment.



Figure 54 : Characterizations of Y-ZrO₂ (top), Al_2O_3 (bottom) diffraction gratings (same grating parameters than Figure 50) imprinted in optimal conditions. From the left to the right panel: AFM profiles, optical images of the diffraction (scale is 2mm) and X-ray diffraction patterns for each material (Y-ZrO₂ was acquired in Bragg-Brentano geometry and indexed with PDF #00-030-1468, Al_2O_3 acquisition was performed in GIXRD configuration).

II.3.b. Study of silica and hybrid SiO₂

Silica is the most known system in sol-gel chemistry and has been extensively studied ⁴. It is used in a plethora of applications in silicon microelectronics industry for instance as an insulator ⁵². Soft lithography of silica is developed industrially and mostly relies on spin-on-glass system (e.g. Hydrogen Silsesquioxane -HSQ-), cage-like silica precursors that ensure a low viscosity and slow condensation rate. Indeed, silica-based systems are known to condensate rapidly especially in highly acidic conditions that acts as catalyst.

The swelling behaviour of silica and hybrid silica (obtained with $40\%_{mol}$ MTEOS and $60\%_{mol}$ TEOS) were studied by environmental ellipsometry as previously (Figure 55). The xerogels swell as much as TiO₂. In contrast, gelation time measurements show a different behaviour for silica systems: at 25°C, gelation occurs after only 14mins for pure silica instead of 20h for TiO₂. If methylated precursors are used the gelation time is found to be around two-fold longer than for pure SiO₂. The condensation rate decreases as less hydroxyl groups are present for cross-linking. Indeed the introduction of Si-CH₃ groups decrease the density of cross-linking points and slow the condensation kinetic. In situ Fourier Transformation Infrared spectroscopy (FTIR) can be used to obtain more information on the condensation of a drying film ³⁵ however this equipment wasn't available in our lab and does not give as much insight on the gel flexibility that in-situ Environmental Ellipsometry especially if coupled with humidity cycling to determine gelation time ¹³⁶.

Imprintability tests show that pure silica xerogel (from TEOS precursor) could not be imprinted even just after deposition and whatever the humidity and temperature, despite its ability to swell. It reveals that as-prepared silica xerogels rapidly crosslinks into a rigid network. In the case of hybrid silica, an imprintability window of up to 4 min after deposition was determined at 70% RH and 22°C. The resulting diffraction grating was analyzed by AFM and displayed in Figure 56.



Figure 55 : a) Water uptake of SiO_2 , hybrid- SiO_2 and TiO_2 xerogels with respect to relative humidity measured by in situ time-resolved ellipsometry. Dashed lines are displayed as guides for the eyes. b) Results of gelation time measurements at 25°C for the various studied xerogels.



Figure 56 : AFM profile and optical image of the imprinted SiO_2 diffraction gratings in optimal conditions.

In this study, we showed that by a careful monitoring of the sol-gel film behaviour it is possible to predict its imprintability in Soft-NIL. The versatility of the sol-gel chemistry allowed us to tune the chemistry of the silica precursor to decrease its condensation rate. Hybrid-silica precursors were successfully imprinted and can be converted to pure silica after annealing treatment as demonstrated elsewhere¹⁴⁵.

Summary

- Water is a good fluidising agent to perform soft-NIL on sol-gel systems without chelatants leading to high quality and homogeneous replicas with a minimal shrinkage
- Optimal conditions for soft-NIL on sol-gel systems correspond to a water uptake equivalent to 30%_{vol} for all studied systems.
- Effect of relative humidity but also of temperature and ageing time before and during imprinting was studied. By accurately controlling those parameters, it is possible to obtain the optimal rheology during the soft-NIL process whatever the temperature and time after deposition
- Optimisation of nanoimprint was studied and shown possible for various sol-gel systems with different behaviours (TiO₂, SiO₂, Al₂O₃, Y-ZrO₂)
- Ellipsometry was proven to be an efficient method to study condensation kinetics through the measurements of gelation times.

III. Towards new development: Micro Transfer Moulding without residual layer

Although the interest in soft-NIL is continuously growing, there are still some issues to be tackled for this technique to supplant well-established lithographic processes such as photolithography. One of the challenges is **to imprint without a residual layer** in the areas between the patterns. Indeed, the nanofabrication of isolated objects is often required for instance, in microelectronics, where stacks of thin layers are used and access to the underlying layers is necessary to deposit the metallic contacts. In general, this thin residual layer is removed in a post processing step by Reactive Ion Etching (RIE) increasing the overall process cost, time, complexity and potentially modifying the patterns shape because of a low etching selectivity.

Nevertheless some studies have shown that direct printing of a material without residual layer in various imprinting processes is indeed possible. In soft-NIL, different methods exist, for instance UV-NIL of polymers followed by a development step^{146,147}, partial filling of the cavities by a flowable polymer^{148,149} or selective filling of the mold patterns by solvent-evaporation-induced shrinkage in direct or reverse NIL (similar to µTM in the reverse NIL configuration with precise control over the deposited prepolymer quantity)^{150,151}. However those techniques show severe limitations and can be applied only on polymeric resist. Microcontact printing is known to give structures without residual layer but it has been limited to the patterning of self-assembled monolayers (SAM) and bio molecules^{65,66}. Examples of microcontact printing on polymers exists even if there are mainly used to create a surface energy contrast between patterned and non-patterned areas at micrometric size¹⁵². In Micromolding in capillaries (MIMIC), no residual layer is obtained but the structures need to be connected to allow the "ink" to flow and fill the cavities^{63,64}. In Microtransfer molding (μ -TM), the mold is filled by a prepolymer before being applied onto a surface and transferring the patterns⁶⁷. In order to remove the prepolymer excess (leading to a residual layer), the surface can be scrapped. Nevertheless, a thin residual layer is often obtained as it is difficult to ensure a complete removal of the excess prepolymer. This technique has been used in one study on sol gel to transfer high aspect ratio patterns with residual layer ⁶⁸. In a different approach, John D. Bass *et al* used disposable watersoluble PVA molds to yield high aspect ratio structures without residual layer on sol-gel⁶⁹.

It emerges that, even if several printing techniques without residual layer exist, very few proof of concept on sol-gel films have ever been reported owing to the complicated rheological behaviour of sol-gel. In this study, starting from a plain sol-gel film, we impregnate a mould and transfer the sol-gel material trapped in the mould cavities onto a final substrate, without residual layer. This work has been the object of a patent¹⁵³.

III.1. Study of the mechanism of Micro Transfer Moulding

Description of the experimental procedure

A sol-gel solution, which composition is detailed in Table 7 was used to obtain a coating on a defatted glass slide (VWR[®]) by dip-coating in a controlled chamber (T = 22°C, RH = 20%). The withdrawal speed was chosen in between 1 and 6 mm.s⁻¹ to obtain a film thickness between 60 and 120 nm after annealing at 400 °C. Moulds are degassed in vacuum for 10 mins before being used (P < 10 mbars). Soon after breaking the vacuum, the degassed mould is first impregnated by direct application onto an as-prepared TiO₂ xerogel. This is done without applying any additional pressure in a custom-made

chamber where the film was allowed to equilibrate with the atmosphere for 1min at 70% RH prior to mould impregnation. After 1min of impregnation, the mould is peeled off at 20% RH without any thermal treatment. The substrate, still coated with a part of the initial xerogel is discarded and the humidity in the chamber is increased to 85% RH. Finally, after stabilization in the chamber at 85% RH for 1 min, the mould is applied onto a different substrate (silicon wafer, glass slide, plastic ...). The assembly is kept in the chamber for 1 min then stabilized at 70 °C for 1 min and finally demoulded. The resulting xerogel after demoulding on the final substrate will be referred here as the replica. To get more insight into the mechanism, the final replica will be systematically analysed, as it gives a good indication of how the xerogel behaved during demoulding and stabilization. Moreover, moulds are harder to image during the process (less contrast, evolving xerogel ...). In any case, moulds are inspected after each transfer to assess if all the xerogel structures have been transferred. If some structures are still present in the mould after transfer and annealing at 70 °C, cleaning of the mould is then necessary in order to reuse it. This cleaning step can be performed by applying sticking tape on the mould or by immersion in a solution of diluted HCl for few hours to dissolve the remaining partially condensed gel.

TiCl₄	EtOH	H ₂ O	F127
1	40	7	2.10 ⁻⁴

Table 7 : Molar ratios used for the formulations in this part

As can be seen from the protocol, the following technique uses extensively the property of xerogels to swell and shrink with varying relative humidity (see Figure 57) as explained in details in the previous part (Effect of Relative Humidity on sol-gel soft-NIL). The equipment used to vary the humidity – consisting of mass flow controllers and water bubbler to obtain a flow of saturated wet air from dry air – is described in the previous part of this chapter (see Figure 43). TiO₂ xerogels will be chosen for this study as their behavior has been well investigated in the previous part and they display a relatively high stability over time (slow ageing) allowing to modify their swelling degree several minutes after deposition.



Figure 57 : Variation of thickness and refractive index of as-deposited TiO_2 xerogel films as a function of RH measured by environmental ellipsometry. Each point was measured independently (equilibrium took less than 1 min). The dotted line is added as a guide for the eyes. This figure, first presented as Figure 45, is presented again for clarity.

Results and discussion

The mechanism of Micro Transfer Molding without residual layer is displayed in Figure 58 and can be divided in four steps. First, in step A, the PDMS mould is applied on the freshly prepared xerogel layer at high humidity (70% in the case of TiO₂) without additional pressure as for standard soft-NIL. The xerogel fills the cavities thanks to capillary forces and mould outgassing. In step B, demoulding is performed **before annealing**, 1 min after application of the mould at low relative humidity (RH=20%). In those conditions, a part of the xerogel sticks to the substrate while the rest stays attached to the mould surface. Straight after demoulding, the xerogel equilibrates with the atmosphere, dries and recedes in the cavities stabilized by capillary forces. Indeed, since the PDMS surface is highly hydrophobic, the xerogel dewets and gather within the cavities. During this step, the relative humidity is kept low to promote dewetting of the remaining xerogel from flat surfaces to the cavities. In step C, the xerogel, stabilized in the cavities, is then swelled at high humidity (85% RH for TiO_2) in order to protrude from the surface of the mould and to ensure good contact of the xerogel with the substrate surface during the transfer step (next step). Finally, the mould is pressed onto another substrate in step D. The xerogel having more affinity for the substrate surface (hydrophilic) than for the PDMS mould (hydrophobic), preferential shrinkage will occur at the latter interface, detaching the xerogel from the mould. After annealing at 70 °C, the mould can be easily removed; the sol-gel material is thus transferred without residual layer. The imprinted structures are finally thermally treated at 400 °C for 10 min, in order to crystallize TiO_2 into its anatase form.





To confirm the mechanism, Micro transfer moulding is performed on a 20 x 20 μ m² squared arrays of pillars of depth 700 nm and pitch 2 μ m following the procedure described above. The resulting replica is shown in Figure 59a. From the centre to the side of the image, three zones can be defined: In the centre, the 20 x 20 μ m² array containing the transferred structures without residual layer is visible. Around this zone, at an intermediate distance from the structures, an area without any xerogel exists (highlighted by dotted lines in Figure 59a). Further away from the structures, large "drops" of xerogel more or less dewetted can be seen. Indeed, two factors promote the mobility and dewetting of the xerogel after impregnation: i) the xerogel shrinks due to the loss of adsorbed water (transition from high to low relative humidity between step A and B), ii) the flat surface of the mould is not energetically favourable (highly hydrophobic). The depletion zone (without xerogel) around the structures thus corresponds to the area where the xerogel dewetted to fill the cavities while, further away, the xerogel stayed on the flat surface and form droplets. Inside the structured array, each wall between two cavities played a similar role with dewetting of the xerogel initially on the walls towards the cavities, leading to the observed well separated structures without residual layer.

Tests were performed trying to obtain the same results (filling of the cavities only) by direct spincoating or dip-coating on the PDMS mould as typically performed in microtransfer molding (μ -TM). However, the fluidity of the xerogel is too large to homogeneously fill the cavities. Moulds are observed directly after deposition with an optical microscope equipped with a camera (Figure 59b). Mobility is seen over very large distances with vast empty zones and local big "drops" of several tens of microns. In addition, the drops of sol-gel material are seen to bridge several mould cavities of a 20 x 20 μ m² array (particularly visible for spin-coating) and even two neighboured structured arrays (in particular for dip-coating) even if they are spaced by 20 μ m. This is in accordance with the literature, where many reports mention that the excess material must be removed from the raised areas of the stamp, either by scraping or with a stream of nitrogen to avoid the formation of a residual layer⁶⁷. Thus, the arrangement obtained by Micro Transfer Moulding seems difficult to reach by other means.



Figure 59: a) Optical microscopy image of a replica after Micro Transfer Moulding showing the dewetting areas around the objects. Dotted lines are added to highlight the depletion zone around the transferred structures. The mould used in this experiment displayed the following features: $20 \times 20 \ \mu m^2$ squared arrays of pillars of depth 700 nm and pitch 2 μm . b) Optical microscopy images of a PDMS mould bearing square cavities of squares. Direct deposition of a sol-gel layer (dip coating or spin coating) on the mould results in the inhomogeneous filling of the cavities.

In order to assess the homogeneity of the transferred structures, moulds displaying squared areas of $20 \times 20 \ \mu\text{m}^2$ with pillars of 700 nm depth and various pitch (from 1 to 2.5 μ m) were used. Impregnation was performed for 1 min on a thin TiO₂ layer which thickness was 60 nm after annealing at 400 °C. Figure 60 shows optical images (bright and dark field) and AFM images of the replicas. No residual layer is visible around or in between the transferred areas confirming that the structures were transferred efficiently. However, compared to standard soft-NIL, the homogeneity is rather poor with visible differences in the size of the pillars while some structures were not transferred at all. The large deviation of the pillars dimensions explains the difference in colours observed in dark field and are caused by an inhomogeneous filling of the mould cavities. In the case of the missing structures, the xerogel did not swell enough to protrude from the cavities and get into contact with the substrate. This is confirmed by looking at the mould after the transfer step (step D): in Figure 60c, the pillars missing in the corresponding replica (Figure 60a) are found in the mould.

Missing structures are expected when filling of the cavities is particularly low which is expected here since the TiO_2 layer was particularly thin. Anyhow, most structures were transferred efficiently as shown in Table 8. For smaller cavities (pitch of 1 µm), the structures revealed to be even harder to transfer as can be observed from the poor percentage of transferred structures. Indeed, since the cavity dimensions is reduced, the xerogel is particularly stabilized by strong capillary forces (which increases with the reduction of the cavity size).

Pitch (µm)	Transferred structures	Missing structures
2.5	92 %	8 %
2	98 %	2 %
1.5	97 %	3 %
1	43 %	57 %

Table 8 : Summary of the transferred/missing structures from imprinted arrays of 20 x 20 μ m² with pillars of 700 nm depth and various pitch.



Figure 60 : **a**, **b**) Optical bright field and dark field images and AFM of the replica transferred from a mould bearing squared arrays of cavities of depth 700 nm and pitch 1.5 μ m and 2 μ m, for a) and b) respectively. Impregnation is carried out from a thin TiO₂ xerogel of 58 nm (thickness is given after annealing at 400 °C). The number of transferred/missing structures is summarized in Table 8. c) Optical image of the mould after incomplete transfer of the structures visible in a). d) Optical image of structures transferred with some portion of residual layer (see arrows). Moulds parameters were the same of a). Impregnation was carried out with a TiO₂ layer of 120 nm.

In the opposite case, when the cavity filling of too large, the xerogel will merge forming large droplets as already seen for direct spin-coating of the mould (Figure 59b). This effect is exacerbated when the size of the cavity is shrunk: since the wall thickness (distance between two cavities) is reduced, the xerogel can be more easily stabilized in-between cavities. This effect was highlighted by using an impregnation layer of 120 nm. The locally transferred residual layer is easy to spot on optical images (see Figure 60d).

During the impregnation step, mobility of the xerogel to fill the cavities happens very quickly (in a matter of seconds) and is hard to control. *In fine*, homogeneity still needs to be improved by a better control over the xerogel quantity dispatch in each cavity. Tailoring the xerogel viscosity might help to improve the homogeneity while using larger structured surfaces might avoid inhomogeneities induced by side effects. As an example, on a $20 \times 20 \ \mu\text{m}^2$ array with a pitch of $2 \ \mu\text{m}$, 44% of the structures are on the edges (28 out of 64 structures). In addition, to obtain more control over the filling of the cavities, the influence of demoulding parameters, for instance the impregnation step length, can also be studied. Further investigations, focusing both on the chemistry of the initial sol-gel formulation and its evolution during the process and on the imprinting process conditions, are needed in order to improve the homogeneity.

III.2. Applications of Micro Transfer Moulding

Transfer of CaTiO₃ layer: application as an etching mask

To confirm the absence of residual layer, diffraction gratings (width 8 μ m, pitch 14 μ m, depth 1.3 μ m) were imprinted in TiO₂; first by using standard soft-NIL (Figure 61a) then by Micro Transfer Moulding (Figure 61b). The imprinted/impregnation layer thickness was chosen to be about 100 nm. When nano-imprinting is carried out by soft-NIL, cracks are visible in between the imprinted lines caused by the building of shrinkage-induced stress during annealing (see arrows in Figure 61a). On the contrary, no cracks were found in between the lines for the Micro Transfer Moulding technique. Since no residual layer was deposited, skrinkage-induced stress could be efficiently relaxed by the system. In addition, grating lines were successfully transferred on a large scale of more than 1 mm². The defects visible in the optical image of Figure 61b with breaking of the lines, are typically observed when the mould cavities are not fully filled by the resist as explained elsewhere¹⁴⁸. This is expected as the mould depth is 1.3 μ m and the xerogel thickness was of only 100 nm and could be avoided by using a shallower mould.



Figure 61 : a) SEM image of TiO₂ replica imprinted by soft-NIL from a mould bearing diffraction gratings of width 8 μ m, pitch 14 μ m, and depth 1.3 μ m. Arrows indicate areas where cracks are visible in the residual layer. b) SEM and optical images of a TiO₂ replica made by Micro Transfer Moulding from the same mould shown in a). No residual layer is found. The optical microscopy image shows the homogeneity over large scales.

In order to validate the absence of any residual layer, the above process is repeated with a similar solgel solution containing a molar ratio of 0.7 TiCl₄: 0.3 CaCl₂ (instead of 1 TiCl₄). By adding CaCl₂ to TiCl₄ in the formulation, CaTiO₃ is deposited. If exposed to a reactive fluorinated gas (typically used in RIE), CaTiO₃ is converted into RIE-resistant CaF₂ ⁴⁵ and thus acts as an etching mask as schematized in Figure 62a. The resulting diffraction gratings are analysed by AFM before and after Reactive Ion Etching (RIE). RIE treatment lasted 4 mins with a power of 300 W using a flow of 2.5 sccm of CF₄ as the etching gas. The etching depth of silicon for such RIE treatment is well known and calculated to be about 800 nm from calibration curves. In Figure 62b, AFM profiles show that the originally transferred lines have a height of 100 nm, a pitch of 12 µm and a width of 6 µm. The fluctuation of the height of the lines is not critical here as CaF₂ is highly resistant to the etching gas (up to a factor 1:25⁴⁵). After RIE, the height increases up to 900 nm, while the pitch and width remain constant. The roughness visible at the bottom of the trenches is inherent to the RIE conditions used here and in principle could be avoided by optimizing the etching step. This result confirms that the CaTiO₃ patterns were successfully transferred onto silicon, without residual layer and acted as an efficient etching mask.



Figure 62 : a) Scheme of the reactive ion etching treatment of a transferred $CaTiO_3$ layer and its conversion into CaF_2 . b) AFM profiles of diffraction lines transferred onto a silicon substrate before and after reactive ion etching. The profiles are stacked with an offset for clarity, the baseline of each profile corresponds to the lowest point of the surface seen by the AFM tip.

Transfer on stainless steel substrates

Another interest of transferring sol-gel structures instead of using standard NIL is that the structures are already partially condensed when transferred. This can be particularly interesting when substrates are sensitive to one of the component present in the formulation. For example, stainless steel substrates are quickly corroded in highly acidic medium, it is thus impossible to coat and imprint a TiO_2 thin film using $TiCl_4$ as a precursor. Here, a transfer of TiO_2 pillars, of the same dimensions and in the same conditions than detailed above, is performed on stainless steel substrate (Figure 63). Optical microscopy shows no visible oxidation likely because the substrate is not directly in contact with the TiO_2 sol and the transfer process involves a condensation step at 70 °C eliminating all the volatile species (such as HCl) that would otherwise be corrosive for the substrate. As discussed above, once again some structures are missing in the transferred areas while others bear a residual layer.

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Figure 63 : Optical image of the transferred structures on a stainless steel substrate. The structured areas of the mould have the following dimensions: $20*20 \mu m^2$ squared areas of squared pillars of depth 700 nm and pitch 2.5, 2 and 1.5 μm (from left to right).

III.3. Perspectives

Micro Transfer printing is very interesting as it allows to imprint without residual layer. Interesting preliminary results were obtained for grating lines and pillars of micron-size dimensions. More work needs to be done to optimize the properties of the initial xerogel (viscosity, ageing, swelling ...) for successful impregnation and homogeneous filling of the mould cavities. Unfortunately, owing to time limitations, this was not possible in the time of this thesis. A system with *in-situ* optical microscopy during transfer, allowing to study the dynamics of the process, including the study of the mobility of the xerogel during demoulding, is expected to be developed in the laboratory for deeper understanding and control of the mechanisms at play. In addition, automatization of the moulding/demoulding process would allow a higher degree of reproducibility and control during the critical step of demoulding after impregnation.

The perspectives offered by this technique are numerous as it allows not only to imprint without residual layer but also to repeatedly transfer structures side by side on the same substrate (see Figure 64). This makes possible to build up large areas of structures from a small PDMS mould, but also to imprint various types of structures side by side or in a 3D-network (i.e. on top of previously formed structures). Moreover, the sol-gel source could be varied in between two transfers allowing for an extra degree of flexibility over the possible structures obtainable by this process.



Figure 64 : a) Scheme of multiple transfers on a same final substrate using small moulds. b) Images of multiple transfer of TiO₂ diffraction gratings transferred side by side on a silicon substrate.

Summary

- Nano imprinting was successfully performed without residual layer by using the developed Micro Transfer printing technique
- A possible mechanism was given with the xerogel receding into the mould cavities when demoulding after impregnation. Transfer was obtained by contacting the swelled xerogel onto a new substrate
- ➤ Transferred CaTiO₃ diffraction gratings were efficiently used as an etching mask
- Systematic studies are now needed to obtain more homogeneous replica and determine the limit of the process

IV. Towards Soft-NIL on large surfaces

As for now, only small patterns (less than 20 x 20 μ m²) had been studied. Indeed, masters were fabricated by Focused Ion Beam with a focus on fast prototyping of structures of various depths and geometries. In this part, inverted PDMS moulds will first be discussed as viable ways to improve the versatility of soft-NIL. Replicas (standard and inverted) made from masters fabricated by dewetting of thick layers on 4 cm² will then be presented.

IV.1. Inverted PDMS mould

Context

In nanoimprint lithography, fabricating a master is time-consuming and represents a huge cost as it is generally done by direct lithography (i.e. E-beam, FIB) to obtain the desired resolution. In this context, the possibility to obtain more diverse structures from the same expensive master is highly interesting. Very importantly, the possibility to invert a mould allows to limit the use (and deterioration) of the original hard master, increasing its lifetime. Moreover, some designs might be very complex or time-consuming to pattern while their inverse is not. For instance, in order to obtain a single pillar on a flat surface by FIB, the substrate's surface needs to be etch all around the pillar on a large area while, in comparison, it is straight forward to etch a single cavity. A simple way is by inverting a mould, as summarized in Figure 65. For instance, a master displaying pillars will give a mould with cavities (negative mould). If PDMS is poured on this mould (that now acts as a master), one can obtain an inverted mould (positive mould) having pillars of the exact same dimensions than those of the original master. From a negative mould, replicas will bear the same structures than the initial master, whereas from a positive mould the structures will be inverted (see scheme in Figure 65).



Figure 65 : Scheme representing the principle of inverted PDMS moulds. First, a mould is made from an initial master by pouring the PDMS reactants and curing it at 70°C for 1h before releasing from the master. This negative mould displays the inverse of the master features. Secondly, after passivation of its surface, the negative mould is used as a master, yielding a positive mould with the same features than the initial master.

However, if PDMS is directly poured on PDMS and cured, cross-linking occurs at the interface and demoulding is impossible. In fact, PDMS is never fully crosslinked, even after extensive annealing some functions can still be reactive. In order to easily separate negative from positive PDMS, different techniques were developed to change the surface functionalization of PDMS. The first occurrence of positive/negative moulds by Giltin *et al*, used hydroxypropylmethylcellulose (HPMC) to ensure effective release of the secondary PDMS layer¹⁵⁴. HPMC is grafted on the PDMS surface which provides a hydrophilic barrier for the penetration of hydrophobic PDMS. Easy demoulding is obtained for structures with large features of several microns and very low aspect ratio. This approach was used for biological applications to grow cells on surfaces replicating the features of the cells membranes¹⁵⁵.

Another technique uses ozone treatment to obtain a hydrophilic PDMS surface, inhibiting the possible cross-linking in between negative and positive PDMS stamps with efficient release of structures of few microns in size¹⁵⁶. However, such techniques revealed harder to implement for the easy release of structures of sub-micron dimensions, in particular when densely packed. In order to tackle this issue, a new technique was developed during the current thesis.

The goal was to obtain a thin buffer layer at the surface of the negative PDMS mould which do not contains PDMS chains and hinder their migrations towards the surface. Ozone treatment and HPMC grafting reduces the PDMS-PDMS interactions, were tested but are not sufficient when the surface area increases in the case of densely packed structures. The approach used here was to deposit a conformal SiO₂ layer of few tens of nanometers by CVD.

Experimental procedure and discussion

To do so, moulds were prepared following this procedure: Si masters were processed with different features and periodicities using FIB or E-beam on Si wafers. Their surfaces were first rendered hydrophobic by immersion for 10 min in a solution of 0.05 M SiCl₂(CH₃)₂ in ethanol before being thoroughly rinsed with ethanol. PDMS reactants (90w% RTV615A; 10w% RTV615B from BLUESIL) were poured onto the master, degassed to remove the trapped air and cured at 70 °C for 1h. After demoulding, the negative moulds are introduced into the PECVD chamber and a given thickness of SiO₂ is deposited. PDMS reactants were then poured onto the SiO₂ treated PDMS, degassed to remove trapped air and cured at 70 °C for 1h before demoulding positive from negative mould. The SiO₂ thickness deposited by PECVD was varied from 5 to 30 nm; results are summarized in Table 9. Positive and negative moulds could not be separated after curing if the thickness of the deposited SiO₂ was less than 10 nm. If instead the thickness of SiO₂ was larger or equal to 15 nm, moulds were easily released.

SiO ₂ thickness deposited	Demoulding of PDMS/PDMS?
5 nm	No
10 nm	No
15 nm	Yes
30 nm	Yes

Table 9 : Results of the variation of the buffer layer thickness deposited by PECVD on the effective release of positive PDMS mould from passivated negative PDMS mould.

Positive and negative moulds, made using 15 nm of SiO₂ as buffer layer, were then used for imprinting TiO₂ films in Soft-NIL conditions (as-deposited layers of 100 nm, HR = 70%, stabilization 70 °C for 1 min, annealing 400 °C for 30 mins after demoulding). To confirm the good quality of the inverted moulds, the replication of two different kinds of patterns were evaluated: a network of densely packed dots (depth 100 nm, diameter 270 nm, pitch 700 nm) and large rings (depth 400 nm, outer diameter D_{ext} 6 μ m, inner diameter D_{int} 3 μ m and pitch 10 μ m). The best way to assess the difference of dimensions of inverted mould be a direct AFM measurement of their morphology. Unfortunately, the AFM equipment available in our lab did not allow to probe the surface of the moulds due to the excessive softness of PDMS. The masters and resulting positive/negative replicas were thus analyzed by AFM in order to compare their dimensions. AFM images are visible in Figure 66 and extracted dimensions are summarized in Table 10. Since TiO₂ layers display large shrinkage upon annealing and the imprinted layers are thin, only the resulting lateral dimensions will be compared. In particular, the difference between positive and negative replicas is indicative of the loss of resolution during the process of inverting moulds. As indicated in Table 10, the depth and lateral size of the imprinted structures vary from master to mould as expected when imprinting TiO₂ thin films. Moreover, the dimensions are

similar for positive and negative replica indicating that there is no notifiable loss in term of dimensions during the inversion of the PDMS moulds.



Figure 66 : AFM images of a) Si masters, b) TiO_2 replicas made from "standard" negative moulds and c) from positive moulds made by inverting mould with SiO_2 buffer layer.

DOTS						
		Depth Diamete		Diameter	Pitch	
Master		100 ± 5 nm		2	70 ± 5 nm	$700\pm10~\text{nm}$
Positive replica	1	28 ± 5 nm		2	85 ± 5 nm	$700\pm10~\text{nm}$
Negative Replic	а	30 ± 5	nm	חm 285 ± 5 nm		$700\pm10~\text{nm}$
RINGS						
		Height	Dev	ct	D _{int}	Pitch
Master	40	00 ± 10 nm	5.5±0.	2 µm	$3\pm0.2~\mu m$	$10\pm0.1\mu m$
Positive replica	15	50 ± 10 nm	5.1±0.	2 µm	$2.8\pm0.2~\mu\text{m}$	$10\pm0.1\mu m$
Negative Replica	16	50 ± 10 nm	$5.6 \pm 0.$	2 µm	$2.7\pm0.2~\mu\text{m}$	$10\pm0.1\mu\text{m}$

Table 10 : Summary of AFM measurements of samples dimensions for masters and corresponding positive and negative replica

Thus inverting PDMS mould could be an efficient alternative to expensive master manufacturing. The structures dimensions and periodicity were demonstrated to be kept during the process. In particular, this technique will be used in the current thesis to replicate and inverse the complex features obtain by spontaneous dewetting to obtain more diverse structures from the same master.

IV.2. Large scale Soft-NIL of dewetted structures

The master was made by depositing a 400 nm thick Ge layer on a silicon substrate at 700°C followed by annealing at 800°C for 4 hours (see Chapter II). The obtained dewetted structures are highly homogeneous over more than 1 cm² (see Figure 67). The difference seen between the sides and the center of the deposited area comes from a slight gradient in temperature inherent to the holder used in the molecular beam epitaxy chamber. Dewetting is thus more advanced on the sides of the substrate (blue square) than in the center (green square).



Figure 67 : a) Optical images showing the connected Ge islands. Dewetting is more advanced on the sides (blue) than on the center of the substrate (green) due to a thermal gradient. b) SEM image of a partially-dewetted interconnected Ge network.

From the original master, positive and negative moulds were obtained following the protocol detailed above. Soft-NIL was performed on various sol-gel formulations: dense TiO_2 , porous TiO_2 and porous SiO_2 . Resulting replicas can be seen in Figure 68 in bright field optical microscopy and in AFM. The structures visible are more or less connected depending on the analyzed zone. Difference in term of the final replica thickness is influenced only by the initial thickness of the xerogel and the film shrinkage during annealing. *In fine*, homogeneous replica are obtained on 2 x 2 cm² on a variety of substrates (silicon, glass, plastic ...). Such structuration is performed in only a few minutes (time necessary to carry out the soft-NIL process).

Such structures are considered for microfluidic devices and the study of biomolecules transport in confined, intricate environment (this study is carried out in Lausanne University by Prof. Pietro De Anna). Moreover, interconnected structures could also be used as robust textured antireflective coatings with superior mechanical resistance. In contrast with the next subchapter, the targeted applications do not necessitate a fine control over the dimensions of the structures (especially since, in the present case, this dimension evolve along the sample). When applied to photonics, the structures dimensions are reduced (as they need to be similar to the wavelength of light) and will play a key role in the final replica properties as will be shown for imprinted Mie resonators.



Figure 68 : (top) Optical image of a porous SiO_2 positive replica on a glass substrate. (bottom) Bright field optical images and AFM profiles of the dewetted master and the corresponding positive/negative replica for various materials.

Summary

- ➤ Fabrication of inverted PDMS mould was demonstrated by casting PDMS on a first PDMS mould after passivation of the surface by deposition of 15nm of SiO₂ by CVD.
- Dewetted structures on 2 x 2 cm² were faithfully replicated in a number of materials with positive and negative print.

V. Applications of nanofabricated structures for photonics

V.1. Principle of Mie resonators

V.1.a. Fundamental aspects of Mie Resonators

Mie resonators can be defined as objects that display Mie scattering. In order to have Mie scattering, objects must have **dimensions similar to the wavelength of the incident light**. In those conditions, exact analytical solutions of the Maxwell's equation, describing the scattering of an electromagnetic plane wave by a perfect sphere, can be obtained ^{157–160}.

According to Mie theory, both metallic and dielectric spherical particles possess strong scattering resonances (see Figure 69a). For non-magnetic and lossless materials, only two parameters define the inherent scattering properties: the dielectric permittivity ε ($\varepsilon = n^2$ for dielectric materials) and the size parameter q that is proportional to the wavelength of the impinging light ($q=2\pi R/\lambda$ where R is the particle radius). For a given size parameter, the dielectric permittivity is negative for metallic particles and positive for dielectrics. For small metallic spheres (q < 1), only local surface plasmon resonances are produced which are purely electric (as the magnetic part is negligible for a spherical geometry). For dielectric particles, both magnetic and electric resonances are of comparable intensity (see Figure 69a). The incoming light induces circular displacement currents of the electric field, i.e. electric resonances, which will in turn give rise to magnetic resonances. This is possible when the wavelength of light inside the particle (λ/n) is comparable to its diameter (Figure 69b):

$$2R = D \approx \frac{\lambda}{n}$$

The calculated field structure of the main resonant modes in dielectric particles of high refractive index (magnetic dipole, electric dipole, magnetic quadripole and electric quadripole) is displayed in Figure 69c.

Many of the plasmonic effects seen in metallic nanomaterials can be found in their dielectric counterparts. Figure 69b shows the efficiency of the various resonances as a function of the refractive index n. For n > 2, Mie resonances are well defined, with spectral positions corresponding to a given ratio of $2R/(\lambda/n)$. Strong resonances, induced by interactions with incoming light, can be achieved in high-index materials for many different geometries (spheres, cylinders, rings ...). Depending on the geometry, the positions of the resonances can be considerably different. Moreover, the relative localization of the electric and magnetic dipole resonances can be tuned separately giving a very high degree of flexibility of the achievable resonances.



Figure 69 : **Mie resonances of a spherical particle.** (A) Scattering efficiency (dimensionless ratio of scattering cross section to geometrical cross section of the particle) for a lossless particle with size parameter q = 0.5, for plasmonic ($\varepsilon < 0$) and dielectric ($\varepsilon > 0$) materials. Abbreviations for resonances: ed, electric dipole; eq, electric quadrupole; md, magnetic dipole; mq, magnetic quadrupole. Only the first resonant modes are shown. (B) Scattering efficiency of a lossless dielectric particle (colour scale at right) as a function of refractive index n and size parameter. (C) Illustration of electric and magnetic field structures for different electric and magnetic resonances supported by a spherical dielectric particle. Reproduced from Kuznetsov et al¹⁶¹.

Mie theory has been developed in the beginning of the twentieth century but the first experimental observations of Mie resonances in dielectric nanostructures at visible wavelength were reported only very recently. The first work published by Schuller et al in 2007 showed electric and magnetic resonances in the mid-infrared wavelengths for silicon carbide microrods of 1 to 2 μ m in diameter¹⁶². The experimental demonstration of Mie resonances, at visible wavelengths, in nanoparticles was first reported in 2012 for silicon particles of size ranging from 100 to 200 nm¹⁶³. In order to experimentally measure the Mie resonances, far-field spectroscopy is generally used. In particular, Dark Field spectroscopy allows to directly measure the scattering spectra by illuminating the sample at a low incident angle. The different colours observed in dark-field optical microscopy can be directly linked to the contribution of the electric and magnetic resonant modes (Figure 70). First, as the dimension of the particles changes, the colours observed in dark-field are seen to change. This is due to a shift in the resonance wavelength with the diameter of the particle and of the relative contributions of the different resonant modes. The peaks visible in the dark-field scattering spectra are seen to increase in number for larger particles: resonant modes of higher orders can be confined when the particle dimension increase. For small silicon particles of ~100 nm of diameter, only the magnetic dipole (fundamental mode of the magnetic resonance) is observed. When the diameter of the particle increases up to 140 nm, a second contribution appears corresponding to the electric dipole. For even larger particles, higher modes, such as quadrupoles, are observed.



*Figure 70 : Dark-field optical microscope images (top left), scanning electron microscope (SEM) images (top right), and dark-field scattering spectra (bottom) of spherical Si nanoparticles with approximate diameters of 100 nm (A), 140 nm (B), and 180 nm (C). Reproduced from ref*¹⁶³.

V.1.b. Properties and applications of Mie Resonators

Mie resonators are a system of choice for light manipulation in nanophotonics. Ways to efficiently manipulate light are typically based on dielectric coatings (i.e. as anti-reflective coatings), on their stacking (i.e. Bragg mirrors) or on nanostructured coatings for graded refractive index. However, all of those systems are often complex bulky and expensive when efficient light manipulation at visible and near-infrared frequencies is needed. Alternatively, plasmonic particles provides efficient solutions as nanosize systems for light manipulation but are limited to sub-infrared wavelength due to their strong absorbance in the visible range. In this context, Mie Resonators (MRs) based on dielectric materials represent an extremely young and promising research topic.

Experimentally, Mie resonators cannot be suspended in air. In the best case of a perfect sphere, the particles are deposited on a substrate with which they will interact. As Maxwell equations do not have exact solutions for such a complicated system, spectra can only be measured or calculated by finitedifference time-domain (FDTD) simulations. The normalized scattering efficiency have been calculated in the literature for three different systems: (blue) a Si sphere in air, (green) a Si sphere on a Si substrate, (red) a Si cylinder on a Si substrate (Figure 71a) ¹⁶⁴. In the case of the spheres, two distinct resonances corresponding to the first and second order modes are clearly visible, confirming that light is confined in the spheres. When the sphere is deposited on a Si substrate, a small modification of the scattering spectrum is observed confirming the poor coupling between the substrate and the particle. In the case of a cylinder on a Si substrate, resonances broaden and merge into a broadband feature. To better understand this behavior, calculated distribution of the electric field allows to visualize the resonances in the near-filed (Figure 71b). Compared to a sphere on a substrate, for which light is well confined within the structure, cylindrical particles present resonant modes that clearly penetrate into the Si substrate. This broadening can be explained by the interaction of the resonant modes with the substrate, creating a leaky channel for the light. Thus, such interactions can be used to guide or trap light into the substrate (e.g. for applications in light detection and photovoltaic). The choice of the geometrical parameters of the structures (height, diameter, spacing ...) is thus extremely important as it will shape the resonant modes and the resulting overall properties of the system.



Figure 71 : a) Calculated scattering efficiency for a Si sphere in air (blue), a Si sphere on a Si substrate (green) and a Si cylinder on a Si substrate (red). b) Simulated electric field intensity for a sphere and a cylinder on a substrate for first and second order Mie resonances. Simulations are given for the wavelength indicated in each panel. The spheres have diameter d = 150 nm, the cylinder has an inplane diameter of 150 nm and height of 100 nm. The field distribution for the cylinder at resonance overlaps with the substrate, thus introducing a loss channel for the light confined in the particle that broadens the resonances. Reproduced from ref ¹⁶⁴.

A pioneer work published by Spinelli et al ¹⁶⁴ uses a single layer of Mie resonators to obtain a broadband omnidirectional anti-reflective coating on a 6-inch wafer. In this work, square arrays of low aspect ratio Si cylinders were fabricated using soft-NIL on a resist followed by reactive ion etching (RIE) to transfer the features in the silicon substrate (see Figure 72a). Such cylinders, once coated with a Si₃N₄ anti-reflective thin layer, induce a strong decrease of reflectivity down to 1.3% with a strongly reduced reflectivity for angles up to 60°. Other examples of applications of simple assemblies of Mie resonators are for instance dielectric mirrors with reflectance over 98% for a 200 nm wide band (see Figure 72b)¹⁶⁵. In this example, Moitra *et al* used polystyrene spheres self-assembly on a Si substrate to fabricate organized Si pillars after RIE etching. Another interesting work, done by Yang *et al* ¹⁶⁶, reported electromagnetically induced transparency with transmittance up to 100% at a given wavelength by using arrays of Si split-ring resonators made by E-beam lithography and RIE. Moreover, they showed that the position of the transmittance band could be used as a highly accurate refractive index sensor. With those few examples, it is clear that by changing the design of the structures very different light manipulation effects can be obtained.

Moreover, complex assemblies of dielectric resonators were shown to be capable of accomplishing more sophisticated optical functions such as Fano resonances¹⁶⁷, surface Enhanced Raman Scattering (SERS) ¹⁶⁸, anapoles ¹⁶⁹, non-linear effects ¹⁷⁰, optical vortices ¹⁷¹ or mechanically tuneable metasurfaces¹⁷². In the light of the first studies (as Mie resonators is a very recent topic), Mie resonators can promisingly outcome or reach the best existing performances in light manipulation.



Figure 72 : **a**) (top) Si cylinders (250 nm diameter, 150 nm height, 450 nm pitch) fabricated using soft-NIL followed by RIE. (bottom) Specular reflection as a function of the angle of incidence at 405 nm. Si Mie resonators provides a very efficient broad-angle antireflective coating. Reproduced from ref¹⁶⁴. **b**) (top) Si resonators fabricated by PS spheres self-assembly followed by RIE. Dimensions are $D_{top} = 460$ nm, $D_{bottom} = 600$ nm, H = 500 nm and the periodicity of lattice is P = 820 nm. (bottom) Simulated and experimental reflectance. Strong reflectance over 98% is found experimentally for a 200 nm bandwidth. The resonator dimensions are $D_{top} = 460$ nm, $D_{bottom} = 600$ nm, H = 500 nm and the periodicity of lattice is P = 820 nm. Reproduced from ref¹⁶⁵. **c**) (top) Si split-ring resonators fabricated by E-beam followed by RIE. (bottom) Simulated (blue solid line) and measured (red dashed line) transmittance spectrum of the metasurface. Reproduced from ref¹⁶⁶.

V.1.c. Sol-gel TiO₂ Mie resonators

Initial studies of the past few years concentrated on silicon systems, and have shown that Mie resonators (MRs) could outperform plasmonic nanoparticles due to their lower ohmic losses (lower absorbance) at visible and near infrared frequencies. Even so, the still significant optical losses associated with silicon's absorption considerably limit their potential applicability. Furthermore, nanofabrication of Si-based MRs typically relies on specific top-down fabrication technologies (i.e. E-beam, RIE ...), which are impossible to scale-up at affordable prices. We propose to overcome both of these drawbacks by enlarging the field of Mie resonators to dielectric oxide materials, and more precisely to titania-based materials, that can be prepared by cheaper and scalable sol-gel processes using soft-NIL.

Titania is already a material of choice that is found as a component in many technological domains. Here again, it is of particular interest as a result of its high dielectric constant and high transparency in the visible spectral region: Indeed, when comparing n and k dispersions of both Si and TiO₂ (Figure 73) it is clear that Titania appears as the most promising oxide material, as an alternative to Si, as it is nonabsorbent over a larger spectral range extending to near-UV. In addition, TiO₂ has many other advantages that are its high chemical, mechanical and thermal stabilities, its non-toxicity, its excellent photocatalytic properties, its natural abundance, and also its compatibility with sol-gel processes. Despite its ideal physical-chemical properties, the use of TiO₂ in dielectric MRs was only shown just recently in a few examples $^{172-174}$, confirming that electromagnetic resonances could be generated in TiO₂ and that remarkable optical systems can be elaborated.



Figure 73 : Comparison of the (n, k) dispersions for anatase TiO₂ and silicon. Inset zoom of the extinction coefficient curves showing the full transparency of Titania above 360nm.

In the next part, spherical TiO_2 nanoparticules are first studied as a fundamental system, validating the fact that TiO_2 structures can indeed hoist Mie resonances and behave in a similar manner than silicon spheres already studied in the literature experimentally and theoretically. In a second time, arrays of imprinted nanopillars will be fabricated and their properties studied in the context of photonics and light manipulation.

Summary

- Mie resonances characterize the interaction of light with any object of a dimension similar to the wavelength of the incoming light.
- In contrast with plasmonic particles, Mie resonators are lossless dielectrics with a high refractive index (n>2) that displays electric and magnetic resonances.
- Mie resonators can be used to modify an incoming light in many different ways: as antireflective coatings, mirrors, transparent coatings etc.
- Structural parameters of the resonators (dimension, shape, pitch) will strongly influence their resulting properties
- TiO₂ is a material of choice to fabricate Mie resonators which avoids the limitation of silicon systems

V.2. Titania-based spherical Mie resonators: single object investigation

To date, three research groups have studied the properties of Titania particles as dielectric resonators prepared using conventional top-down microfabrication technologies (*e.g.* E-beam)^{139,174,175} or Soft-Nano Imprint Lithography ^{133,137}. They all confirmed that electromagnetic resonances could be generated within these metal oxide objects. However, the limited exploitation of this material is mainly due to the difficulty in applying conventional top-down fabrication methods to TiO₂. Additionally, such approaches do not allow the preparation of spherical resonators, which may be interesting for many applications with effective metamaterials, such as beam steering and backscattering- free optics ^{159,176}, enhanced light extraction¹⁷⁷, resonant transmission¹⁷⁸, light detectors ¹⁵⁸ and much more.

Here, we focus on the investigation of the scattering properties of individual, dense, spherical TiO_2 particles of different sizes. The particles were prepared by a high throughput aerosol generation method. Their structural properties were characterized by scanning electron microscopy and X-ray diffraction, whereas their scattering properties were assessed using dark field microscopy and spectroscopy. The optical resonances observed in experiments are interpreted on the basis of analytical solutions of Mie scattering from a sphere. We demonstrate that spherical Titania particles are efficient scattering objects and can be tuned in size to scatter in a relatively broad range of frequencies (from blue to near-infrared).

Experimental procedure

The spherical particles were prepared by atomizing a hydroalcoholic solution (molar ratios of reactant and solvents are displayed in Table 11 in a carrying air flux using a TOPAZ ATM 210 aerosol generator (Figure 74).

TiCl₄	EtOH	H ₂ O
1	20	5

Table 11 : Molar ratios used for the aerosol.

The nominal size of the droplets varies between 0.1 to several microns. The suspended microdroplets/air mixture passed within a circular furnace at 300 °C for a few seconds to complete evaporation and pre-stabilization of the dry particles. The suspended particles/air mixture was then accelerated at the furnace output using a nozzle and impacted over the target surface (e.g. a Si wafer). This last deposition step lasted for about 10 sec preventing the clustering of the particles and keeping their density sufficiently low, thus allowing for spectroscopic investigation of single objects. The Si wafer sample was then heated at 600 °C for 10 min for densification and crystallization of the spheres. In this configuration, particles of different diameters are generated, which is ideal for the present investigation.



Figure 74 : (a) Schematic representation of the process used to prepare dense TiO_2 Anatase particles on a Si wafer. (b) SEM image of two distinct spheres deposited on Si taken at 55 degrees tilting angle.

In parallel, the same solution was dip-coated using an ACEdip equipment from Solgelway to prepare a homogeneous thin layer on a Si wafer. The as-prepared coating was thermally treated in the same conditions, and analyzed by spectroscopic ellipsometry (Woollam M2000V) to extract the (n, k) dispersion used for the analytical model.

V.2.a. Structural investigation

The GIXRD pattern measured on a substrate with densely packed spheres reveals that they have crystallized under Anatase structure (Figure 75b)). With the GIXRD geometry used for this analysis, the Si (311) Bragg reflection is also detectable around $2\vartheta = 55$ degrees. This is ascribed to the X-Ray beam average divergence and to the huge substrate signal. From the fitting of the Anatase (101) Bragg reflection, the broadening of the peak was calculated to be H_c = 0.29 degrees, giving an average crystallite size of 27 ± 3 nm.

The SEM investigation revealed that the Titania particles have a spherical shape (as evidenced in Figure 74b), Figure 75a) and Figure 77a)). This is ascribed to the fact that aerosol generation atomizes liquid, spherical, micro-droplets that keep their morphology upon evaporation of water and ethanol within the furnace. This fast evaporation also initiates the poly-condensation of the Titania precursors. As a consequence, a stiff shell is formed on the spheres skin, preventing their collapse upon impaction on the receiving surface and keeping a small contact point with the underlying substrate. These spheres are composed of densely packed nanoparticles with a size of the order of tens of nanometers (Figure 75a)). As a result, the surface roughness is estimated to be much lower than the wavelength in the visible range, so that the sphere surface can be considered smooth, with negligible influence on the Mie scattering features.



Figure 75 : a) GIXRD pattern of Titania spheres deposited onto a Si (001) substrate. The diffraction pattern is indexed with PDF #00-021-1272 for the TiO_2 Anatase phase. The peak indexed with a star likely corresponds to a parasite peak due to unknown impurities from the process. b & c) High-resolution SEM image at high magnification of a typical crystalline Titania sphere.

The optical constants of the material composing the particles cannot be measured directly on the spheres. Thus, they were deduced from ellipsometry investigation on a thin, plain film. The ellipsometric curves have been fitted with a Cauchy dispersion with k = 0 and $n(\lambda) = A + B/\lambda^2$ (with A = 2.007, B = 0.058), which gives n = 2.293 at 450 nm. Due to such relatively high index of refraction combined with a high transparency window for wavelength longer than 350 nm and inter-band transitions outside the visible spectral range, TiO₂ spheres are expected to show Mie resonances in the visible range for dimensions above 200 nm in diameter¹⁶⁰.

Spheres featuring diameters ranging from about 200 to 500 nm were first spotted by SEM, then imaged in dark field optical microscopy. Thus, the corresponding scattering spectra were collected via dark field microscopy. The excitation/collection geometry used in experiments and in the analytical model is shown in Figure 76.



Figure 76 : a) Scheme of the excitation/collection geometry used in experiments. NA is the numerical aperture of the objective lens spanning over an angle of ± 48.6 degrees; $< \Im >$ is the average illumination angle determined by the condenser of the microscope (see b) for details). b) Polar diagram highlighting the excitation and collection geometry used in experiments and theory. The theoretical excitation angle was chosen to be the average between the maximum and minimum experimental excitation angles (respectively \Im max and \Im min). The collection angle within the NA of the objective lens is also highlighted.

V.2.b. Spectroscopic investigation

SEM images of TiO_2 spheres with their measured radius (r), corresponding DF images, as well as experimental and theoretical scattering spectra are displayed in Figure 77. This analysis shows that

increasing the size of the particle, the wavelength of the corresponding fundamental resonance (the broader and more intense peak in the spectrum) red-shifts accordingly. This behavior is also reflected on the optical appearance of the spheres (Figure 77b)), where one can observe a marked change of colour (from blue to red) corresponding to a shift of the fundamental resonance.

In small particles (r < 126 nm), only one main resonance is visible corresponding to the fundamental resonant mode. For larger particles (starting from r = 126 nm), multiple and sharper peaks emerge in the spectra at shorter wavelength than the main resonance. The emergence of these multiple peaks accounts for the onset of higher order resonant modes (e.g. electric and magnetic quadrupoles) within the Titania spheres. Finally, for even larger particles (r > 180 nm) the fundamental mode shifts to near-infrared frequencies (non-accessible with our spectroscopic setup) and the higher order modes are quenched: they are spectrally broader and less intense with respect to those found in smaller particles.



Figure 77 : **a)** From bottom to top: high-resolution SEM images of TiO_2 spheres on a Si substrate with increasing radius size. The scale bar corresponds to 200 nm. **b)** From bottom to top: dark-field optical microscope images of the TiO_2 spheres shown in a). The scale bar corresponds to 500 nm. **c)** From bottom to top: scattering spectra produced by the TiO_2 spheres shown in a) and b). **d)** Analytical models of the scattering spectra of TiO_2 spheres in vacuum for radii corresponding to those shown in a), b) and c). The shaded area highlights the spectral range accessible in experiments.

The observations made here correspond fairly well to what could be expected theoretically from a dielectric sphere scattering the incoming light in the far field. From the literature^{157,160}, the lowest order resonant mode is ascribed to the magnetic dipole and is expected at a wavelength of about $\lambda_{MD} = 2.r.n$. For instance, for a sphere featuring a radius of 96 nm and n = 2.3, λ_{MD} is expected at about 440 nm. This is not far from the peak measured in our case at about 460 nm (bottom panel of Figure 77c). At a shorter wavelength with respect to λ_{MD} , the electric dipolar mode can be found followed by higher order modes such as magnetic and electric quadrupoles. These modes are visible in the spectra of particles with a radius larger than 126 nm and come with sharper peaks than the ones of the fundamental resonances.

In spite of the reduced size of the contact point between a sphere and the substrate, the photonic modes are expected to leak in the underlying bulk Si. This is seen in the experimental spectra with: i) a slight red-shift of the resonances, ii) their spectral broadening, and iii) a stronger quenching of the higher order modes with respect to the lowest order modes^{164,179}. This latter feature can be interpreted as a more efficient coupling with the substrate for the modes with intense resonances in the skin of the sphere (typically higher order modes). Nonetheless, in the present case, it is worth highlighting the presence of sharp resonances in the near-UV range, not accessible by conventional Si-based Mie resonators¹⁰⁸.

Finally, it is worth mentioning that the versatility of the aerosol technique in use may be adapted for a plethora of applications, as it allows for a direct transformation of the precursors solution in ready-touse Mie resonators to be sprayed on a surface in a few seconds. In the present case, the poly-disperse size distribution of the particles would lead to an overall broad-band response of the particles, which may be adapted for the production of a structural white paint. However, other techniques compatible with aerosol, such as electrospray¹⁸⁰, can be exploited to produce particles with much narrower size distribution. This suggests the possibility to produce structurally-coloured aerosol sprays for large scale applications.

In this perspective, we show the changes in colour response evaluating the 1931 CIE chromaticity coefficients¹⁸¹ for the smaller investigated particles (r < 150 nm) as their spectra lies in the visible range (and colorimetry functions are defined between 380 and 780 nm). Using a chromaticity gamut allows to evaluate the quality of the colour: the purest colours are the furthest away from the center. In spite of the presence of the Si substrate (featuring a larger refractive index with respect to the Titania composing the spheres), our Mie resonators present neat colours in the visible range, spanning from blue-green up to orange of the CIE chromaticity gamut. Thus, even if TiO₂ has a lower refractive index with respect to Si and Ge, Titania spheres have the potential to be exploited for coloured metasurfaces^{137,139} in analogy with the IV-IV counterpart^{95,175,182}.



Figure 78 : CIE chromaticity gamut for selected TiO_2 spheres with radius ranging from 96 to 150 nm (obtained from non-normalized, raw spectra). The position of the source is specified in the map as a white full circle.

These results support the possibility to exploit our particles for structural colours and for efficient light manipulation from near-UV up to near-infrared frequencies, confirming the relevance of these spherical Titania-based resonators. The bright and sharp resonances found in experiments agree fairly well with very simple, analytical model for isolated perfect spheres, confirming that magnetic and

electric dipolar modes can be sustained even if the spheres are deposited on a high-n material (such as the Si substrate in use).

Spectroscopic investigation of single spherical TiO₂ particle was performed Spherical TiO₂ particles can support Mie resonances. Resonances are seen to red-shift with increasing radius Good correlation is found between experiments and the analytical model used Neat structural colours are obtained for the spheres with the smallest radius (r < 150 nm) confirming that such spheres could be exploited for structural colours

V.3. Sol-gel imprinted Mie resonators: "Black Titania"

In contrast with the previous investigation on single objects made by aerosol spray, Soft-Nano Imprint Lithography allows to prepare large areas of closely packed nanostructures of the same dimension and morphology. In the next part, Soft-NIL will be used to obtain sol-gel imprinted Mie resonators. The properties of such surfaces will be thoroughly investigated.

V.3.a. Structural features of Master and TiO₂ replica coatings

Experimental procedure

Masters are elaborated by Focused Ion Beam (FIB) milling of a porous silica matrix in order to increase the milling rate (see details in Chapter II). Arrays of square motifs of different lateral and transversal dimensions and periodic separation were prepared using a dual-beam liquid-metal focused ion beam (LMAIS-FIB) from Orsay Physics (selected Au⁺ from AuSi source / 30 keV / 130 pA). After hydrophobisation using SiCIMe₃, PDMS is poured on the master, degassed in vacuum and cured at 70°C for 1h. The PDMS mould is then peeled off the master surface after cooling. Soft-NIL of sol-gel layers is performed on TiO₂ xerogels prepared by dip-coating (Table 12) (see details above in Chapter III.II). Dip-coating is carried out at room temperature, RH=40% and withdrawal speed between 2 and 6 mm.s⁻¹ to obtain as-prepared xerogels with a homogeneous thickness between 100 and 250 nm. A degassed mould was then applied onto the xerogel without additional pressure at 70% relative humidity for 1min before consolidation at 120°C for 3mins (temperature ramp for reaching that temperature is about 2 minutes). After demoulding, the coatings are annealed at 350°C for 10 min to ensure complete removal of the F127 polymer and to complete the TiO₂ xerogel condensation and crystallisation into anatase without extensive diffusive sintering ¹⁸³.

TiCl ₄	EtOH	H ₂ O	F127
1	75	6	5.10-4

Table 12 : Molar ratios used for the dense TiO₂ formulation.

Refractive index and porosity of Titania coatings.

The refractive index of the materials is known to be a key parameter in Mie resonances and must thus be determined with precision. The use of different substrates for the implementation of sol-gel coatings (*e.g.* on glass and on Si wafers) could lead to different crystallization kinetics, due to differences in adhesion and in thermal coefficient, and thus to changes in the optical properties of the TiO₂. Nevertheless, the presence of a thin SiO₂ layer on the Si matrix (native oxide, typically few nm thick), renders the influence of the two substrate *quasi* equivalent. In order to confirm this point, we systematically measured the refractive index of the different replicas via ellipsometry on zones located aside the arrays (measuring by ellipsometry the refractive index of a single pillar is impossible).



Figure 79 a) Refractive index dispersion of the TiO_2 material measured aside the zone containing the motifs on SiO_2 (black curve) and on Si (red curve). b) Adsorption and desorption curves recorded by ellipsometric porosimetry on the stabilized TiO_2 film as a function of the relative pressure of water (analysis performed aside the zone containing the motifs). c) Corresponding pore size distribution derived from the adsorption and desorption curves.

As shown in Figure 79, the results are very similar and the optical constant dispersions of the final TiO₂ material were $n(\lambda) = 2.05 + 0.05/\lambda^2$ (Cauchy model with λ/μ m) and k(λ)=0 in the visible range, as expected for sol-gel TiO₂¹⁸³. The obtained tendency is lower than with bulk crystalline TiO₂ as a results of the sol-gel process that leads to the formation and arrangement of small anatase crystallites, leaving small interstices (voids, pores) between them ^{136,184}. This refractive index was obtained for an annealing treatment at 350°C for 10min. The temperature was chosen to be just above the temperature of crystallisation and compatible with the thermal resistance of many kinds of substrates. Therefore, a denser TiO₂ film, exhibiting higher refractive index, can be obtained by sintering at higher temperatures (see Figure 52a).

At 350°C, the presence of the void has been confirmed by environmental ellipsometric porosimetry. In Figure 79b, the adsorbed water quantity is seen to increase progressively up to $P/P_0 = 0.4$. After $P/P_0 = 0.5$, a plateau is visible confirming that no larger pores are present. The sample is thus mainly constituted of micro and small mesopores with broad size distribution. The desorption curve almost overlaps the adsorption one (small hysteresis). This isotherm is characteristic of interstitial voids between randomly packed small particles (as it is the case here with small Anatase particles). From the isotherm and the corresponding pore size distribution (Figure 79b & c), one can deduce that the total porosity of the TiO₂ thin film is ~16% in volume (V_{ads} at P/P_0=1) and is composed of pore having diameter < 4 nm (average pore diameter = 2.5 nm +/- 1 nm). In this experiment, Pluronic F127 agent wasn't used to create a controlled ordered mesoporosity but only to ensure a good wetting of the substrate by the solution. For such a reason, the quantity of F127 added in the solution is too low to induce the formation of micellar templated mesoporous titania film as conventionally reported with higher F127 content ¹³⁶. However, it is likely participating to the formation of the latter residual porosity.
Structural characterization

Starting from a master designed with $20*20 \,\mu\text{m}^2$ square array of square pillars, the TiO₂ replica exhibits slightly smaller pillars (dimensions are given in Table 13) with an isotropic shrinkage of 35% vol inherent to the TiO₂ sol-gel chemistry and with the same pitch.

Fourier transform analysis of HR-SEM images is shown in the inset of Figure 80 and reveals a broadening and a doubling of the spots for the replica with respect to the master, suggesting a slight deformation of the mould during imprinting. In addition, careful statistical analysis over the arrays of pillars reveals that the master as well as the replica have pillars that are slightly asymmetrical (one dimension is about 10% bigger than the other) probably caused by astigmatism during the FIB milling process. In the top-view HR-SEM images, the measured lateral dimensions are considered to be equivalent at the top and at the base of the motif.

	Height (H)	Width (L)	Pitch (P)
Master	$320\pm20~\text{nm}^{*}$	$640\pm30~\text{nm}$	$800\pm30~\text{nm}$
Replica	200 ± 15 nm	$415\pm20~\text{nm}$	800 ± 30 nm

Table 13 : Dimensions of the master and the corresponding TiO_2 replica. All values were deduced from HR-SEM images except the value noted with * that was deduced from the FIB etching calibration.

In order to determine more precisely the morphology of the structures, important for the calculation of Mie resonances, profile view of the arrays were obtained by HR-SEM after sample milling by liquid metal ion source focused ion beam (LMIS-FIB), as shown in Figure 80b (this image is obtained from a similar sample to that shown in Figure 80a). A typical truncated square-pyramidal morphology of the motifs is observed together with a residual layer of an estimated thickness around 25 nm. The height of the pillars from the top level of the residual layer is H = 200 ± 15 nm, while the base and the top of the pyramids have dimension of L_{BASE} = 400 ± 25 nm and L_{TOP} = 200 ± 10 nm, respectively. The value of the base extension corresponds to the dimension measured in Table 13. The reduction in the pillar dimensions is a volume shrinkage, attributed to the typical elimination of the volatile species during drying and thermal annealing of the sol-gel.

In order to investigate the influence of the array structural characteristics, other samples with different motifs height (H), side (L_{BASE} , L_{TOP}) and pitch (P) were prepared following the same procedure. These characteristics will be systematically mentioned for each sample in the following text. Aside, the roughness of the TiO₂ surface was estimated from AFM measurement to be as small as 0.25nm (RMS), allowing for a negligible light scattering from the flat surface (see Figure 81).



Figure 80 : **a)** HR-SEM images of the master (left) and the TiO_2 replica on glass (right). The Fourier transforms of the corresponding HR-SEM image are given in the bottom left inset. **b)** Statistical analysis of the width distribution of the pillars for the master and for the replica. A size reduction of about 35% is observed from master to replica. **c)** HR-SEM image of the pattern profile (from a similar sample of that shown in a)). The relevant parameters of the pillars (height H, base size L_{BASE} , top size L_{TOP}) and of the pattern periodicity (P) are highlighted. The sample was prepared via FIB milling.



Figure 81 : a) AFM analysis of a TiO_2 coating collected on a flat zone under the PDMS (non-patterned) after thermal annealing. Calculated mean square roughness (RMS) is 0.25 nm. b) Light scattering in dark field configuration from a flat zone of TiO_2 with very low diffusion.

V.3.b. Optical properties of titania-based Mie resonators

Resonant scattering of TiO₂ MRs array on glass

First of all, we want to confirm that our imprinted TiO_2 structures are able to support Mie resonances. To do so, dark field microscopy (DF) allows selecting the resonant part of the light scattering rejecting the non-resonant part (*e.g.* the reflection from the substrate). Thus, the bright colours scattered in DF images are accounted for by the formation of resonant modes in the MRs. Figure 82 dispatches a Dark-Field optical microscopy and the corresponding scattering spectrum of a typical TiO_2 array of MRs on glass. In this case, MRs are truncated pyramids having H = 300 nm, L_{BASE} = 230 nm, and L_{TOP} = 185 nm (with typical size variation in the range of 5%). Even if the colour appears homogeneous for each resonator, a precise understanding of these features requires a spectroscopic investigation of the scattered light. This characterization is shown in Figure 81b and a scheme of the custom-made experimental setup used in this thesis is shown in the appendix.

In our case, the MRs are around 200-300 nm in dimension so we expect the fundamental resonant peak to be at around 500 nm for a refractive index slightly above 2 (from the approximation $D \sim \lambda/n$). In the spectra displayed in Figure 81b, a broad peak is observed centered at 480nm fitting quite well the expected values provided by the previous approximation and confirming the possibility to create resonant modes within our TiO₂ motifs. The peak is very broad (around 150 nm for full width at half maximum) and shoulders are visible on the sides of the peak. This shape can be attributed to size and shape variations of the pillars within the etched pattern. Indeed, the scattered colours in the DF image are not uniform across the pattern, consistent with the small structural and dimension fluctuations obtained upon imprinting and seen in the HR-SEM characterization. In addition, the overall area probed with the spatial filter of the confocal microscope is about 50 μ m² meaning that the full imprinted array (20*20 μ m²) is measured. In summary, the sol-gel prepared TiO₂ pillars have a high enough refractive index to efficiently induce the formation of Mie resonances at visible frequencies.



Figure 82 : a) Dark field optical microscope image of a TiO₂ MRs array (P = 800 nm; H = 300 nm; $L_{BASE} = 230 \text{ nm}$; $L_{TOP} = 185 \text{ nm}$; Residual TiO₂ layer = 25 nm) deposited on glass. Bottom left inset: HR-SEM image of a portion of the array. b) Resonant scattering intensity as a function of wavelength.

Reflection and transmission of TiO₂ MRs arrays on glass

In order to assess the influence of the MRs morphology on light propagation through the sample, reflection and transmission were studied on three arrays of pillars elaborated on glass (A, B and C). The three patterns were fabricated to have a different aspect ratio η :

$$\eta = H_i/L_i$$

with $L_i=1/2(L_{BOTTOM,i} + L_{TOP,i})$. The dimensions are deduced from AFM and HR-SEM (see Table 14 and Figure 83). The pitch remains the same for the three samples and the aspect ratio increases from sample A to C (from $\eta = 0.75$ to $\eta = 1.1$).

	Aspect ratio (η)	Height (H)	Width (L)	Pitch (P)
С	1.1	$440\pm20~\text{nm}$	$390\pm20~\text{nm}$	$1000\pm30~\text{nm}$
В	0.92	$390\pm20~\text{nm}$	$425\pm20~\text{nm}$	$1000\pm30~\text{nm}$
Α	0.75	$330\pm20~\text{nm}$	$440\pm20~\text{nm}$	$1000\pm30~\text{nm}$

C 440 m 440 m 40 m 40 m 40 m 40 m 10 m 10

Table 14 : Structural dimensions of the three arrays of pillars imprinted in TiO₂

Figure 83 : From left to right : SEM, AFM images and corresponding AFM profiles for the three arrays of pillars imprinted in TiO_2 on glass. The aspect ratio increases from A to C (from bottom to top).

Given that the non-patterned layer has a thickness of 90 nm (measured by ellipsometry), the residual layer thickness is estimated to be around $t_{A,B,C} \sim 25 \pm 5$ nm for all three samples in agreement with the HR-SEM investigations (Figure 80c). This value is deduced from a volume conservation law considering that the initial layer volume is divided, after imprinting, between residual layer volume and the volume of the structures. For a straightforward comparison of the TiO₂ MRs performances, all the spectra are normalized to the reference spectrum measured on a bare flat silica substrate.



Figure 84 : a) Bright field reflection microscope image of nano-imprinted sample and of a flat zone nearby. The inset shows a scheme of the illumination used for microscopy imaging. b) Reflection spectrum for 3 patterns having different pillar aspect ratio ($\eta_A = 0.75$, $\eta_B = 0.92$, and $\eta_C = 1.1$). The reflected intensity is normalised to the reflection of a SiO₂ substrate without TiO₂. c) and d) Same as for a) and b) for the transmission case. Note that the sample orientation is reversed with respect to the previous case of reflection.

All samples show a pronounced reduction of the light intensity with respect to the flat TiO₂ layer as accounted by the optical microscope images (see Figure 84a) and c)). These optical images obtained in reflection and in transmission modes, show clearly that patterned zones appear much darker than the non-patterned zone aside. The corresponding spectra of this "black TiO₂" coating show a large reduction over a broad wavelength interval both for reflection and transmission configurations (see Figure 84 b) and d)). Reflection spectra show two minima centered at 450nm and 700nm for all samples. The greatest reduction of reflection is observed for pattern C (higher aspect ratio, η_c =1.1) with a minimum of about 37% at ~700nm. This is in stark contrast with what was found for the non-patterned coating, which exhibits enhanced reflection over the whole range of investigated frequencies as expected for a 90 nm thick TiO₂ layer on glass (see Figure 85). Interestingly, the pillar arrays play the role of an antireflective layer.



Figure 85 : Simulated reflectance for bare glass and glass coated with a 90nm thin layer of TiO₂.

The transmitted intensities from the patterns show a marked reduction, with a minimum of about 35% over a broad spectral interval. Differently from the reflection case, the most marked effect is found for pattern A (lower aspect ratio), which exhibits reduced transmission on a broader interval. Here, the pillar arrays play the role of filters by cutting more than 60% of the incident light, this part being thus certainly trapped and scattered. These combined effects explain why the patterns appear "black" in both transmission and reflection configurations. These spectral features lead to the conclusion that a strong redirection of light occurs during *propagation* through the TiO₂ arrays and a large portion of light is trapped within the coating/substrate.

These results highlight the importance of the pillar morphology and aspect ratio. One can infer that a simple array of sub-micron pillars, made by imprinting a TiO_2 coating, has radically different optical properties with respect to the pristine 2D layer as a result of the Mie resonances. Moreover, it reveals that an intrinsically "transparent" material, such as titanium oxide, can become an "absorber" if patterned with the proper structure to form Mie resonances. Finally, the relative transmission and reflection intensities can be modulated with the pillar aspect ratio.

Theoretical simulations

In order to understand the impact of the different parts of the sample on light reflection, finitedifference time-domain (FDTD) simulations were performed with varying pillars' aspect ratio η and different thickness of the underlying TiO₂ layer *t*. The results are summarized in Figure 86. This investigation shows that an increase in η leads to a red shift of the spectral features, as expected when increasing the MRs' dimension. For the tallest pillar ($\eta = 1.1$), an additional mode at shorter wavelengths appears (see Figure 86a). This is not surprising as the overall increase in the pillar volume allows it to accommodate higher order modes (*e.g.* quadrupolar modes) featuring a sharper band in the spectrum. More striking is the role of the TiO₂ residual layer below the MRs (see Figure 86b). The FDTD simulations demonstrate that a large increase of reflection can be obtained by increasing *t*. At the same time, an overall red-shift of the resonances is observed together with the onset of higher order modes.



Figure 86 : **a)** Simulated reflection spectra as a function of wavelength for t = 0 nm and the 3 different pillar aspect ratios of interest for this study (patterns A, B and C). The spectra are normalised to the SiO₂ substrate reflection (thus, 100% corresponds to the reflection of the SiO₂). **b)** Simulated reflection spectra as a function of wavelength for $\eta = 0.92$ (corresponding to the case B of Figure 84) and 3 different thicknesses of the residual TiO₂ layer.

For a deeper understanding of these features, the internal field distributions within the pillar motifs (see Figure 87b) is plotted for the labelled minima in the simulated reflection spectra in Figure 86b). The relevant features are summarized as follows. For the case $\eta_B = 0.92$ (H=390 nm) and t = 25 nm (corresponding to sample B in Figure 84 and to the red curve in Figure 86b)) three minima, labelled I, II, and III are present. In the central column of Figure 87b, the simulated E² (electric component of the confined mode) and H² (magnetic component of the confined mode) are displayed at the specific wavelengths corresponding to the minima. Minima I and II respectively at $\lambda_{simulation} = 750$ nm and $\lambda_{simulation} = 550$ nm, correspond to first order electric and magnetic Mie resonances, which are strongly confined in the pillar and coupled to the substrate underneath them. A further resonance (minimum III) at $\lambda_{sim} = 420$ nm appears to be a second order magnetic dipolar mode.



Figure 87 : **a**) Scheme of the different parts of the sample considered in FDTD simulations. The thickness of the residual TiO_2 layer underneath the MR is denoted as t. **b**) Internal field distribution at the labelled minima in the reflection spectra in Figure 86b). Left, central and right columns show respectively the cases t = 0 nm, 25 nm and 50 nm at the wavelengths indicated on the spectra shown in Figure 86b). For each case the field intensity (E^2 or H^2) is plotted in the corresponding plane of detection (yz or xz). The intensity of the field in each panel of d) is self-normalized and are in arbitrary units, thus, their relative intensities cannot be directly compared. (More details on FDTD simulations is available in the appendix)

Increasing the thickness *t* of the 2D layer underneath the pillars from 0 to 50 nm (from the left to the right panels in Figure 87b leads to the onset of several phenomena: firstly, an overall increase in the reflected intensity is observed. This is due in part to the high refractive index of the TiO₂ increasing the substrate's Fresnel reflection coefficient with increasing thickness of the 2D layer, and also due to the onset of constructive interference after reflection over the wavelength range considered. Furthermore, the minima observed in the reflectance spectra in Figure 86b are seen to double, for example minimum II for t=25nm transitions to minima A and B at t=50nm. This phenomenon can be better understand by plotting the near field distributions at wavelengths corresponding to minima A and B (Figure 87b). Two distinct effects are visible: minimum A is still attributed to a substrate coupled Mie-resonance (as for no residual layer). However minimum B is associated with a trapping of light in the residual layer, as shown by the confined nature of the fields in this region.

These findings show that t is a critical factor for tuning the optical properties of the MRs from highly reflective (for larger t) to less reflective (for thinner t). Indeed, for optimal anti-reflection performance, it must be as close to zero as possible, meaning that all of the TiO_2 must be patterned during imprinting so as to leave no residual layer. The near field distributions of Figure 87b explain the origins of the reduction of the reflection at the specific wavelengths yielding reflection minima and corroborates the efficiency of titania pillars acting as dielectric Mie resonators.

The FDTD simulations accounts for the formation of Mie modes as shown above. I, II and III minima also appear in the experimental reflectivity spectrum in Figure 86a) for pattern B, although they feature a blue-shift and a lower intensity. These discrepancies with the simulated spectra may be attributed to slight differences in the chosen structural parameters for the simulation (shape, asymmetry, residual layer homogeneity, size distribution), with respect to the real experimental pattern characteristics. Moreover, the dispersion of the refractive index is disregarded in the simulations, where it was assumed as constant (n=2.2) over the full spectral range. Importantly, the simulations refer to the case of excitation at normal incidence with respect to the sample surface and collection over the full upper half space above this surface (angle of collection = 180 degrees). However in the experimental spectroscopic investigations, the incident and collected light only spans over a limited collection angle of about 60 degrees. As a result, the cone of detection limited by the numerical aperture of the microscope objective lens cannot be 180 degrees as in the simulation, leading to larger simulated values of reflection (on this point see also Figure 88b)). In summary, all these issues lead to the observed significant differences in the measured and simulated reflection spectra.

V.3.c. Anti-reflection coating on silicon

As a second example of application, TiO₂ MRs with the same structural parameters of pattern B in Figure 84b) (H = 390 nm, η_B = 0.92, and t = 25 nm) were imprinted on a silicon substrate. A broadband anti-reflection effect, ranging from 400 to 1000 nm and reducing the reflection by up to 70% with respect to that of the bare silicon, is observed (see Figure 88 a)). The reflection does not manifest any resonant features, which is likely due to the large broadening induced by the presence of the high

refractive index of Si underneath¹⁷⁹. The measured values of reflection are close to those found by Spinelli et al. for a similar system ¹⁷³. Here again, the measured spectra are integrated over a solid angle of ~60 degrees, leading to an overestimated reflectivity with respect to experiments performed at normal incidence shown by Spinelli et al ¹⁷³. As it is difficult to quantify this effect from simulation with resonators, we compared the theoretical normalised reflectivity of a 90 nm TiO₂ plain coating at normal incidence on silicon, to the experimental reflectivity of the same layer integrated over an angle of 60 degrees. As expected, a significant overestimation in the reflectivity is found for the measurements compared to the simulations due to the broader angular range of excitation and collection. Note that, even if the reflectivity of the plain layer reaches extremely low values at specific wavelengths, it must be underlined that this effect occurs only at a certain incident angles. This is not the case with MR arrays that feature reduced reflectivity over a wide angle range¹⁶⁴. These optical properties can be further improved through careful optimisation of the resonator structural characteristics. Nevertheless, this first result allows one to conclude that the present method, based on sol-gel/NIL TiO₂, can be efficiently used to prepare broad-band and broad-angle antireflection coatings on silicon.



Figure 88 : a) Reflection spectrum measured from pattern B on silicon (same as Figure 84) normalised to the measured reflection from a flat Si substrate. b) Same as a) for a flat un-patterned TiO_2 layer (90 nm thick). The dashed line corresponds to the theoretical prediction of reflection at normal incidence from a TiO_2 layer of 90nm thickness normalised to the reflection of silicon. The refractive index of the TiO_2 layer in the simulations is n=2.1 (red line). The two insets on the right show the excitation/collection configuration used for simulations (bottom) and for experiments (top).

V.3.d. Conclusion

In summary, we have demonstrated a sol-gel dip-coating/soft-NIL method for the fabrication of TiO_2 based MRs on arbitrary glass and silicon substrates. The imprinted coatings exhibit optical properties that are very different to those of pristine plain coatings on glass as a result of Mie resonances. Lighttrapping is responsible for the "black titania" appearance in transmission mode and we estimated that over roughly 60% of light remains strongly coupled in the system. Moreover, with the same technique, a reduction of ~70% of the direct reflection was achieved on bulk silicon at visible and near infrared frequencies. Even though these values are obtained in non-optimised conditions, they demonstrate that sol-gel/soft NIL is a pertinent strategic method for the fabrication of these novel 3D structures. Advantages include high flexibility, speed, and cost effectiveness with respect to common top-down fabrication methods. Moreover, in contrast with most common top-down etching methods, our soft-NIL process does not damage the wafer surface thus avoiding any carrier loss by recombination with surface states ¹⁷³. Finally, the annealing process to consolidate the TiO₂ structures does not exceed 350°C, which is perfectly compatible with all substrates withstanding this temperature (*e.g.* polyimide, glass, metallic and semi-conducting alloys), and with Back End processes in silicon electronics. This opens the way to a direct printing of MRs on photovoltaic cells, and many other optical devices.

Summary

- > TiO₂ nanostructures imprinted by Soft-NIL can support Mie resonances.
- ➢ Morphology and aspect ratio of the imprinted TiO₂ pillars strongly influence the resulting properties (reflection, transmission)
- ➤ Used on glass, imprinted TiO₂ pillars display a lower reflection and lower transmission than bare glass in complete contrast with plain TiO₂
- > Imprinted "black titania" coatings trap over 60% of the incoming light on glass
- > If used on silicon, reduction of about 70% of the reflection is achieved

V.4. Large scale demonstrator

Mie resonators made out of pillars have been shown to be interesting for light manipulation and in particular as anti-reflective and light-trapping devices as explained above for "Black Titania". One of the main challenges remaining is to obtain structured arrays over large surfaces. Indeed, for now, only arrays of 20 x 20 μ m² were studied which complicate the measurements of the optical and structural properties. To measure those small arrays, a confocal microscope mounting with an optical fiber was used to reduce the detection area to a spot size of about 10 x 10 μ m². Moreover, demonstrating optical effects induced by Mie resonances on large scales would bring this technology one step closer to realistic industrial applications.

Experimental procedure and structural characterization

Here, we use masters having structured arrays of 1 mm² made by E-beam lithography and RIE. An Ebeam resist is first patterned and selectively removed; then a nickel mask is deposited and used to etch silicon by reactive ion etching. Finally, the nickel mask (located at the top of the pillars) is dissolved by chemical treatment followed by ion milling (to remove the nickel silicon alloy). Master fabrication is performed in a PLANETE CT PACA cleanroom facility, thanks to Frédéric Bedu and Igor Ozerov (Aix-Marseille Univ, CNRS, CINaM). 9 arrays of squared pillars of height 500nm, gap (distance between two structures) of 150 nm and pitch varying between 380 and 600 nm were fabricated (see Figure 89).



Figure 89 : a) Image of the master with large arrays (1 cm^2) of pillars of sub-micron size. b) SEM image of one of the arrays with pillars of the following dimensions: pitch 460nm, height 500 nm, width 280 nm.

The master was replicated using Hard PDMS as introduced above (see part on h-PDMS). Experimentally, an h-PDMS blend (h-PDMS from Gelest Inc) is directly poured on the hydrophobized master and partially cured for 10 mins at 50°C then a thick PDMS buffer layer (RTV615 from Momentive) is poured and annealed at 50°C for 12 hours then at 70°C for 2 hours. Moreover, in order to obtain a surface tension as low as possible to ease demoulding, the master surface is previously grafted with a fluorinated precursor. For instance, 1H,1H,2H,2H-perfluorodecyltrichlorosilane has been widely studied as anti-adhesive¹⁸⁵ and will be used here. TiO₂ replicas were made using the same set-up and protocol than before. A TiO₂ xerogel is first deposited on glass by dip-coating in controlled environment (22°C, 20% RH) then placed in a specially designed chamber in which RH = 70%. Previously

pumped for 10 min, the mould is put into contact with the xerogel after allowing its equilibrium for 1min. Finally, after 1min, the assembly mould + substrate is annealed at 70 °C for 5 min and demoulded. The replica is then annealed at 450 °C for 30 min.

Figure 90 displays the optical and SEM images of a TiO_2 replica. The structured areas are visible by eye and looks sensibly darker than glass coated with a plain TiO_2 layer. From bright field microscopy investigations, homogeneous colours are visible on a large scale, the slight variation of the colour from side to middle of the 1 mm² array is expected from side effects. Indeed, high mobility of the xerogel will result in more material filling the cavities on the sides of the pattern which would lead to higher pillars. Anyhow, pillars are homogeneous on more than 400 μ m².

The dimensions of the master and TiO_2 replica are summarized in Table 15 for structures of 460 nm pitch. Well-ordered pillars of 160 nm depth, 220 nm width and 460 nm pitch are obtained after soft-NIL. The diminution of the pillars dimension from replica to master and the cracks visible in the SEM image are caused by the large shrinkage inherent to TiO_2 xerogel (volumic shrinkage of 70%). This reveals that a thin residual layer is present underneath the pillars which is expected to play an important role on the properties of the structures as seen in the previous example.

A similar evolution, between the master dimensions and the replica dimensions, can be expected whatever the pitch. In addition, the width of the pillars are expected to increase with increasing pitch as the gap in-between pillars remains the same.



Figure 90 : (left) Image of a TiO_2 replica on glass with large arrays (1 cm²) of pillars of sub-micron size. (right) Bright field optical image, SEM image and AFM map of one of the arrays imprinted from a mould with the following cavities dimensions: pitch 460 nm, depth 500 nm, and width 280 nm. The mould is prepared from the master which SEM images are displayed in Figure 89.

	Height	Width	Pitch	
Master	$500\pm10~\text{nm}$	280 ± 5 nm	$460\pm10~\text{nm}$	
Replica	$160\pm10~\text{nm}$	220 ± 5 nm	$460\pm10~\text{nm}$	

Table 15 : Summary of the dimensions of the master and the resulting TiO₂ replica for a motif of a squared array of squares, measured from AFM and SEM images.

Optical properties

The optical properties of the structures were collected for the various arrays using a confocal microscope in a similar configuration than used previously (see Appendix).

Figure 91a & c shows the spectra of the array studied above with nanopillars of 160 nm height, 220 nm width and a pitch of 460 nm. Complex spectra with sharp peaks can be seen both in reflection and

dark field configuration. In order to get an idea of the evolution of the spectra with the pitch, chromaticity gamut were calculated from the corresponding spectra and are displayed in Figure 91b & d. Sharp structural colours (*i.e.* data points far from the center of the gamut) are obtained whatever the pitch. In reflection, only a small variation of the colour is observed with increasing pitch (see arrow in Figure 91b) whereas in scattering, the colour is highly dependent on the pitch. For instance, starting with an orange light source, it is possible to obtain orange scattering colour for structures with a pitch of 400 nm, sharp blue for structures with a pitch of 500 nm and green for a pitch of 550 nm.

Further investigations are needed to understand the origin of the structural colours obtained here. In particular, FDTD simulations would allow to get insight into the Mie resonances and the relative contribution of the structures dimensions and their coupling with the substrate.



Figure 91 : **a)** Reflection spectrum corresponding to an array with pillars of height 160 nm, width 220 nm and pitch 460 nm. **b)** Reflection CIE chromaticity gamut for nanoimprinted arrays of pillars with pitch varying from 380 to 600 nm (obtained from non-normalized, raw spectra). The arrow is a guide for the eyes to follow the evolution of the colour from 380 to 600 nm pitch. The position of the source is specified in the map as a white full circle. **c)** Scattering spectrum corresponding to the same array than a). **d)** Scattering CIE chromaticity gamut (obtained from non-normalized, raw spectra) for the same array than a).

In addition, the structures were illuminated using the guided modes of the glass slab on which they are fabricated (see Figure 92a). This is similar to dark-field imaging as the incoming light is not collected by the detector: only the scattering induced by Mie resonances will be detected. To do so, a white LED light source was shined on the edge of the glass slide, far from the samples, to make sure that light could not reach the structured arrays by other means that through the glass (see scheme in Figure 92a). The resulting optical images are displayed in Figure 92b. Bright colours are seen homogeneously over 1 mm² with very different colours from one array to another. Slight differences between forward and backward scattering are probably due to the internal reflection of the scattered light in the glass slide but also to the directionality of the resonant modes.



Figure 92 : a) Schematic representation of the set-up used to measure the scattering resulting from the interaction of the Mie resonators with the guided light. b) Optical image of the backward and forward scattering. Really different colours are visible from one array to the other.

This investigation proved the feasibility of Soft-NIL to directly yield large surfaces of nano-sized pillars (each 1 mm^2 array contains 4.10^6 pillars) from sol-gel TiO₂. Spectroscopic investigations confirmed the interest of such structures as metasurfaces with sharp structural colours.

Much remains to be done, as further spectroscopic investigations and simulations would allow to understand the origin of the properties observed here and their potential applications for light manipulation. In any case, the applications of Mie resonators are numerous especially when large surfaces are available. For instance, such structured arrays could be examined in the light of other fields of applications such as sensors with optical transduction.

VI. Conclusion

In this chapter, we started by shedding light on the principle and context of Soft-Nano Imprint Lithography (Soft-NIL) on sol-gel thin films and we highlighted recent innovations that allowed to decrease the pressure used during the process (*i.e.* Degassed Assisted Patterning) and the achievable resolution (*i.e.* hard-PDMS).

Our first objective was to optimize the Soft-NIL process for sol-gel films. We proposed new sol-gel formulations as NIL resists. By a simple control over the Relative Humidity in the NIL chamber, water was used as fluidizing agent and a quantity corresponding to $30\%_{vol}$ of the film was found to give optimal imprinting. An in-depth study of the imprinting parameters (RH, T, aging ...) was performed for TiO₂ and extended to three other sol-gel materials (Al₂O₃, SiO₂, Y-ZrO₂) confirming that this approach could be extrapolated to the imprinting of most sol-gel films. This study proves that sol-gel films with no organic moieties (such as chelating agents) can be successfully imprinted. Furthermore, Micro Transfer Printing was introduced with similar sol-gel formulations. By taking advantage of the high mobility inherent to freshly deposited sol-gel coatings, residual layer free nanostructures were obtained by the latter technique. The mechanism and potential of this technique was explored with examples on various substrates such as silicon, glass or stainless steel. In addition, we showed that it is possible to fabricate inverted PDMS moulds by using a first PDMS stamp as a master after passivation of its surface. All the improvements made to the Soft-NIL technique in this chapter focused on the increase of its throughput and on its scalability. To confirm the latter point, nanostructures made by solid state dewetting on very large surfaces (4 cm²) were used as masters and were successfully replicated on sol-gel thin films.

Then, the nanostructures fabricated by Soft-NIL were applied to photonics. After introducing Mie theory and the interest of Mie resonances for light management, we proved, through several examples, that structured surfaces with nano-sized objects can indeed display Mie resonances. First, TiO_2 spheres produced by aerosol spray were studied. Spectroscopic investigation confirmed that the spheres can indeed support Mie resonances and a good correlation was found between experiments and the analytical model used. Next, photonic properties of nanoimprinted surfaces with 20 x 20 μ m² arrays of nanopillars were investigated and compared to FDTD simulations. Study of the optical properties of such surfaces revealed an anti-reflective behavior on glass and on silicon. In particular, trapping of 70% of the incoming light in the structured coatings was obtained on glass, coining the term "black" titania coatings.

Finally, a demonstrator on 1 mm² with nanopillars was successfully fabricated and showed sharp structural colors visible with the naked eye. Complementary spectroscopic investigations are still on the way. This result proved the feasibility of the Soft-NIL technique to produced nanostructured surfaces on a large scale with very interesting photonic properties.

Chapter IV: Nanofabrication by directed solid state dewetting

Self-assembly via dewetting can be modified and controlled by taking advantage of the surface chemical or topographical inhomogeneities. In this chapter, different strategies will be studied to organize nanometric objects via solid state dewetting and obtain narrow size distribution. First, inorganic nanopatterns will be exploited for the dewetting of germanium thin layers. Dewetting parameters and pre-deposition treatments will be underlined as key to control the process. Inorganic nanopatterns will then be presented as a substrate to direct the dewetting of gold thin layers following a different strategy than in the case of semiconductors thin films. Finally, controlled dewetting of thick germanium layers will be demonstrated by using sol-gel nanoimprinted surfaces.

I. Organization of Ge nanocrystals by double selfassembly

In this chapter, we show the use of hybrid self-assembled surfaces yielding **inorganic nanopatterns (INPs)**. Interestingly, INPs have been previously used to modify solid state dewetting. In this study, Rowell *et al*⁴⁸ deposited a thin layer of germanium directly on TiO₂ INPs, without any pre-treatment, at room temperature in ultra-high vacuum followed by annealing at 450 °C for 20 minutes in order to induce the complete dewetting and formation of islands. The resulting substrate showed Ge nano-dots of about 20 nm in size, randomly dispersed on the TiO₂ surface. Size distribution was reduced compared to non-patterned surfaces and interesting photoluminescence results were obtained⁴⁸. However, in this case, no organization was found, highlighting the difficulty of directing the growth and dewetting of semiconductor NPs even on patterned substrates such as the INPs.

Here we report on a method to obtain large surfaces of highly organized Ge nano-dots through a double self-assembly procedure. Ceramic nano-patterned surfaces bearing organized nano-perforations arranged in hexagonal lattice are first prepared through chemical solution deposition, self-assembly of block copolymer and annealing. After appropriate hydrofluoric acid (HF) etching treatment, such layers display topographical and **chemical inhomogeneity** between the surface of the template and the perforations. This unique feature can be exploited to modify the solid state dewetting of a Ge thin layer and obtain Ge-based nano-crystals at the bottom of the perforations. Precise 2D arrangements of monocrystalline Ge dots with narrow size distribution can be achieved on a scale of several centimeters. This work led to a patent¹⁸⁶.

Experimental

Sol-gel initial solutions were prepared with the respective molar ratio presented in Table 16. $PB_{12.5}$ -b-PEO₁₅ refers to polybutadiene-block polyethylene oxide with blocks of 12500 and 15000g/mol.

TiCl ₄	EtOH	H ₂ O	PB _{12.5} -b-PEO ₁₅	PB5.5-b-PEO30
1	320	42	0.0015	/
1	320	42	/	0.001

Table 16 : Molar ratios of the precursors and solvents needed to make inorganic nanopatterns.

The solution is divided in two parts: in part A, PB-b-PEO is dissolved in 2/3 of the ethanol and water; part B contains TiCl₄ and the remaining ethanol. The solutions are aged for 2 h at 70 °C then part A is slowly cooled down to room temperature in about 30 mins. Finally, both parts are mixed together before use. Films were deposited on cleaned silicon wafer by dip coating at a temperature of 40 °C and a relative humidity below 20%, using a withdrawal speed ranging between 1 and 3 mm/s in order to obtain a film thickness of less than 10 nm. The resulting film is then annealed at 450 °C for 30 mins. As explained in Chapter I, PB-b-PEO block copolymers are chosen because they form large micelles in solution and display high thermal stability as assessed by thermal gravimetric analysis TGA (see Figure 93).



Figure 93 : TGA analysis of Pluronics F127 and a larger block copolymer $PB_{12.5k}$ -b-PEO_{15k}. TGa was performed in air with a ramp of 5 °C/min. F127 is seen to start degrading at 250 °C whereas PB-b-PEO is stable up to 400 °C.

Substrates, previously dip-coated to obtain self-assembled perforations, are cleaned by thoroughly rinsing with EtOH then immersed into a diluted hydrofluoric acid (HF) solution of 1.17 mol/L for 20 seconds. Quickly after HF treatment, the substrates are placed under vacuum in an epitaxy chamber (Riber Molecular Beam Epitaxy) at a pressure of 10^{-10} Pa and 2 nm of germanium are deposited from an effusion cell (T_{Ge cell} = 1150 °C). The temperature of the substrate during the process is first of 450 °C to remove any remaining impurities then placed at the required temperature.

Structural characterization of the resulting films are performed using Atomic Force Microscopy (AFM) (PSIA XE-100 AFM), high resolution scanning electron microscopy (SEM) (Dual-beam FIB HELIOS 600) and high resolution transmission electron microscopy (HRTEM, MET FEI Tecnaï G2, used at 200 kV). Their refractive index and thickness, before Ge deposition, were measured by spectroscopic ellipsometry (Woollam M2000V) using a Cauchy model for dielectric films. X-ray Diffraction (XRD) patterns were recorded on a conventional diffractometer in Bragg–Brentano geometry (PANalytical Empyrean) using Cu radiation ($\lambda = 0.154$ nm), a rapid detector (PANalytical PIXcel) and an offset of 4 degrees to avoid Si substrate contribution. Grazing incidence XRD (GIXRD) analyses were performed on the same set-up with a parallel plate collimator 0.27 degrees at two different incident angles (w from 1 and 1.6 degrees) and different in plane angle measured from the Si substrate [010] direction (j = 45 to 60 degrees). Before any analysis the sample was carefully oriented with the Si (001) perpendicular to the diffraction plane.

I.1. Discussion

Highly organized Ge nano-dots were obtained following the procedure schematized in Figure 94. The SEM picture, visible at the bottom right of the figure, shows an example of a substrate bearing a TiO_2 layer with nano-perforations inside which perfectly dispatched Ge nanocrystals are found.



Figure 94 : Scheme representing the process used to obtain organized Ge nano-dots. A monolayer of micelles embedded in a titania gel is first deposited on a silicon substrate. After annealing, TiO_2 inorganic nano-patterns are formed revealing the surface of the substrate. In the appropriate conditions (discussed later), a single Ge nano-dot per perforation is obtained.

Comparison dewetting vs. directed dewetting

On bare silicon, dewetting of a thin layer of Ge is known to form randomly disperse islands with a large size distribution. To direct dewetting and reduce size distribution, a self-assembled network of micelles embedded in a titania matrix are deposited by dip-coating on the surface forming, after annealing, inorganic nano-patterns (INPs). A layer of 2 nm of germanium is deposited at 650 °C under ultra-high vacuum then annealed at 650 °C for 20 mins.

Without the INPs layer, large dots of different sizes are found randomly dispersed on the surface (Figure 95a). Analysis of the SEM images gave an average diameter of the Ge dots of 40 nm with a very large diameter distribution ranging from 10 to 65 nm (Figure 95d). If instead dewetting takes place on the INPs surface, Ge nanodots feature a much narrower size distribution of 23 ± 10 nm in diameter (Figure 95b) as already demonstrated in a previous study⁴⁸. With this additional surface texturation, the presence of energetically favorable points leads to a more homogeneous size distribution with respect to the spontaneous dewetting case. However, even if the size distribution is drastically reduced compared to a flat surface, no precise spatial organization is found.

In order to obtain a precise organization of the dots, the position of defects must be controlled which could be the case with the INPs network as it bears organized perforations. However, without any additional treatment, the bottom of the perforations still consist of the native silicon oxide having a low affinity with Ge. *In fine*, Ge nanodots will preferably nucleate on the TiO₂ INPs network where defects, such as grain boundaries between anatase crystals, will locally increase the surface energy, providing narrow size distribution but no organization.

In contrast, with the appropriate chemical etching, the native oxide can be eliminated from the bottom of the perforations revealing the silicon surface while keeping the TiO_2 structure intact. Silicon is a convenient nucleation point for Ge growth since Ge is highly miscible in Si. In the right deposition conditions (discussed in details later), the nucleation of Ge nanodots will lead to an organized network of dots, with one dot per perforation.

Figure 95c displays the results of the deposition of 2 nm of Ge, a sharp size distribution of 17 ± 2 nm is found without any dot on the INPs network. Ge nano-dots are well organized in a hexagonal lattice with the same network parameters than the INPs. Importantly, as the dot parameters (size, arrangement) are directly dependent on the INPs network, they can be easily varied by simply changing the network parameters.



Figure 95 : Deposition and dewetting of 2 nm of Ge at 650 °C followed by annealing at 650 °C for 30 mins on a) a bare silicon surface, b) TiO_2 INPs without chemical etching, c) TiO_2 INPs after appropriate etching. d) Size distribution in diameter of Ge nano-dots after deposition in different conditions, deduced from image analysis.

Optimization of the HF treatment

TiO₂ nano-patterns before germanium deposition are visible in Figure 96a. After annealing, a network of round perforations, in place of the micelles, is obtained through diffusive sintering⁴⁰. The surface of the silicon wafer is clearly visible through the perforations. Compact hexagonal lattice is found at a length of few micrometers while, at a larger scale, hexagonal domains with different orientations are found. With the copolymer PB_{12.5k}-b-PEO_{15k}, perforations have a diameter of 20 ± 3 nm with a spacing of 40 nm between perforations (center-to-center). Thickness of the INPs was measured to be 7 nm with a refractive index of $n_{\lambda} = 1.66 + 0.05/\lambda^2$. This refractive index is lower than dense TiO₂ has expected for a porous layer.

Very importantly, the surface visible through the perforations is silicon dioxide (SiO_2) because of the native oxide originally present at the surface of the silicon wafer. To remove this oxide, typically of a thickness of about 2 nanometers, substrates are immersed into a solution of diluted HF (1.17 mol/L). The calibration curve, displayed in Figure 96b, was measured by ellipsometry on a flat SiO₂ layer initially 50 nm thick, by immersion in the HF solution during a time ranging from 5 sec to 1 min while actively stirring. With a HF concentration of 1.17 mol/L, a time of 20 seconds will be used which is sufficient to remove about 4 nm of SiO₂. This duration is optimal to remove the silicon oxide thickness without damaging the INPs. Indeed, titania is also dissolved by HF but at a lower speed than SiO₂. Figure 96c shows that the resistance of TiO_2 to HF is highly dependent on the annealing temperature. After annealing at 350°C for 30 mins, the INPs are totally removed after a HF treatment of 20 seconds. Only partial damages are visible on the INPs network after thermal treatment at 400°C for 30 mins whereas no damage can be seen after annealing at 450°C for 30 mins. Extended crystallization of the titania INPs seems to be necessary to obtain better chemical resistance to the acid. Indeed, in the case of thin films, crystallization of titania in anatase starts around 300°C and crystallites, of only a few nanometers at first, grow larger with increasing temperature through diffusive sintering (see Chapter I)^{49,184}. Anyhow, if the etching duration exceeds 40 seconds, even in the case of annealing at 450 °C, the INPs network is totally removed from the surface. This is caused by the lift-off of the INPs by etching of the SiO_2 underneath. Once the native oxide at the bottom of the perforations is removed, the substrates are placed under vacuum in order to avoid the oxidation of the bare silicon surface. At this point, the diameter of the perforations is measured to be 28 ± 4 nm.



Figure 96 : a) SEM image of the INPs surface before HF etching. b) Calibration curve displaying the etched thickness of a flat SiO₂ layer as a function of time. c) SEM images of the INPs surface after immersion in HF (1.17 mol/L) for 20 secs after annealing the TiO₂ INPs for 30 mins at different temperatures.

Optimisation of Ge deposition parameters

Deposition of 2 nm of Ge is performed in an epitaxy chamber under ultra-high vacuum (P = 10^{-10} torr), while the substrate is maintained at a given temperature T_{evap} . After deposition, the substrate is annealed at a temperature $T_{annealing}$ for a certain time to dewet the thin germanium layer. The process is summarized in Figure 97. The pre-deposition annealing step ("Flash", Figure 97), at 450 °C for 20 mins, leads to the transformation of anatase TiO₂ into rutile as deduced from subsequent XRD analysis. Even if the transition from anatase to rutile is generally expected above 600 °C for thin films¹⁸⁴, ultra-high vacuum conditions is promoting the diffusion enough to lead to this transition at a temperature as low as 450 °C.

To assess the state of the surface after deposition, the number of Ge nanodots in the perforations (N_{Ge1}) and on the substrate (N_{Ge2}) is calculated from SEM images for a given area covering at least 150 dots for each measurement and is summarized by the percentage of coverage ($%_{coverage}=N_{Ge1}/(N_{Ge2}+N_{Ge1})$). If nano-dots are only found in the perforations, $%_{coverage}=1$. Different deposition conditions were assessed and results are summarized in Table 17 and Figure 98.



Figure 97 : Scheme representing the Ge deposition process in Molecular Beam Epitaxy (MBE) chamber under ultra-high vacuum conditions. Parameters that are varied during the study are written in red. After HF treatment, the substrate is introduced in the chamber. A flash thermal treatment is systematically performed to remove impurities, followed by Ge evaporation at a given temperature (T_{evap}) and dewetting of the deposited layer at a temperature $T_{annealing}$ and a time $t_{annealing}$.

If Ge is deposited on the INPs at room temperature, the percentage of coverage is seen to be around 60% whatever the post-annealing treatment. For instance, a coverage of 55% is found after annealing at 450 °C for 20 mins while coverage is 58% for 650 °C for 20 mins. This means that almost as many dots are found on the INPs network than those present in the perforations. In all the investigated samples, one dot per perforation is always found while the number of dots found on the INPs surface is variable.

This shows that the bottom of the perforations (silicon) are indeed energetically favorable for the nucleation and dewetting of Ge. Indeed, Ge and Si have very similar crystalline structures and specific nucleation of Ge on silicon is expected. Moreover, this could also be explained by the fact that the surface energy of silicon is slightly higher than the one of rutile titania ($\gamma_{Si(100)} = 2.13 \text{ J/m}^2$ against $\gamma_{TiO2(211)} = 1.91 \text{ J/m}^2$)^{187,188}. Nevertheless, even if the surface energy of the later is lower than the one of silicon, the presence of defects on the TiO₂ INPs surface (topological roughness, crystal defects or grain boundaries) will also similarly lead to the nucleation of Ge islands. From these results exposed above, post-deposition annealing doesn't seem to have any effect on the placement of the dots. Once deposited at a particular position (on the Si surface or on TiO₂), the barrier for the diffusion of germanium is too high to be overcome by an increase of the temperature.

In order to promote the placement of the dots solely in the perforations, a higher deposition temperature is necessary. Indeed, better results are found at 450 °C with a coverage of about 80% whatever the post-annealing conditions. Following the same trend, perfect coverage if found at 650 °C with Ge dots only in the perforations.

This result shows that the mobility of germanium can only be promoted during the nucleation step before the formation and growth of Ge crystals on TiO_2 . Above a threshold temperature, germanium will specifically nucleate at the interface with silicon: inside the perforations. As the surface energy of silicon is slightly higher than the one of TiO_2 , the increase of the atomic diffusion with temperature leads to specific nucleation on silicon. More probably, the number of defects on the TiO_2 INPs decreases with the temperature. Indeed, TiO_2 crystallites grow in size with increasing temperature through diffusive sintering which will reduce the number of grains boundaries and the overall number of defects able to trigger the nucleation of Ge. This is similar to what was reported for the annealing

of anatase TiO_2 INPs (see Chapter I), in this case, for rutile TiO_2 INPs and under ultra-high vacuum conditions.

	а	b	С	d	е	f
T_{evap}	20°C	20°C	20°C	450°C	450°C	650°C
$T_{annealing}$	450°C/20'	450°C/2h	650°C/20'	450°C/48h	650°C/20'	650°C/20'
% coverage	55%	64%	58%	79%	78%	100%

Table 17: Resulting placement of the nanodots for various temperatures during the deposition of 2 nm of Ge (T_{evap}) and various post-deposition annealing conditions $T_{annealing}$. Letters in the first row corresponds to SEM images in Figure 98.



Figure 98 : SEM images of the TiO_2 INPs surface after the deposition of 2 nm of germanium in various conditions summarized in Table 17.

Advanced characterization of Ge dots

HRTEM analysis in Figure 99 revealed that the dots are indeed in direct contact with the silicon surface confirming that silicon oxide has been removed from the bottom of the perforations. A thin layer of SiO_2 native oxide can still be seen in the TEM images but it is mainly a projection of the thin layer present underneath the inorganic perforations. At the location of the Ge dot, in the perforation, the atomic lattice of Ge is seen to extend up to the crystalline surface of silicon. The monocrystalline nature of germanium is clearly visible and confirmed by Fourier Transformation. Moreover, (001) facets are visible with no apparent defects confirming the perfect hetero-epitaxy of the Ge nanocrystals on silicon.



Figure 99 : TEM analysis of Ge dots in TiO_2 perforations with corresponding Fourier Transform. Facets are easily visible on the Ge crystals.

XRD analysis is shown in Figure 100. The inset corresponds to the XRD pattern recorded in Bragg-Brentano geometry with an offset of 4 degrees: it shows no detectable diffraction peaks due to either very few crystallized volume or highly textured film (preferred crystallographic orientation along specific directions).

To observe the diffraction peaks of silicon and germanium in GIXRD, several points have to be taken into account: (i) in the configuration used here, at $\varphi = 0$ degree, the in-plane orientation of the Si (001) substrate is along the [010] direction. (ii) In a cubic system, the angle between the (001) and (311) planes is of $\alpha = 25.24$ degrees. (iii) The theoretical 2 θ angle for (311) reflections is $2\theta = 53.68$ degrees for Ge and $2\theta = 56.12$ degrees for Si. In this case, the corresponding diffraction peaks should appear at $\omega = 1.6$ degrees for Ge (311) and $\omega = 2.8$ degrees for Si (311) in GIXRD geometry. In other words, for germanium, $2\theta_{\text{theoritical}} = 53.68^\circ = 2$ ($\alpha + \omega$); since $\alpha = 25.24^\circ$ thus $\omega = 1.6^\circ$. GIXRD measurements will thus be taken with ω around 1.5 degrees and $\varphi = 45$ degrees in order to detect the (311) planes.

Experimentally, Figure 100 clearly shows that the diffractions peaks are only visible around $2\theta = 55$ degrees and that the diffraction peaks disappear when the sample is in plane rotated ($\varphi \neq 45$ degrees) as expected. Moreover, Ge (311) peak detection is optimized at $\omega = 1.6$ degrees. Concerning the Si (311) Bragg reflection, it is also detectable at incident angle of $\omega = 1$ degrees and 1.6 degrees, which are close to the expected value of $\omega = 2.8$ degrees considering the X-Ray beam average divergence and the huge substrate signal. At $\omega = 1$ degrees, the peak at $2\theta = 53.91$ degrees corresponds to an average between the Ge (311) and TiO₂(211) reflection, these peaks being clearly dissociated when the incident angle is 1.6. At $\omega = 2.8$ degrees, the Si (311) reflection is optimized and only small parts of the Ge (311)

and TiO_2 (211) are visible. This analysis thus confirms the unique Ge crystallite orientation, with (001) plane parallel to the Si substrate (001) plane, thus in agreement with HRTEM analysis.



Figure 100 : **a**) Schematic representation of the set-up used in GI-XRD. The incident angle is ω , the collection angle 2 θ , the in-plane angle φ and the angle between the surface (100) and the planes (311) is α . **b**) XRD analysis of TiO₂ INPs bearing Ge nanocrystals: patterns recorded in GIXRD geometry with two different incident (ω) and in plane (φ) angles (in plane angle is measured from the Si substrate [010] direction); inset: XRD recorded in Bragg Brentano geometry with 4 degrees offset.

Variation in the INPs network parameters: smaller perforations

Inorganic nano-perforations with a smaller perforation diameter were deposited using a smaller block copolymer ($PB_{5.5k}$ -b-PEO_{30k}). Such films display the well-ordered perforated network as seen for the larger perforations (Figure 101). The mean diameter, deduced from SEM, is 12 ± 2nm.



Figure 101 : SEM images of the TiO_2 INPs network after annealing for: a) small perforations of 12 nm (PB_{5.5}-b-PEO₃₀), b) large perforations of 20 nm (PB_{12.5}-b-PEO₁₅).

Deposition was carried out following the procedure optimized for larger perforations (HF treatment 20 sec, 2 nm of Ge deposited at 650 °C then annealing at 650 °C for 20 mins). SEM imaging after deposition shows that one Ge crystal is found in each perforation with a few large Ge dots visible on the TiO_2 network (Figure 102a). This corresponds to a $%_{coverage} = 92$ %. Thus, it seems that in the case of smaller perforations, a deposition at a temperature of 650 °C doesn't give enough mobility to Ge in order to diffuse entirely towards the perforations even if the later are small. The temperature was then gradually increased until no dots were found on the INPs surface. At a temperature of 800 °C, the INPs network starts to lose organization with a collapse of the inorganic nano-perforations, merge to form larger dots as the TiO_2 topographical barrier is breaking apart. We note that, in this case, no Ge dots are found on the INPs.

A narrow window thus seems to exist with full organization of germanium in the perforations before the TiO₂ INPs become instable. Results of deposition at 775 °C show organized Ge dots with full diffusion in the perforations (Figure 102b). The TiO₂ network begins to collapse but the extent is not large enough to allow the Ge dots to merge. In this case, a percentage of coverage of 98% is found with very few dots on the INPs. The average diameter of the dots on the INPs is about the same than the ones in the perforations in contrast with the previous case when Ge deposition was performed at 650°C. The very small size of the Ge dots in the perforations did not allow to obtain SEM images with sufficient resolution to extract a size distribution. Nevertheless, as Ge crystals are located within the INPs perforations, their size diameter is bound to be smaller than the one of the perforation (12 ± 2 nm) and can be roughly estimated to 9 ± 3 nm. HRTEM analyses are on the way. Note that, in the case of smaller perforations, the annealing step after evaporation (see scheme, Figure 97) was suppressed from the process as similar results were obtained with or without post-annealing. Since the temperature is maintained for a shorter time, this allows to work at higher temperature without damaging the INPs.



Figure 102 : SEM images of the TiO₂ INPs after the deposition of 2 nm of germanium at different temperatures: a) deposition at 650 °C, b) deposition at 775 °C and c) deposition at 800 °C. No annealing is performed after deposition.

I.2. Conclusion

By using inorganic nano-patterns, local chemical inhomogeneity was obtained between the layer surface and the bottom of the perforations directing the assembly of Ge nanocrystals into the perforations. Nano-dots were highly organized with one dot per perforation leading to a very narrow size distribution and hexagonal organization. Inspection of the Ge crystals by HRTEM and XRD revealed the hetero-epitaxy of Ge on silicon with visible facets and without any crystal defect. Finally, smaller perforations were used to decrease the Ge crystals size distribution. The Ge dot assembly can be thus easily tailored in terms of dot size and spacing by simply changing the INPs network parameters. Samples were sent for photoluminescence characterization, strong photoluminescence signal is expected from Ge crystals of sub-20nm diameter with narrow size distribution.

Summary

- Thanks to the chemical heterogeneity brought by the INPs, Ge dots are highly organized with one dot per perforation
- Sharp size distribution of 17 ± 2 nm with hexagonal compact organization is found (for a perforation diameter of 28 ± 4 nm of the inorganic nanopatterns)
- > Germanium crystals are monocrystalline and facetted in heteroepitaxy on Si without defects
- It is possible to change network parameters (dot size, spacing) by varying INPs network parameters.

II. Self-assembly of Au nanodots by directed dewetting on INPs

In this part, we will use the heterogeneity given by INPs to direct the dewetting of a thin Au layer. Indeed, Au dots are of great interest (especially if organized) since they can be used in microelectronics as catalyst for the growth of wires such as silicon nanowires by Vapor Liquid Solid (VLS) mechanism but also for sensing for instance in Surface Enhanced Raman Scattering (SERS).

If dewetting of a thin Au layer is performed on bare silicon, a very large size distribution with dots between few nanometers and few hundred of nanometers is expected¹⁸⁹. The mean diameter of the droplets is expected to be roughly thirty times the Au deposited thickness; which means, in the present case of a 3.5 nm Au layer, droplets of about 100 ± 50 nm in diameter. Obtaining narrow size distribution is thus inachievable by spontaneous dewetting. Various strategies have been proposed to obtain Au dots of less than 100 nm in diameter with a small size distribution^{86,190,191} but these processes are unfortunately more or less cumbersome with various resist patterning and etching steps impractical for scaling over large surfaces. For instance, Choi et al¹⁹⁰ showed nicely organized Au dots of 30 ± 5 nm in diameter: by using laser interference lithography to pattern a resist, silicon oxide is localy removed by wet etching followed by gold deposition. After annealing and lift-off of the photoresist, gold dots are left only in the etched areas with one dot per pit. In addition, direct lithography techniques have also been demonstrated to produce similar results with highly organized sub-100nm Au dots¹⁸⁹ however these techniques are inherently limited to small surfaces.

By following the procedure schematized in Figure 103, a network of well-organized gold nanoparticles with one dot per perforation is obtained with a narrow size distribution. This technique, using INPs to direct the Au dewetting, can be very easily applied to the wafer scale.



Figure 103 : a) Scheme representing the process used to obtain organized Au nano-dots. A monolayer of micelles embedded in a titania inorganic gel is first deposited on a silicon substrate. After annealing, TiO_2 inorganic nano-patterns are formed revealing the surface of the substrate. Following a chemical etching, a thin layer of gold is deposited and annealed to form Au droplets. With an appropriate mechanical etching, droplets on the TiO_2 INPs network are removed leaving only the Au dots in the perforations. b) SEM image of the obtained, well-organized, Au nano-dots with one dot per perforation.

A TiO₂ network of inorganic nano-perforations (INPs) is deposited by dip-coating using the same procedure than that one developed in the previous part (see Experimental section of Chapter IV, part 1). After deposition of a monolayer (about 7 nm) of block copolymer micelles embedded into an

inorganic TiO₂ gel, the substrate is annealed at 450 °C for 30 mins. Samples are then etched in diluted HF (1.17 mol/L for 20 seconds) in order to remove the native silicon oxide at the bottom of the perforations and reveal the silicon surface without damaging the INPs. Open perforations of 28 ± 4 nm in diameter are obtained with accessibility of the substrate surface. Quickly after HF treatment, the substrates are placed in a sputtering chamber (P = 4.10^{-6} mbar) and a layer of 3.5 nm of Au is evaporated on the substrates at room temperature.

Figure 104a shows the surface of the layer straight after deposition. The gold layer broke down into islands of various size and shape that covers the entire substrate. The presence of the TiO_2 network can be guessed with smaller islands inside the perforations and large elongated islands on the network.

In order to obtain more homogeneous Au domains, an annealing step is performed in an epitaxy chamber under ultra-high vacuum ($P = 10^{-10} Pa$) at 450 °C for 30 mins. In those conditions, Au thin layers are known to dewet and form isolated islands¹⁸⁹. The film after annealing shows round gold droplets confirming the high mobility of gold at this temperature (Figure 104b). A large size distribution of the Au dots is found with size ranging from 10 to 45 nm (Figure 104d). Moreover, dots are randomly arranged without any specific interaction with the bottom of the perforations or with the INPs network. This is probably due to the fact that Au does not have a specific affinity for silicon compared to TiO₂. In this case, only topographical defects are directing dewetting which is not sufficient to obtain organized arrays of dots.

Even if higher temperature could have been beneficial to give higher mobility to the dots, gold could not be annealed in ultra-high vacuum at temperatures higher than 600 °C in order to avoid evaporation of gold and contamination of the epitaxy chamber. In any case, in comparison with Ge, appropriate dewetting and localization of the dots could only be obtained by varying the temperature during the deposition step while no effect was found on the organization with post-annealing. However, in our case, the same strategy could not be tested as the sputtering chamber was not equipped with an annealing module.

As ordering of Au dots could not be obtained solely via dewetting, another approach we developed was to selectively remove the dots on the INPs network while keeping only those formed within the perforations. To do so, various chemical etching were tested (HF, HNO₃, H₂SO₄) and various mechanical etching (ultrasonic bath, sticking tape, embedded PDMS layer) but without success. Finally, abrasion of the surface by gently rubbing with fabric was found to be the most effective method for removing the dots on the TiO₂ without impacting those formed within the perforations. Indeed, as gold has a poor affinity for the surface, it can be removed mechanically quite easily. By rubbing the surface only the raised areas will be impacted: the Au dots on the INPs. Figure 104c presents the image of the surface of 0.75 N/cm². Nice organization with hexagonal arrangement is found corresponding to the INPs network parameter as confirmed by Fourier Transformation (FT). The size distribution of the Au dots after such mechanical treatment, statistically measured on a minimum of 150 objects, is narrow with a measured dot diameter of 28 ± 5 nm which is in good agreement with the size of the perforations (Figure 104d). The slight broadening towards smaller dots can be explained by the fact that not all the perforations are fully filled by gold.



Figure 104 : SEM images of a) TiO_2 INPs after the deposition of a thin Au layer, b) TiO_2 INPs with Au droplets after annealing at 450 °C for 30 mins in ultra-high vacuum, c) TiO_2 INPs with Au droplets after annealing and mechanical etching. Insets display the corresponding Fourier Transformation. d) Distribution of the Au dots diameter after annealing, before and after mechanical etching.

Whereas, in the case of Ge, dewetting could be precisely directed to yield a dot per perforation; Au does not have the same affinity for the silicon substrate. Thus mechanical treatment is performed to remove the Au dots on the INPs network to obtain optimal arrangement in term of organization and size distribution with one Au dot per perforation. Such samples are expected to be interesting structured surfaces for VLS growth. For this purpose, samples were produced on Si (111) substrates following the same protocol and sent for preminilary VLS tests to grow silicon nanowires. In addition, our team is currently working closer with SERS specialists to determine the interest of such Au dots surfaces for spectroscopic analyses.

Summary

- Au was evaporated and dewetted on inorganic nanopatterns
- Mechanical rubbing of the surface is necessary to remove Au dots on the INPs network
- Narrow size distribution (28 ± 5 nm) was found
- Hexagonal organization of the Au dots with one dot per perforation

III. Dewetting of Ge thick layers on Soft-NIL nanopatterned surfaces

Nanoimprinted surfaces have never been used to direct the dewetting of semiconductor thin layers. In this part, we will used soft-NIL on sol-gel layers to fabricate structures able to direct the dewetting of germanium layers as schematized in Figure 105. Polycrystalline germanium crystals are obtained in a controlled configuration.



Figure 105 : a) Scheme representing the direct dewetting process with: first the deposition of a sol-gel layer; its imprinting to obtain a TiO_2 layer bearing 3D structures; the deposition of a conformal Ge layer; and its dewetting at high temperature giving Ge dots. b) SEM image of the obtained Ge dots complying with the organization of the imprinted squared pillars.

Structures were imprinted from a FIB master having square arrays of squares of various heights. Softnanoimprinting was performed using a PDMS stamp on a TiO₂ sol-gel layer deposited by dip-coating (see chapter III for detailed description of Soft-NIL on sol-gel). Conditions during soft-NIL were: RH= 70%, imprinting time = 1 min, stabilization at 70 °C for 1 min then stabilization at 120 °C for 1 min in an oven before demolding. Finally, annealing at 450 °C was performed in order to fully condense TiO₂ and obtain the anatase phase. Figure 106 shows the SEM image of the TiO₂ replica, in each square of 20 x 20 μ m², pillars of different size are visible. The height of the pillars increase from left to right (better contrast can be seen). Cracks visible on the edge of the squares are caused by TiO₂ strong shrinkage during annealing and do not impact the imprinted zones with pillars.



Figure 106 : a) SEM image of imprinted TiO_2 replica bearing squared arrays of squares. From top to bottom: pitch of 1000, 1500, and 2000 nm. From left to right: height of 150, 300, 500, and 700 nm. b) Close-up on imprinted TiO_2 pillars of 1500 nm pitch and 500 nm height.

The substrate was then placed under ultra-high vacuum and 200 nm of germanium were deposited at 700 °C. Such deposition conditions will lead to a very high surface roughness which will trigger the dewetting of the thick layer when annealed at 800°C for 4 hours (see Chapter II). The topographical inhomogeneity, brought by the nanoimprinted substrate, can then be used to direct the dewetting of the Ge layer to yield organized Ge dots with one dot per motif as schematized in Figure 105. This uses a purely topographical control whereas chemical inhomogeneities were used in the case of Ge dewetting on INPs. Indeed, defects are known to be the starting points of dewetting. On such imprinted TiO₂ films, defects such as crystal defects or grain boundaries are homogeneously dispersed on the surface such that they should not impact dewetting. On the contrary, imprinted pillars create a large changes in the local substrate curvature. It is this topographical anisotropy that directs dewetting: The material deposited on the film surface flows down the gradient of the local chemical potential μ , which is proportional to the local curvature of the surface k (if the surface energy is considered isotropic, thus neglecting the anisotropy related to the crystallographic directions). The high curvature created by the nano-imprinted patterns leads to the retraction of the deposited Ge and then to the formation of islands.

Influence of surface curvature

In order to better apprehend the impact of surface curvature on dewetting, a system with lines will be studied. Nano-imprinting of TiO_2 diffraction gratings (2 µm width, 7 µm pitch and 150 nm height) was carried out on silicon substrates following a standard protocol. *In fine*, the imprinted substrate displays heterogeneous zones side by side, with flat surface of 5 µm width (in between the imprinted lines) and zones with curved surface of 2 µm width (onto the lines) (Figure 15a). 200 nm of germanium is deposited at 700 °C then annealed at 800 °C for 4 h. SEM images of the sample surface were taken after annealing (Figure 107b). As expected, dewetting of the germanium occurred when such annealing conditions are used. In the SEM image, the thin lines, visible by the presence of isolated germanium dots, correspond to the raised zones with the imprinted lines. In between those lines, larger zones are visible with an interconnected germanium network which corresponds to the flat surfaces in between the diffraction lines.

During the dewetting of thick semiconductors layers, specific stages of dewetting have been highlighted: first, a fully interconnected network is formed which will then evolved towards isolated islands (see Chapter II). Moreover, the surface curvature is expected to have a strong influence on the dewetting kinetics since the dewetting rate increases with the surface curvature as described by Mullins equation⁸³ (see Chapter I). In this example, dewetting is more advanced on the curved surface of the diffraction gratings, with the presence of isolated germanium dots, confirming that the diffusion was locally promoted. This proves than even a small variation in the substrate curvature (diffraction gratings with an aspect ratio of 0.075) can greatly enhance the diffusion. It is this strategy that will be used to direct dewetting on nano-imprinted pillars.



Figure 107 : a) Scheme representing the partially dewetted germanium layer on a substrate imprinted with diffraction gratings. Dewetted objects are still connected in flat zones (in between diffraction lines) while isolated islands are already visible on the lines confirming the impact of surface curvature on the kinetic of dewetting. b) SEM image of a 200 nm layer of germanium after dewetting on imprinted TiO_2 diffraction gratings. Germanium deposition parameters are the following: deposition at 700 °C followed by annealing at 800 °C for 4 hours.

Optimization of the dewetting conditions

In order to obtain precisely located Ge dots, nano-imprinted samples with arrays of square pillars were used as templates (see Figure 106) for the dewetting of 200 nm of Ge in the same conditions than previously. Figure 108 shows the resulting Ge layer after annealing and dewetting. Ge dots, more or less elongated, are randomly dispersed on the whole substrate. On the imprinted areas, in between and on the pillars, the surface curvature is greatly increased such that the diffusion is promoted enough to lead to complete dewetting. Only isolated germanium islands are found which corresponds to the final dewetting stage. Organization of the Ge dots is visible. With a closer view (Figure 108b), dots can be seen to follow the pillar organization with one large dot per pillar. Some residual dots in between pillars are also observed. Indeed, higher diffusion will likely lead to the agglomeration of dots into the positions of highest energy which could be on or in between the pillars.

Better organization of the dots is found for taller structures (height increases from left to right) as expected for surfaces displaying higher curvatures. The pitch between two pillars also impacts the organization: no organization is found for a pitch of 1000 nm (blue square) whereas dots are organized with one dot per pillar for a pitch of 1500 nm and 2000 nm (green and orange squares respectively).

This is probably because, in those dewetting conditions, the scale of the Ge thin film instability (i.e. the average distance between two dots spontaneously dewetting) needs to be of about the same order than the pitch between defects. In other words, if the distance between two defects is too short, a dot will not spontaneously break apart to form two separate dots.



Figure 108 : a) SEM image of a substrate where a layer of 200nm of germanium was dewetted on imprinted TiO_2 squared arrays of squared pillars. b) Zoom on 3 areas with different pitch (1000, 1500, and 2000 nm from left to right) and with a height of 500 nm.

In order to obtain a better organization whatever the pitch, the temperature and time of the dewetting step is increased to promote diffusion towards the points of higher energy. In other words, the system might not be in its state of equilibrium, which would need more energy to be reached. In addition, the deposition of a thinner Ge film should decrease the scale of the natural instability thus increasing the degree of organization on the motifs with the smallest pitch. To do so, a film of 25 nm of Ge was deposited at 700 °C then annealed at 900 °C for 8h. A clear improvement is seen with highly organized dots whatever the pitch (Figure 109b). Some very small dots remain visible in between the large dots sitting on the pillars. High resolution SEM confirmed that the Ge dots are polycrystalline with visible facets (Figure 109c). TEM analyses are on the way to obtain more information on the structures of the germanium dots.



Figure 109 : SEM images of Ge dots after dewetting on nanoimprinted TiO_2 pillars of 500 nm height and 1000, 1500, 2000 nm pitch for blue, green & orange frames respectively. Dewetting conditions were a) 200 nm Ge deposited at 700°C, annealed at 800°C for 4 hours (similar to Figure 108), b) 25 nm Ge deposited at 700°C, annealed at 900°C for 8 hours. c) Closer view showing the polycrystalline germanium dots in the dewetting conditions corresponding to b), with a pitch of 1000 nm.

More systematic experiments need to be performed in order to fully understand the parameters improving the organization of the dots. In particular, the relative influence of the germanium initial thickness and the annealing temperature and time needs to be clearly addressed.

This study proves that substrates, pre-patterned by nanoimprint lithography, can be used to accurately control the dewetting of semiconductor layers. By taking advantage of the gradient of diffusion induced by the variation of surface curvature, germanium dots were organized and obtained at chosen location. In contrast with the inherent limitations of the currently used pre-patterning techniques (*i.e.* FIB, E-beam), using NIL is straight-forward and is not restricted to small surfaces. This opens the way to large-scale directed dewetting of semiconductor thin films.

Summary

- > Directed dewetting of Ge layers on imprinted substrates was performed for the first time
- Obtained Ge dots were highly organized with one dot per imprinted structure (pillar)
- > The higher the pillar the better the dot formation
- Experimental conditions and/or pitch between structures need to be optimized to control dewetting

IV. Conclusion

In this chapter, we presented and developed various strategies in order to direct solid state dewetting.

To organize germanium nanocrystals, we took advantage of the chemical heterogeneity brought by inorganic nanopatterns (INPs) thanks to an appropriate HF chemical treatment. After a careful study of the germanium deposition and annealing conditions, highly organized germanium nanocrystals were obtained in epitaxy and with a sharp size distribution. The density and organization of the germanium nanocrystals can be easily tailored by changing the INPs network parameters. Next, inorganic nanopatterns were exploited to obtain a topographical control over gold dewetting. With an appropriate rubbing of the surface, gold nanodots were obtained in an organized fashion with a narrow size distribution. Finally, we demonstrated, for the first time, the viability of surface pre-patterning by nanoimprint lithography for the templated dewetting of semiconductor layers.

In contrast with direct lithography techniques generally used for templated dewetting, all the nanofabrication techniques developed in this thesis can be easily implemented on large scales allowing a unique control of solid state dewetting at the wafer scale.
General Conclusion

The approach followed during this thesis - dedicated to the study of possible combinations of topdown and bottom-up approaches – was fruitfully implemented to various lithography techniques and enabled the development of original photonic systems. Results obtained here show the tremendous potential of combining different approaches and open the way to many different opportunities and potential developments.

Concerning the development of lithography techniques, sol-gel porous layers were first successfully used for direct lithography by Focused Ion Beam. After a detailed study of the mechanism, we showed that this technique could be directly applied for the fast structuration of surfaces to fabricate masters for Soft-NIL. The throughput was increased by a factor 15 compared to classical silicon substrates. In addition, the development of angular dip-coating allowed to obtain large surfaces coated on a single face while giving more flexibility on the range of thickness accessible by this liquid deposition process.

Concerning Soft-Nano Imprint Lithography (Soft-NIL) of sol-gel coatings and its applications in photonics, we proposed new sol-gel formulations as NIL resists. By a simple control over the Relative Humidity, water was used as fluidizing agent and a quantity corresponding to $30\%_{vol}$ was found to give optimal imprinting. A new soft lithography technique called Micro Transfer Printing (combining Soft-NIL and Micro Transfer Molding) was introduced and applied to sol-gel coatings, highlighting its mechanism and potentials. The knowledge gathered in the latter studies, in particular by the development of fast master fabrication and sol-gel soft-NIL, was put into contribution to obtain nanostructured surfaces with arrays of nano-sized pillars displaying Mie resonances. The presence of Mie resonances was first demonstrated on the simple system of single TiO2 spheres. Then, nanoimprinted surfaces with 20 x 20 μ m² arrays of nanopillars were produced and their photonic properties investigated and compared to simulations. Trapping of 70% of the incoming light in the structured coatings was obtained, coining the term "black" titania surfaces. A demonstrator on 1 mm² was then presented and showed sharp structural colors visible with the naked eye.

The promising sol-gel soft-NIL and Micro Transfer Printing techniques detailed here could be pushed forward towards industrial implementation with the development of an automatized system (roll-to-roll, step-and-repeat). In particular, further investigations are needed to fully understand and control the Micro Transfer Printing. Discussions, concerning the two patents deposited on these techniques, are on the way with two companies and may lead to a technological transfer. Moreover, this thesis proved the feasibility of sol-gel soft-NIL to fabricate Mie resonators and detailed studies focused on targeted applications could be further performed. For instance, nanostructured surfaces could be designed and fabricated according to simulations in order to obtain textured coatings optimized for tailored light management (anti-reflective, highly transmissive, light trapping ...). In particular, Mie resonances are highly sensitive to slight changes in the refractive index. The previous nanostructured surfaces could thus be used as gas sensors; since the adsorption of specific molecules can modify the refractive index of the resonators.

Concerning the self-assembly of thin semiconductors or metallic layers, templated solid state dewetting was studied and originally combined with sol-gel surfaces. Inorganic nanopatterns (INPs)

were first applied to the dewetting of germanium thin layers to yield – in optimized conditions – perfectly organized Ge nanocrystals in epitaxy on Si, with one dot per perforation. Using the same system, organized Au dots with a sharp size distribution were obtained after an appropriate subsequent rubbing step. Finally, nanoimprinted sol-gel films also proved to be interesting candidates when applied to the directing of solid state dewetting of thick semiconductor layers.

Proof of concept and applications of the various dewetted surfaces are still needed to give value to the directed self-assembly approach developed during this thesis. For instance, Ge nanocrystals are expected to show interesting photoluminescence properties while Au dots are foreseen as nanowire growth catalysts. In addition, dewetted surfaces showing complex organization could also be used as masters and applied to various applications such as anti-reflective coatings or microfluidic channels.

In general, we showed that the combination of bottom-up and top-down approaches can bring interesting new advances in the existing lithography techniques for the fabrication of low-cost and large scale nanostructured surfaces. We proposed new sol-gel materials to tackle some of the limitations of the current lithography technologies increasing their throughput, flexibility and resolution. In particular, soft-NIL on sol-gel resists – once optimized - revealed to be of a method of choice to obtain nanostructured surfaces for photonic applications. Moreover, we proved the feasibility of the latter technique by making a demonstrator opening the way to sol-gel soft-NIL processes for industrial applications, in photonics but also in other fields.

Appendix

I. Ellipsometry

Ellipsometry is a non-destructive characterization technique based on the measurement of the depolarization of a beam of light after being reflected by a material (Figure 110a). This material is usually one or a stack of thin films of optical quality. The optical response is dependent of the thickness and the refractive index of each layer. To determine the contribution of each of those parameters, a model is built to represent the stack and is fitted to the measured depolarization Ψ and Δ with a software (WVase 32 software from Woollam). Ψ and Δ are the differential changes of the polarization of light in term of amplitude and phase respectively. The ellipsometer spot has a size of about 1.2 x 0.3 cm² at an angle of 70 degrees and can be decreased to about 300 μ m² by using focus probes (Figure 111).



Figure 110 : a) Illustration of the ellipsometry. The incident light is reflected on the stack of layers, the polarization changes when the beam interact with the stack and is analyzed. A chamber can be mounted to control the atmosphere. b) Typical optical properties of a transparent dielectric layer fitted with a Cauchy model (here anatase TiO_2 with A=1.9 B=0.05)



Figure 111 : Image of the ellipsometer used during this thesis. The polarized light source is on the left and the detector on the right. The ellipsometer is equipped with focus probes to decrease the area analyzed by the beam.

The optical properties (**refractive index n**, extinction coefficient k) and the **thickness** of each layer can then be deduced from this fit (Figure 110b). If the studied material is dielectric and transparent in the visible range, which is the case for most materials studied in this thesis, it can be modeled by a simple **Cauchy dispersion model** where $n=A+B/\lambda^2$. If the material is absorbent (for instance Si, Ge or Au), a more complex model need to be use such as the general oscillator model (Gen-Osc) where multiple oscillators can be added to correctly fit the studied layer.

In-situ ellipsometry

In-situ ellipsometry can be used to study the evolution of the thickness and refractive index of a layer with time. A modification of the thickness and refractive index with time can be the result of chemical reactions within the film for instance during aging of a gel. External stimulus can also induce modifications in the film parameters. For instance, by **heating** the substrate, condensation or crystallization can occur in sol-gel films. For this purpose, a programmable heating stage (Linkam T96-HT with temperature range $10 - 600^{\circ}$ C) can be mounted on the ellipsometer. Furthermore, changes in the film can also result from a dynamic **equilibrium with the atmosphere**. Indeed, wet gels are able to swell or shrink by absorbing solvent vapors leading to modification in the film thickness but also in the film refractive index. To change the atmosphere composition, an in-situ ellipsometry chamber has been designed where a controlled flow of gas is injected. The atmosphere in the chamber is modified by changing the carrying gas from dry air to wet air (change of humidity) or by using other solvents (Isopropanol, toluene) (P/P₀ = 1) which allows a precise control of the solvent relative vapor pressure.

Environmental Ellipsometric Porosimetry

In the case of porous layers, when the relative solvent pressure increases, adsorption and capillary condensation occurs in the pores. By carefully monitoring the film evolution, it is possible to know the **percentage of porosity** and the **pore size**.

This technique called **Environmental Ellipsometric Porosimetry (EEP)** measures the refractive index evolution with the relative solvent vapor pressure (P/P_0) (see Figure 112a). The solvent used is generally water but can be switched to isopropanol in the case of hydrophobic films. The pore size distribution can be extracted for nanoporous films (up to pores of 50nm in diameter). Since pores are far smaller than the wavelength of light, the porous layer can be considered as a homogeneous media. The volume fraction of adsorbate is then deduced from the Bruggeman Effective Medium Approximation (BEMA):

$$f \frac{\widetilde{\varepsilon_1} - \tilde{\varepsilon}}{\widetilde{\varepsilon_1} + 2\tilde{\varepsilon}} + (1 - f) \frac{\widetilde{\varepsilon_2} - \tilde{\varepsilon}}{\widetilde{\varepsilon_2} + 2\tilde{\varepsilon}} = 0$$

with $\tilde{\varepsilon_1}$ the dielectric function of the material, $\tilde{\varepsilon_2}$ the dielectric function of the pores, f the volume fraction of $\tilde{\varepsilon_1}$ compared to $\tilde{\varepsilon_2}$ and, for transparent dielectrics, $\tilde{\varepsilon} = n^2$. During the adsorption, the pores first containing air (n=1) are progressively filled with solvent (n water= 1.326, n isopropanol=1.383). From the substitution of air, the overall refractive index will increase at a specific relative vapor pressure. The porous volume of the film Vp is first measured in dry atmosphere then by measuring experimentally the refractive index of the film at each relative humidity (relative water pressure), the adsorption

isotherm can be calculated V_{water}/V_{film} = f(RH) from V_{water}/V_{film} = f V_p (Figure 112a). The pore size distribution was determined from the isotherm via Kelvin equation:

$$\operatorname{RT}\ln\frac{P}{P_0} = \gamma V_L \cos\theta \ \frac{dS}{dV}$$

with P/P₀ the partial pressure, γ the surface tension, V_L the molar volume of the liquid, θ the contact angle between the solid and the adsorbate, dS and dV the surface and volume variations between the solid and the adsorbate. A modified Kelvin equation is generally used to take into account the nonspherical geometry of the pores and the thickness of the water layer adsorbed in the pores before capillary condensation as described by Boissiere *et al*¹⁹². This analytical treatment results in the curve visible in Figure 112b and gives the pore size distribution.



Figure 112 : a) Adsorption (blue) and desorption (red) curves as a function of the relative vapour pressure (i.e. for water on a titania film). b) Pore diameter distribution extracted from a).

In this thesis, the measurements were carried out with a Wollam M200V (350nm – 1000nm) ellipsometer.

II. Optical characterization

The optical characterizations were performed with a commercial LEICA DMI5000 M optical microscope (M=100×, numerical aperture NA=0.75). The spectroscopic properties were probed with a home-made confocal microscope (M=50×, NA=0.5) coupled with a 30 cm spectrometer (grating 1200 gpmm) and a Si phototube for visible light detection. White light illumination was provided by a tungsten lamp. The measured spectrum of the lamp and a scheme of the experimental setup in given in Figure 113.



Figure 113 : Scheme of the experimental setup used for optical characterizations. Illumination of the sample can be done in different configurations: reflection, transmission and dark field. A spectrometer coupled with a detector is then used to obtain the different spectra.

III. FDTD simulations

The simulations presented were carried out by **Dr. Tom Wood** using a home-made FDTD (Finite Difference Time Domain) code, written in C++. The objects in the simulation space were discretized onto a 3D grid of 15nm resolution and of overall dimensions $1 \times 1 \times 1 \mu m$, using the following fixed values for the refractive indices of materials: $n_{TiO2} = 2.2$, $n_{SiO2} = 1.45$. The simulation space, in which the substrate occupied the <xy> plane used periodic boundary conditions on the x and y extrema, and absorbing boundary conditions in z. Light was injected using a broadband plane wave source at normal incidence on the substrate, and the reflection coefficients were obtained using a Poynting vector surface monitor covering the full <xy> plane above the substrate and resonator. The plane wave injected was polarized such that the electric field was oriented along the x axis and the magnetic field along the y axis. The near field distributions were collected by frequency domain monitors in the <xz> plane (electric field) and <yz> plane (magnetic field).

IV. Molecular Beam Epitaxy (MBE)

Molecular Beam Epitaxy is a physical technique for the deposition of thin films. The chamber is placed in ultra-high vacuum (10⁻¹⁰ torrs). The deposition rate is very low (few angstroms per minutes) allowing to grow films in epitaxy with an extremely good control over the thickness and composition of the layers (down to the atomic layer). The conditions of ultra-high vacuum give high mobility to the atoms to grow layers without defects and to avoid any contamination. Germanium is deposited from an effusion cells and a silicon source heated by an electron beam is used to deposit silicon.



Figure 114 : Image of the Molecular Beam Epitaxy chamber (RIBER-MBE 32) used for silicon and germanium deposition and for annealing in ultra-high vacuum.

V.X-ray diffraction

In X-ray diffraction, the sample is illuminated with an X-ray beam producing a diffraction pattern of regularly spaced dots which corresponds to the constructive interferences between the X-ray waves scattered by the crystal lattice atoms. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law: $2dsin\theta = n\lambda$. With θ the incident scattering angle (Bragg angle), d the distance between two lattice planes, λ the wavelength of the incident light and n an integer (Figure 115). By varying the angle θ , the Bragg's Law conditions are satisfied by different d-spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffraction peaks produces a pattern which is characteristic of the sample.



Figure 115 : Representation of the x-ray diffraction of a crystal by a beam. Each atom scatters a part of the X-ray beam. If scatterers are arranged in an organized manner, the interferences can add constructively giving diffraction spots.

The typical symmetrical X-ray geometry - called Bragg-Brentano or $\theta - 2\theta$ – is generally used in XRD measurements. In this case, the incident angle ω is equal to the Bragg angle and the position of the detector (2 θ) moves following $\omega = \theta$. This mode, adapted for powders, is however difficult to apply to thin films as the intensity of the film will be very small compared to the one of the substrate. In grazing incident X-ray diffraction (GIXRD), the incident angle ω is inferior to 5 degrees and fixed at a given value while the position of the detector (2 θ) is free. In this configuration, radiation does not penetrate far into the substrate which results in higher intensity of the layer peaks relative to the substrate peaks. It is this configuration that will be used in this thesis. The substrate can be rotated in plane (angle ϕ) in order to get the diffraction lines in the detector path (the detector can move only in one axis following the angle 2 θ).



Figure 116 : **a)** Schematic representation of the set-up used in GI-XRD. The incident angle is ω , the collection angle 2θ and the in-plane angle φ .

References

- (1) Livage, J. .; Henry, M. .; Sanchez, C. . Sol-Gel Chemistry of Transition Metal Oxides. *Solid State Chem* **1989**, 259–342.
- (2) Livage, J.; Henry, M. Ultrastructure Processing of Advanced Ceramics; Wiley-VCH Books, 1988.
- (3) Béteille, F.; Livage, J. Optical Switching in VO2 Thin Films. *J. Sol-Gel Sci. Technol.* **1998**, *921*, 915–921.
- (4) C. J. Brinker; G. W. Scherer. *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*; Elsevier, 1990.
- (5) Bradley, D. C. Metal Alkoxides. In *Metal-Organic Compounds*; American Chemical Society: Washington, 1959; pp 10–36.
- (6) Crepaldi, E. L.; Soler-Illia, G. J. D. a. a.; Grosso, D.; Sanchez, C. Nanocrystallised Titania and Zirconia Mesoporous Thin Films Exhibiting Enhanced Thermal Stability. *New J. Chem.* 2002, *27* (1), 9–13.
- Sanchez, C.; Boissiere, C.; Grosso, D.; Laberty, C.; Nicole, L. Design, Synthesis, and Properties of Inorganic and Hybrid Thin Films Having Periodically Organized Nanoporosity. *Chem. Mater.* 2008, 20 (3), 682–737.
- (8) Grosso, D.; Boissière, C.; Faustini, M. Thin Film Deposition Techniques. In *Handbook of Sol-Gel*; Levy, D., Zayat, M., Eds.; Wiley-VCH Books, 2014.
- (9) Grosso, D. How to Exploit the Full Potential of the Dip-Coating Process to Better Control Film Formation. *J. Mater. Chem.* **2011**, *21* (43), 17033–17038.
- (10) Brinker, C. J. *Chemical Solution Deposition of Functional Oxide Thin Films*; Schneller, T., Waser, R., Kosec, M., Payne, D., Eds.; Springer US, 2013.
- (11) Landau, L.; Levich, B. Dragging of a Liquid by a Moving Plate. *Acta Physicochim. U.R.S.S.* **1942**, 17 (1–2), 42–54.
- (12) Brinker, C. J.; Frye, G. C.; Hurd, A. J.; Ashley, C. S. Fundamentals of Sol-Gel Dip Coating. *Thin Solid Films* **1991**, *201*, 97–108.
- (13) Higgins, B. G.; Silliman, W. J.; Brown, R. A.; Scriven, L. E. Theory of Meniscus Shape in Film Flows. A Synthesis. *Ind. Eng. Chem. Fundam.* **1977**, *16* (4), 393–401.
- (14) Lee, C. Y.; Tallmadge, J. A. Meniscus Shapes in Withdrawal of Flat Sheets. 3. A Quasi-One-Dimensional Flow Model Using a Stretch Boundary Condition. *Ind. Eng. Chem. Fundam.* **1976**, 15 (4), 258–266.
- (15) Spiers, R. P.; Subbaraman, C. V.; Wilkinson, W. L. Free Coating of a Newtonian Liquid onto a Vertical Surface. *Chem. Eng. Sci.* **1974**, *29* (2), 389–396.
- (16) Kistler, S. F.; Schweizer, P. M. *Liquid Film Coating: Scientific Principles and Their Technological Implications*; Springer Netherlands, 1997.
- (17) Kuznetsov, A. .; Xiong, M. Effect of Evaporation on Thin Film Deposition in Dip Coating Process.

Int. Comm. Heat Mass Transf. 2002, 29 (I), 35–44.

- (18) Faustini, M.; Louis, B.; Albouy, P. A.; Kuemmel, M.; Grosso, D. Preparation of Sol Gel Films by Dip-Coating in Extreme Conditions. *J. Phys. Chem. C* **2010**, *114* (17), 7637–7645.
- (19) Faustini, M.; Ceratti, D. R.; Louis, B.; Boudot, M.; Albouy, P.-A.; Grosso, D. Engineering Functionality Gradients by Dip Coating Process in Acceleration Mode. ACS Appl. Mater. Interfaces 2014, 6, 17102–17110.
- (20) Ceratti, D. R.; Louis, B.; Paquez, X.; Faustini, M.; Grosso, D. A New Dip Coating Method to Obtain Large-Surface Coatings with a Minimum of Solution. *Adv. Mater.* **2015**, *27* (34), 4958–4962.
- (21) Bindini, E.; Naudin, G.; Faustini, M.; Grosso, D.; Boissière, C. Critical Role of the Atmosphere in Dip-Coating Process. J. Phys. Chem. C **2017**, 121 (27), 14572–14580.
- (22) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism. *Nature* **1992**, *359* (6397), 710–712.
- (23) Soler-Illia, G. J. D. A. A.; Sanchez, C.; Lebeau, B.; Patarin, J. Chemical Strategies to Design Textured Materials: From Microporous and Mesoporous Oxides to Nanonetworks and Hierarchical Structures. *Chem. Rev.* **2002**, *102* (11), 4093–4138.
- (24) Tanev, P. T.; Pinnavaia, T. J. A Neutral Templating Route to Mesoporous Molecular Sieves. *Science* **1995**, *267* (5199), 865–867.
- Templin, M.; Franck, A.; Chesne, A. Du; Leist, H.; Templin, M.; Franck, A.; Chesne, A. Du; Leist, H.; Zhang, Y.; Ulrich, R.; Schadler, V.; Wiesner, U. Organically Modified Aluminosilicate Mesostructures from Block Copolymer Phases. *Science* 2016, *278* (5344), 1795–1798.
- (26) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. Block Copolymer Templating Syntheses of Mesoporous Metal Oxides with Large Ordering Lengths and Semicrystalline Framework. 2014, No. 21, 2813–2826.
- (27) Kuemmel, M.; Allouche, J.; Nicole, L.; Boissière, C.; Laberty, C.; Amenitsch, H.; Sanchez, C.; Grosso, D. A Chemical Solution Deposition Route to Nanopatterned Inorganic Material Surfaces. *Chem. Mater.* **2007**, *19* (15), 3717–3725.
- (28) Ogawa, M. Preparation of Layered Silica–Dialkyldimethylammonium Bromide Nanocomposites. *Langmuir* **1997**, *13* (6), 1853–1855.
- (29) Brinker, C. J.; Lu, Y.; Sellinger, A.; Fan, H. Evaporation-Induced Self-Assembly: Nanostructures Made Easy. *Adv. Mater.* **1999**, *11* (7), 579–585.
- Grosso, D.; Cagnol, F.; Soler-Illia, G. J. D. A. A.; Crepaldi, E. L.; Amenitsch, H.; Brunet-Bruneau, A.; Bourgeois, A.; Sanchez, C. Fundamentals of Mesostructuring through Evaporation-Induced Self-Assembly. *Adv. Funct. Mater.* 2004, *14* (4), 309–322.
- (31) Grosso, D.; Soler-Illia, G. J. D. A. A.; Crepaldi, E. L.; Cagnol, F.; Sinturel, C.; Bourgeois, A.; Brunet-Bruneau, A.; Amenitsch, H.; Albouy, P. A.; Sanchez, C. Highly Porous TiO2 Anatase Optical Thin Films with Cubic Mesostructure Stabilized at 700 °C. *Chem. Mater.* **2003**, *15* (24), 4562–4570.
- (32) Boudot, M.; Gaud, V.; Louarn, M. Sol–Gel Based Hydrophobic Antireflective Coatings on Organic Substrates: A Detailed Investigation of Ammonia Vapor Treatment (AVT). *Chem. Mater.* 2014, 26 (5), 1822–1833.
- (33) Faustini, M.; Grenier, A.; Naudin, G.; Li, R.; Grosso, D. Ultraporous Nanocrystalline TiO2-Based Films: Synthesis, Patterning and Application as Anti-Reflective, Self-Cleaning, Superhydrophilic

Coatings. Nanoscale 2015, 7 (46), 19419–19425.

- (34) Cagnol, F.; Grosso, D.; Soler-Illia, G. J. d. A. A.; Crepaldi, E. L.; Babonneau, F.; Amenitsch, H.; Sanchez, C. Humidity-Controlled Mesostructuration in CTAB-Templated Silica Thin Film Processing. The Existence of a Modulable Steady State. *J. Mater. Chem.* **2003**, *13* (1), 61–66.
- (35) Innocenzi, P.; Malfatti, L.; Kidchob, T.; Costacurta, S.; Falcaro, P.; Piccinini, M.; Marcelli, A.; Morini, P.; Sali, D.; Amenitsch, H. Time-Resolved Simultaneous Detection of Structural and Chemical Changes during Self-Assembly of Mesostructured Films. *J. Phys. Chem. C* 2007, 111 (14), 5345–5350.
- (36) Crepaldi, E. L.; De, G. J.; Soler-Illia, A. A.; Grosso, D.; Cagnol, F.; Ribot, F. O.; Ment Sanchez, C. Controlled Formation of Highly Organized Mesoporous Titania Thin Films: From Mesostructured Hybrids to Mesoporous Nanoanatase TiO 2. J. Am. Chem. Soc. 2003, 125, 9770– 9786.
- (37) Brezesinski, T.; Fischer, A.; limura, K. I.; Sanchez, C.; Grosso, D.; Antonietti, M.; Smarsly, B. M. Generation of Self-Assembled 3D Mesostructured SnO2 Thin Films with Highly Crystalline Frameworks. *Adv. Funct. Mater.* **2006**, *16* (11), 1433–1440.
- (38) Kuemmel, M.; Grosso, D.; Boissière, C.; Smarsly, B.; Brezesinski, T.; Albouy, P. A.; Amenitsch, H.; Sanchez, C. Thermally Stable Nanocrystalline γ-Alumina Layers with Highly Ordered 3D Mesoporosity. Angew. Chemie 2005, 44 (29), 4589–4592.
- (39) Fisher, A.; Kuemmel, M.; Järn, M.; Linden, M.; Boissière, C.; Nicole, L.; Sanchez, C.; Grosso, D. Surface Nanopatterning by Organic/Inorganic Self-Assembly and Selective Local Functionalization. *Small* **2006**, *2* (4), 569–574.
- (40) Faustini, M.; Grosso, D. Self-Assembled Inorganic Nanopatterns (INPs) Made by Sol-Gel Dip-Coating: Applications in Nanotechnology and Nanofabrication. *Comptes Rendus Chim.* 2015, 1–18.
- (41) Vayer, M.; Hillmyer, M. A.; Dirany, M.; Thevenin, G.; Erre, R.; Sinturel, C. Perpendicular Orientation of Cylindrical Domains upon Solvent Annealing Thin Films of Polystyrene-B-Polylactide. *Thin Solid Films* **2010**, *518* (14), 3710–3715.
- (42) Roland, S.; Gaspard, D.; Prud'homme, R. E.; Bazuin, C. G. Morphology Evolution in Slowly Dip-Coated Supramolecular PS- B - P4VP Thin Films. *Macromolecules* **2012**, *45*, 5463–5476.
- (43) Faustini, M.; Drisko, G. L.; Boissiere, C.; Grosso, D. Liquid Deposition Approaches to Self-Assembled Periodic Nanomasks. *Scr. Mater.* **2014**, *74*, 13–18.
- (44) Faustini, M.; Marmiroli, B.; Malfatti, L.; Louis, B.; Krins, N.; Falcaro, P.; Grenci, G.; Laberty-Robert, C.; Amenitsch, H.; Innocenzi, P.; Grosso, D. Direct Nano-in-Micropatterning of TiO2 Thin Layers and TiO2/Pt Nanoelectrode Arrays by Deep X-Ray Lithography. *J. Mater. Chem.* 2011, *21* (11), 3597–3603.
- (45) Faustini, M.; Drisko, G. L.; Letailleur, A. A.; Montiel, R. S.; Boissière, C.; Cattoni, A.; Haghiri-Gosnet, A. M.; Lerondel, G.; Grosso, D. Self-Assembled Titanium Calcium Oxide Nanopatterns as Versatile Reactive Nanomasks for Dry Etching Lithographic Transfer with High Selectivity. *Nanoscale* **2013**, *5* (3), 984–990.
- (46) Laberty-Robert, C.; Kuemmel, M.; Allouche, J.; Boissière, C.; Nicole, L.; Grosso, D.; Sanchez, C. Sol–gel Route to Advanced Nanoelectrode Arrays (NEA) Based on Titania Gold Nanocomposites. J. Mater. Chem. 2008, 18 (11), 1216.
- (47) Martínez-Ferrero, E.; Forneli, A.; Boissière, C.; Grosso, D.; Sanchez, C.; Palomares, E. Tailored

3D Interface for Efficiency Improvement in Encapsulation-Free Hybrid Light-Emitting Diodes. *ACS Appl. Mater. Interfaces* **2011**, *3* (9), 3248–3251.

- Rowell, N. L.; Lockwood, D. J.; Amiard, G.; Favre, L.; Ronda, A.; Berbezier, I.; Faustini, M.; Grosso,
 D. Photoluminescence Efficiency and Size Distribution of Self Assembled Ge Dots on Porous
 TiO2. J. Nanosci. Nanotechnol. 2011, 11 (10), 9190–9195.
- (49) Faustini, M.; Nicole, L.; Boissière, C.; Innocenzi, P.; Sanchez, C.; Grosso, D. Hydrophobic, Antireflective, Self-Cleaning, and Antifogging Sol-Gel Coatings: An Example of Multifunctional Nanostructured Materials for Photovoltaic Cells. *Chem. Mater.* **2010**, *22* (15), 4406–4413.
- (50) Lepoutre, S.; Grosso, D.; Sanchez, C.; Fornasieri, G.; Rivière, E.; Bleuzen, A. Tailor-Made Nanometer-Scale Patterns of Photo-Switchable Prussian Blue Analogues. *Adv. Mater.* **2010**, *22* (36), 3992–3996.
- (51) Schulze, C.; Faustini, M.; Lee, J.; Schletter, H.; Lutz, M. U.; Krone, P.; Gass, M.; Sader, K.; Bleloch, a L.; Hietschold, M.; Fuger, M.; Suess, D.; Fidler, J.; Wolff, U.; Neu, V.; Grosso, D.; Makarov, D.; Albrecht, M. Magnetic Films on Nanoperforated Templates: A Route towards Percolated Perpendicular Media. *Nanotechnology* **2010**, *21* (49), 5701–5710.
- (52) Cressler, J. Introduction to Microelectronics and Nanotechnology, second edi.; Taylor & Francis Group, L., Ed.; 2016.
- (53) Industry Association for Semiconductor. ITRS Section 5: More Moore; 2015.
- (54) Yu, C. C.; Chen, H. L. Nanoimprint Technology for Patterning Functional Materials and Its Applications. *Microelectron. Eng.* **2015**, *132*, 98–119.
- (55) Grigorescu, A. E.; van der Krogt, M. C.; Hagen, C. W.; Kruit, P. 10 Nm Lines and Spaces Written in HSQ, Using Electron Beam Lithography. *Microelectron. Eng.* **2007**, *84* (5–8), 822–824.
- (56) Doshi, D. A. Optically Defined Multifunctional Patterning of Photosensitive Thin-Film Silica Mesophases. *Science* **2000**, *290* (5489), 107–111.
- (57) Stehlin, F.; Bourgin, Y.; Spangenberg, A.; Jourlin, Y.; Parriaux, O.; Reynaud, S.; Wieder, F.; Soppera, O. Direct Nanopatterning of 100 Nm Metal Oxide Periodic Structures by Deep-UV Immersion Lithography. *Opt. Lett.* **2012**, *37* (22), 4651–4653.
- (58) Stehlin, F.; Wieder, F.; Spangenberg, A.; Le Meins, J.-M.; Soppera, O. Room-Temperature Preparation of Metal-Oxide Nanostructures by DUV Lithography from Metal-Oxo Clusters. *J. Mater. Chem. C* **2014**, *2* (2), 277–285.
- (59) Xia, Y.; Whitesides, G. M. Soft Lithography. Angew Chem Int Ed. 1998, 37 (5), 550–575.
- (60) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. Imprint of Sub-25 Nm Vias and Trenches in Polymers. *Appl. Phys. Lett.* **1995**, *67* (21), 3114–3116.
- (61) Verschuuren, M. A.; Megens, M.; Ni, Y.; Van Sprang, H.; Polman, A. Large Area Nanoimprint by Substrate Conformal Imprint Lithography (SCIL). *Adv. Opt. Technol.* **2017**, *6* (3–4), 243–264.
- (62) Cattoni, A.; Mailly, D.; Dalstein, O.; Faustini, M.; Seniutinas, G.; Rösner, B.; David, C. Sub-10 Nm Electron and Helium Ion Beam Lithography Using a Recently Developed Alumina Resist. *Microelectron. Eng.* 2018, 193, 18–22.
- (63) Xia, Y.; Kim, E.; Whitesides, G. M. Micromolding of Polymers in Capillaries: Applications in Microfabrication. *Chem. Mater.* **1996**, *8* (7), 1558–1567.
- (64) Kim, E.; Xia, Y. N.; Whitesides, G. M. Polymer Microstructures Formed by Molding in Capillaries. *Nature*. 1995, pp 581–584.

- (65) Alom Ruiz, S.; Chen, C. S. Microcontact Printing: A Tool to Pattern. *Soft Matter* **2007**, *3* (2), 168–177.
- (66) Gooding, J. J.; Mearns, F.; Yang, W.; Liu, J. Self-Assembled Monolayers into the 21st Century: Recent Advances and Applications. *Electroanalysis* **2003**, *15* (2), 81–96.
- (67) Zhao, X.; Xia, Y.; Whitesides, G. M. Fabrication of Three-Dimensional Micro-Structures: Microtransfer Molding. *Adv. Mater.* **1996**, *8* (10), 837–840.
- (68) Fernandez-Sanchez, C.; Cadarso, V. J.; Darder, M.; Dominguez, C.; Llobera, A. Patterning High-Aspect-Ratio Sol-Gel Structures by Microtransfer Molding. *Chem. Mater.* **2008**, *20* (8), 2662– 2668.
- (69) Bass, J. D.; Schaper, C. D.; Rettner, C. T.; Arellano, N.; Alharbi, F. H.; Miller, R. D.; Al, B. E. T. Transfer Molding of Nanoscale Oxides Using Water-Soluble Templates. ACS Nano 2011, 5, 4065–4072.
- (70) Liu, B.; Ho, S.-T. Sub-100 Nm Nanolithography and Pattern Transfer on Compound Semiconductor Using Sol-Gel-Derived TiO2 Resist. *J. Electrochem. Soc.* **2008**, *155* (5), P57.
- (71) Hozumi, A.; Cheng, D. F. Facile Micropatterning of Mesoporous Titania Film by Low-Energy Electron Beam Irradiation. *Mater. Chem. Phys.* **2011**, *129* (1–2), 464–470.
- (72) Zanchetta, E.; Della Giustina, G.; Grenci, G.; Pozzato, A.; Tormen, M.; Brusatin, G. Novel Hybrid Organic-Inorganic Spin-on Resist for Electron- or Photon-Based Nanolithography with Outstanding Resistance to Dry Etching. *Adv. Mater.* **2013**, *25* (43), 6261–6265.
- (73) Grenci, G.; Zanchetta, E.; Pozzato, A.; Della Giustina, G.; Brusatin, G.; Tormen, M. High Resolution Spin-on Electron Beam Lithography Resist with Exceptional Dry Etching Resistance. *Appl. Mater. Today* 2015, 1 (1), 13–19.
- (74) Wu, C. W.; Aoki, T.; Kuwabara, M. Electron-Beam Lithography Assisted Patterning of Surfactant-Templated Mesoporous Thin Films. *Nanotechnology* **2004**, *15* (12), 1886–1889.
- (75) Arias-Zapata, J.; Böhme, S.; Garnier, J.; Girardot, C.; Legrain, A.; Zelsmann, M. Ultrafast Assembly of PS-PDMS Block Copolymers on 300 Mm Wafers by Blending with Plasticizers. *Adv. Funct. Mater.* **2016**, 5690–5700.
- (76) Kim, H. C.; Park, S. M.; Hinsberg, W. D.; Division, I. R. Block Copolymer Based Nanostructures: Materials, Processes, and Applications to Electronics. *Chem. Rev.* **2010**, *110* (1), 146–177.
- (77) Garnier, J.; Arias-Zapata, J.; Marconot, O.; Arnaud, S.; Böhme, S.; Girardot, C.; Buttard, D.; Zelsmann, M. Sub-10 Nm Silicon Nanopillar Fabrication Using Fast and Brushless Thermal Assembly of PS-B-PDMS Diblock Copolymer. ACS Appl. Mater. Interfaces 2016, 8 (15), 9954– 9960.
- Girardot, C.; Böhme, S.; Archambault, S.; Salaün, M.; Latu-Romain, E.; Cunge, G.; Joubert, O.;
 Zelsmann, M. Pulsed Transfer Etching of PS-PDMS Block Copolymers Self-Assembled in 193 Nm
 Lithography Stacks. ACS Appl. Mater. Interfaces 2014, 6 (18), 16276–16282.
- Salaün, M.; Kehagias, N.; Salhi, B.; Baron, T.; Boussey, J.; Sotomayor Torres, C. M.; Zelsmann,
 M. Direct Top-down Ordering of Diblock Copolymers through Nanoimprint Lithography. J. Vac.
 Sci. Technol. B Microelectron. Nanom. Struct. 2011, 29 (6), 208–214.
- (80) Kadiri, H. Auto-Organisation Assistée Pour La Nano-Impression À Grande Échelle et Surfaces Optiques Multifonctionnelles, Universite de Technologie de Troyes, 2017.
- (81) Malaquin, L.; Kraus, T.; Schmid, H.; Delamarche, E.; Wolf, H. Controlled Particle Placement

through Convective and Capillary Assembly. Langmuir 2007, 23 (23), 11513–11521.

- (82) Danielson, D. T.; Sparacin, D. K.; Michel, J.; Kimerling, L. C. Surface-Energy-Driven Dewetting Theory of Silicon-on-Insulator Agglomeration. *J. Appl. Phys.* **2006**, *100* (8), 1–10.
- (83) Mullins, W. W. Theory of Thermal Grooving. J. Appl. Phys. 1957, 28 (3), 333–339.
- (84) Abbarchi, M.; Naffouti, M.; Vial, B.; Benkouider, A.; Lermusiaux, L.; Favre, L.; Ronda, A.; Bidault, S. S.; Berbezier, I.; Bonod, N. Wafer Scale Formation of Monocrystalline Silicon-Based Mie Resonators via Silicon-on-Insulator Dewetting. ACS Nano 2014, 8 (11), 11181–11190.
- (85) Masuda, H.; Fukuda, K. Ordered Metal Nanohole Arrays Made by a Two-Step Replication of Honeycomb Structures of Anodic Alumina. *Science* **1995**, *268* (5216), 1466–1468.
- (86) Altomare, M.; Nguyen, T.; Schmuki, P. Chemical Science Templated Dewetting : Designing Entirely Self- Organized Platforms for Photocatalysis. *Chem. Sci.* **2016**, *7*, 6865–6886.
- Lockwood, D. J.; Rowell, N. L.; Barbagiovanni, E. G.; Goncharova, L. V.; Simpson, P. J.; Berbezier,
 I.; Favre, L.; Amiard, G.; Ronda, a.; Faustini, M.; Grosso, D. Photoluminescence Efficiency of Germanium Dots Self-Assembled on Oxides. *ECS Trans.* 2013, *53*, 185–206.
- (88) Bublat, T.; Goll, D. Large-Area Hard Magnetic L10-FePt Nanopatterns by Nanoimprint Lithography. *Nanotechnology* **2011**, *22* (31), 5301–5307.
- (89) Wang, D.; Ji, R.; Schaaf, P. Formation of Precise 2D Au Particle Arrays via Thermally Induced Dewetting on Pre-Patterned Substrates. *Beilstein J. Nanotechnol.* **2011**, *2* (1), 318–326.
- (90) Giermann, A. L.; Thompson, C. V. Solid-State Dewetting for Ordered Arrays of Crystallographically Oriented Metal Particles. *Appl. Phys. Lett.* **2005**, *86* (12), 1–3.
- (91) Zhang, C.; Miao, X.; Mohseni, P. K.; Choi, W.; Li, X. Site-Controlled VLS Growth of Planar Nanowires: Yield and Mechanism. *Nano Lett.* **2014**, *14* (12), 6836–6841.
- (92) Shiraki, Y.; Sunamura, H.; Usami, N.; Fukatsu, S. Formation and Optical Properties of SiGe/Si Quantum Structures. *Appl. Surf. Sci.* **1996**, *102*, 263–271.
- (93) Yakimov, A. I.; Dvurechenskii, A. V.; Kirienko, V. V.; Yakovlev, Y. I.; Nikiforov, A. I.; Adkins, C. J. Long-Range Coulomb Interaction in Arrays of Self-Assembled Quantum Dots. *Phys. Rev. B* 2000, 61 (16), 10868–10876.
- (94) Naffouti, M.; David, T.; Benkouider, A.; Favre, L.; Ronda, A.; Berbezier, I.; Bidault, S.; Bonod, N.; Abbarchi, M. Fabrication of Poly-Crystalline Si-Based Mie Resonators via Amorphous Si on SiO2 Dewetting. *Nanoscale* **2016**, *8* (5), 2844–2849.
- (95) Wood, T.; Naffouti, M.; Berthelot, J.; David, T.; Claude, J. B.; Métayer, L.; Delobbe, A.; Favre, L.; Ronda, A.; Berbezier, I.; Bonod, N.; Abbarchi, M. All-Dielectric Colour Filters Using SiGe-Based Mie Resonator Arrays. ACS Photonics **2017**, *4* (4), 873–883.
- (96) Karmous, A.; Berbezier, I.; Ronda, A. Formation and Ordering of Ge Nanocrystals on SiO2. *Phys. Rev. B Condens. Matter Mater. Phys.* **2006**, *73* (7), 1–5.
- (97) Naffouti, M.; Backofen, R.; Salvalaglio, M.; Bottein, T.; Lodari, M.; Voigt, A.; David, T.; Benkouider, A.; Fraj, I.; Favre, L.; Ronda, A.; Berbezier, I.; Grosso, D.; Abbarchi, M.; Bollani, M. Complex Dewetting Scenarios of Ultrathin Silicon Films for Large-Scale Nanoarchitectures. *Sci. Adv.* 2017, 3 (11), 1472–1482.
- (98) Abbarchi, M.; Naffouti, M.; Lodari, M.; Salvalaglio, M.; Backofen, R.; Bottein, T.; Voigt, A.; David,
 T.; Claude, J.-B.; Bouabdellaoui, M.; Benkouider, A.; Fraj, I.; Favre, L.; Ronda, A.; Berbezier, I.;
 Grosso, D.; Bollani, M. Solid-State Dewetting of Single-Crystal Silicon on Insulator: Effect of

Annealing Temperature and Patch Size. *Microelectron. Eng.* 2018, 190, 1–6.

- (99) Bottein, T.; Loizillon, J.; Grosso, D. A Full Investigation of Angle Dependence in Dip-Coating Sol-Gel Films. J. Phys. Chem. B **2017**, 121 (25), 6620–6625.
- (100) Arfsten, N. J.; Eberle, A.; Otto, J.; Reich, A. Investigations on the Angle-Dependent Dip Coating Technique (ADDC) for the Production of Optical Filters. J. Sol-Gel Sci. Technol. 1997, 8 (1–3), 1099–1104.
- (101) Mennig, M.; Oliveira, P. W.; Frantzen, A.; Schmidt, H. Multilayer NIR Reflective Coatings on Transparent Plastic Substrates from Photopolymerizable Nanoparticulate Sols. *Thin Solid Films* **1999**, *251* (40), 225–229.
- (102) Tallmadge, J. A. A Theory of Entrainment for Angular Withdrawal of Flat Supports. *AlChE J.* **1971**, *17* (1), 243–246.
- (103) Lee, C. H.; Lu, Y.; Shen, A. Q. Evaporation Induced Self Assembly and Rheology Change during Sol-Gel Coating. *Phys. Fluids* **2006**, *18* (5), 1–12.
- (104) Ziegler, J. F.; Biersack, J. P.; Littmark, U. The Stopping and Range of Ions in Matter, Vol. 1. In *Treatise on Heavy-Ion Science*; US, S., Ed.; 1985; pp 93–129.
- (105) Berbezier, I.; Ronda, A.; Portavoce, A. SiGe Nanostructures: New Insights into Growth Processes. J. Physics-Condensed Matter **2002**, *14* (35), 8283–8331.
- (106) Aqua, J. N.; Berbezier, I.; Favre, L.; Frisch, T.; Ronda, A. Growth and Self-Organization of SiGe Nanostructures. *Phys. Rep.* **2013**, *522* (2), 59–189.
- (107) Ma, Z.; Torquato, S. Random Scalar Fields and Hyperuniformity. J. Appl. Phys. 2017, 121 (24), 1–16.
- (108) Naffouti, M.; David, T.; Benkouider, A.; Favre, L.; Cabie, M.; Ronda, A.; Berbezier, I.; Abbarchi, M. Fabrication of Core-Shell Nanostructures via Silicon on Insulator Dewetting and Germanium Condensation: Towards a Strain Tuning Method for SiGe-Based Heterostructures in a Three-Dimensional Geometry. *Nanotechnology* **2016**, *27* (30), 1–12.
- (109) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. Imprint Lithography with 25-Nanometer Resolution. *Science* **1996**, *272* (5258), 85–87.
- (110) Heuberger, K.; Lukosz, W. Embossing Technique for Fabricating Surface Relief Gratings on Hard Oxide Waveguides. *Appl. Opt.* **1986**, *25* (Number 9), 1499.
- (111) Delamarche, E.; Schmid, H.; Michel, B.; Biebuyck, H. Stability of Molded Polydimethylsiloxane Microstructures. *Adv. Mater.* **1997**, *9* (9), 741–746.
- (112) Sharp, K. G.; Blackman, G. S.; Glassmaker, N. J.; Jagota, A.; Hui, C. Y. Effect of Stamp Deformation on the Quality of Microcontact Printing: Theory and Experiment. *Langmuir* 2004, 20 (15), 6430– 6438.
- (113) Hsia, K. J.; Huang, Y.; Menard, E.; Park, J. U.; Zhou, W.; Rogers, J.; Fulton, J. M. Collapse of Stamps for Soft Lithography due to Interfacial Adhesion. *Appl. Phys. Lett.* **2005**, *86* (15), 1–3.
- (114) Hui, C. Y.; Jagota, A.; Lin, Y. Y.; Kramer, E. J. Constraints on Microcontact Printing Imposed by Stamp Deformation. *Langmuir* **2002**, *18* (4), 1394–1407.
- (115) Verschuuren, M. Substrate Conformal Imprint Lithography for Nanophotonics, 2010.
- (116) Schmid, H.; Michel, B. Siloxane Polymers for High-Resolution, High-Accuracy Soft Lithography. *Macromolecules* **2000**, *33* (8), 3042–3049.

- (117) Lee, N. Y.; Lim, J. R.; Lee, M. J.; Kim, J. B.; Jo, S. J.; Baik, H. K.; Kim, Y. S. Hydrophilic Composite Elastomeric Mold for High-Resolution Soft Lithography. *Langmuir* **2006**, *22* (21), 9018–9022.
- (118) Trimbach, D.; Feldman, K.; Spencer, N. D.; Broer, D. J.; Bastiaansen, C. W. M. Block Copolymer Thermoplastic Elastomers for Microcontact Printing. *Langmuir* **2003**, *19* (26), 10957–10961.
- (119) Schmid, H.; Michel, B. Siloxane Polymers for High-Resolution, High Accuracy Soft Lithography. *Macromolecules* **2000**, *33* (8), 3042–3049.
- (120) Peroz, C.; Heitz, C.; Barthel, E.; Sońdergård, E.; Goletto, V. Glass Nanostructures Fabricated by Soft Thermal Nanoimprint. *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* **2007**, *25* (4), 27–30.
- (121) Peroz, C.; Chauveau, V.; Barthel, E.; Søndergård, E. Nanoimprint Lithography on Silica Sol-Gels: A Simple Route to Sequential Patterning. *Adv. Mater.* **2009**, *21* (5), 555–558.
- (122) Letailleur, A.; Teisseire, J.; Chemin, N.; Barthel, E.; Søndergård, E. Chemorheology of Sol-Gel Silica for the Patterning of High Aspect Ratio Structures by Nanoimprint. *Chem. Mater.* **2010**, 22 (10), 3143–3151.
- (123) Yang, K. Y.; Yoon, K. M.; Choi, K. W.; Lee, H. The Direct Nano-Patterning of ZnO Using Nanoimprint Lithography with ZnO-Sol and Thermal Annealing. *Microelectron. Eng.* 2009, 86 (11), 2228–2231.
- (124) Brigo, L.; Mattei, G.; Michieli, N.; Brusatin, G. 2D Photonic Gratings from Thermal Imprinting of ITO-Based Films. *Microelectron. Eng.* **2012**, *97*, 193–196.
- (125) Dalstein, O.; Ceratti, D. R.; Boissière, C.; Grosso, D.; Cattoni, A.; Faustini, M. Nanoimprinted, Submicrometric, MOF-Based 2D Photonic Structures: Toward Easy Selective Vapors Sensing by a Smartphone Camera. Adv. Funct. Mater. 2016, 26, 81–90.
- (126) Park, H. H.; Choi, D. G.; Zhang, X.; Jeon, S.; Park, S. J.; Lee, S. W.; Kim, S.; Kim, K. D.; Choi, J. H.; Lee, J.; Yun, D. K.; Lee, K. J.; Park, H. H.; Hill, R. H.; Jeong, J. H. Photo-Induced Hybrid Nanopatterning of Titanium Dioxide via Direct Imprint Lithography. J. Mater. Chem. 2010, 20 (10), 1921–1926.
- (127) Kim, W.-S.; Yoon, K. B.; Bae, B.-S. Nanopatterning of Photonic Crystals with a Photocurable Silica–titania Organic–inorganic Hybrid Material by a UV-Based Nanoimprint Technique. *J. Mater. Chem.* **2005**, *15* (42), 4535.
- (128) Richmond, D. a.; Zhang, Q.; Cao, G.; Weiss, D. N. Pressureless Nanoimprinting of Anatase TiO2 Precursor Films. J. Vac. Sci. Technol. B Microelectron. Nanom. Struct. **2011**, 29 (2), 21603.
- (129) Hlaing, H.; Lu, X.; Nam, C. Y.; Ocko, B. M. Water-Vapor-Assisted Nanoimprinting of PEDOT:PSS Thin Films. *Small* **2012**, *8* (22), 3443–3447.
- (130) Kothari, R.; Beaulieu, M. R.; Hendricks, N. R.; Li, S.; Watkins, J. J. Direct Patterning of Robust One-Dimensional, Two-Dimensional, and Three-Dimensional Crystalline Metal Oxide Nanostructures Using Imprint Lithography and Nanoparticle Dispersion Inks. *Chem. Mater.* 2017, 29 (9), 3908–3918.
- (131) Hosokawa, K.; Sato, K.; Ichikawa, N.; Maeda, M. Power-Free Poly(dimethylsiloxane) Microfluidic Devices for Gold Nanoparticle-Based DNA Analysis. *Lab Chip* **2004**, *4* (3), 181–185.
- (132) Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D.; Pinnau, I. Gas Sorption, Diffusion, and Permeation in Poly(dimethylsiloxane). *J. Polym. Sci. Part B Polym. Phys.* **2000**, *38* (3), 415–434.
- (133) Bottein, T.; Dalstein, O.; Putero, M.; Cattoni, A.; Faustini, M.; Abbarchi, M.; Grosso, D.

Environment-Controlled Sol-Gel Soft-NIL Processing for Optimized Titania, Alumina, Silica and Yttria-Zirconia Imprinting at Sub-Micron Dimensions. *Nanoscale* **2017**.

- (134) Grosso, D.; Faustini, M.; Dalstein, O.; Bottein, T.; Cattoni, A. Nanoimprint Lithography Process and Patterned Substrate Obtainable Therefrom. EP17305286.1, 2017.
- (135) Ogieglo, W.; van der Werf, H.; Tempelman, K.; Wormeester, H.; Wessling, M.; Nijmeijer, A.; Benes, N. E. N-Hexane Induced Swelling of Thin PDMS Films under Non-Equilibrium Nanofiltration Permeation Conditions, Resolved by Spectroscopic Ellipsometry. J. Memb. Sci. 2013, 437, 313–323.
- (136) Soler-Illia, G. J. A. A.; Angelomé, P. C.; Fuertes, M. C.; Grosso, D.; Boissiere, C. Critical Aspects in the Production of Periodically Ordered Mesoporous Titania Thin Films. *Nanoscale* **2012**, *4* (8), 2549.
- (137) Bottein, T.; Wood, T.; David, T.; Claude, J. B.; Favre, L.; Berbézier, I.; Ronda, A.; Abbarchi, M.; Grosso, D. "Black" Titania Coatings Composed of Sol-Gel Imprinted Mie Resonators Arrays. Adv. Funct. Mater. 2016, 27 (2), 1604924.
- (138) Barrie, J. a.; Machin, D. The Sorption and Diffusion of Water in Silicone Rubbers: Part I. Unfilled Rubbers. *J. Macromol. Sci. Part B* **1969**, *3* (4), 645–672.
- (139) Sun, S.; Zhou, Z.; Zhang, C.; Gao, Y.; Duan, Z.; Xiao, S.; Song, Q. All-Dielectric Full-Color Printing with TiO2 Metasurfaces. *ACS Nano* **2017**, *11* (5), 4445–4452.
- (140) Rowland, H. D.; Sun, A. C.; Schunk, P. R.; King, W. P. Impact of Polymer Film Thickness and Cavity Size on Polymer Flow during Embossing: Toward Process Design Rules for Nanoimprint Lithography. *J. Micromechanics Microengineering* **2005**, *15* (12), 2414–2425.
- (141) Agostinelli, G.; Delabie, A.; Vitanov, P.; Alexieva, Z.; Dekkers, H. F. W.; De Wolf, S.; Beaucarne, G. Very Low Surface Recombination Velocities on P-Type Silicon Wafers Passivated with a Dielectric with Fixed Negative Charge. *Sol. Energy Mater. Sol. Cells* 2006, *90* (18–19), 3438–3443.
- (142) Hoex, B.; Heil, S. B. S.; Langereis, E.; Van De Banden, M. C. M.; Kessels, W. M. M. Ultralow Surface Recombination of c-Si Substrates Passivated by Plasma-Assisted Atomic Layer Deposited Al2O3. *Appl. Phys. Lett.* **2006**, *89* (4), 5–8.
- (143) Lin, Z.; Yang, H.; Zhou, S.; Wang, H.; Hong, X.; Li, G. Pattern Design of and Epitaxial Growth on Patterned Sapphire Substrates for Highly Efficient GaN-Based LEDs. *Cryst. Growth Des.* 2012, *12* (6), 2836–2841.
- (144) Reddy, B. M.; Khan, A. Recent Advances on TiO2-ZrO2 Mixed Oxides as Catalysts and Catalyst Supports. *Catal. Rev. Sci. Eng.* **2005**, *47* (2), 257–296.
- (145) Gallardo, J.; Galliano, P.; Duran, A. Thermal Evolution of Hybrid Sol-Gel Silica Coatings : A Structural Analysis. *J. Sol-Gel Sci. Technol.* **2000**, 393–397.
- (146) Cui, Y.; Lu, J.; Fu, X. X.; Bian, J.; Yuan, C.; Ge, H.; Chen, Y. Near-Zero-Residual Layer Nanoimprint Based on Hybrid Nanoimprint Soft Lithography. *Appl. Phys. A Mater. Sci. Process.* **2015**, *121* (2), 371–375.
- (147) Kolli, V. R.; Woidt, C.; Hillmer, H. Residual-Layer-Free 3D Nanoimprint Using Hybrid Soft Templates. *Microelectron. Eng.* **2016**, *149*, 159–165.
- (148) Yoon, H.; Lee, H.; Lee, W. B. Toward Residual-Layer-Free Nanoimprint Lithography in Large-Area Fabrication. *Korea Aust. Rheol. J.* **2014**, *26* (1), 39–48.

- (149) Yoon, H.; Lee, K. M.; Khang, D. Y.; Lee, H. H.; Choi, S. J. Rapid Flash Patterning of Nanostructures. *Appl. Phys. Lett.* **2004**, *85* (10), 1793–1795.
- (150) Fernandez, A.; Medina, J.; Benkel, C.; Guttmann, M.; Bilenberg, B.; Thamdrup, L. H.; Nielsen, T.; Sotomayor Torres, C. M.; Kehagias, N. Residual Layer-Free Reverse Nanoimprint Lithography on Silicon and Metal-Coated Substrates. *Microelectron. Eng.* **2015**, *141*, 56–61.
- (151) Dai, X.; Xie, H. A Simple and Residual-Layer-Free Solute–solvent Separation Soft Lithography Method. J. Micromechanics Microengineering **2015**, 25 (9), 95013.
- (152) Kaufmann, T.; Ravoo, B. J. Stamps, Inks and Substrates: Polymers in Microcontact Printing. *Polym. Chem.* **2010**, *1*, 371–387.
- (153) Bottein, T.; Grosso, D. Microtransfer Molding Process and Patterned Substrate Obtainable Therefrom. EP 17305823.1, 2017.
- (154) Gitlin, L.; Schulze, P.; Belder, D. Rapid Replication of Master Structures by Double Casting with PDMS. *Lab Chip* **2009**, *9* (20), 3000.
- (155) Mutreja, I.; Woodfield, T. B. F.; Sperling, S.; Nock, V.; Evans, J. J.; Alkaisi, M. M. Positive and Negative Bioimprinted Polymeric Substrates: New Platforms for Cell Culture. *Biofabrication* 2015, 7 (2), 25002.
- (156) He, R.; Xiao, J.; Zhang, M.; Zhang, Z.; Zhang, W.; Cao, Y.; Liu, Y.; Chen, Y. Artificial Honeycomb-Inspired TiO2 Nanorod Arrays with Tunable Nano/micro Interfaces for Improving Poly(dimethylsiloxane) Surface Hydrophobicity. J. Mater. Sci. 2016, 51 (6), 2935–2941.
- (157) Evlyukhin, A. B.; Reinhardt, C.; Seidel, A.; Luk'Yanchuk, B. S.; Chichkov, B. N. Optical Response Features of Si-Nanoparticle Arrays. *Phys. Rev. B - Condens. Matter Mater. Phys.* 2010, 82 (4), 1– 12.
- (158) Garín, M.; Fenollosa, R.; Alcubilla, R.; Shi, L.; Marsal, L. F.; Meseguer, F. All-Silicon Spherical-Mie-Resonator Photodiode with Spectral Response in the Infrared Region. *Nat. Commun.* 2014, *5*, 3440.
- (159) Gómez-Medina, R.; Garcia-Camara, B.; Suarez-Lacalle, I.; Gonzalez, F.; Moreno, F.; Nieto-Ves. Electric and Magnetic Dipolar Response of Germanium Nanospheres: Interference Effects, Scattering Anisotropy, and Optical Forces. J. Nanophotonics 2011, 5 (1), 53512.
- (160) Garcia-Etxarri, A.; Gomez-Medina, R.; Froufe-Perez, L. S.; Lopez, C.; Chantada, L.; Scheffold, F.; Aizpurua, J.; Nieto-Vesperinas, M.; Saenz, J. J. Strong Magnetic Response of Submicron Silicon Particles in the Infrared. *Opt. Express* **2010**, *19* (6), 4815–4826.
- (161) Kuznetsov, A. I.; Miroshnichenko, A. E.; Brongersma, M. L.; Kivshar, Y. S.; Lukyanchuk, B. Optically Resonant Dielectric Nanostructures. *Science* **2016**, *354* (6314), 2472.
- (162) Schuller, J. A.; Zia, R.; Taubner, T.; Brongersma, M. L. Dielectric Metamaterials Based on Electric and Magnetic Resonances of Silicon Carbide Particles. *Phys. Rev. Lett.* **2007**, *99* (10), 1–4.
- (163) Kuznetsov, A. I.; Miroshnichenko, A. E.; Fu, Y. H.; Zhang, J.; Luk'yanchuk, B. Magnetic Light. *Sci. Rep.* **2012**, *2*, 492.
- (164) Spinelli, P.; Verschuuren, M. a; Polman, A. Broadband Omnidirectional Antireflection Coating Based on Subwavelength Surface Mie Resonators. *Nat. Commun.* **2012**, *3*, 692.
- (165) Moitra, P.; Slovick, B. A.; Li, W.; Kravchencko, I. I.; Briggs, D. P.; Krishnamurthy, S.; Valentine, J. Large-Scale All-Dielectric Metamaterial Perfect Reflectors. *ACS Photonics* **2015**, *2* (6), 692–698.
- (166) Yang, Y.; Kravchenko, I. I.; Briggs, D. P.; Valentine, J. All-Dielectric Metasurface Analogue of

Electromagnetically Induced Transparency. Nat. Commun. 2014, 5, 5753.

- (167) Chong, K. E.; Hopkins, B.; Staude, I.; Miroshnichenko, A. E.; Dominguez, J.; Decker, M.; Neshev, D. N.; Brener, I.; Kivshar, Y. S. Observation of Fano Resonances in All-Dielectric Nanoparticle Oligomers. *Small* 2014, *10* (10), 1985–1990.
- (168) Albella, P.; De La Osa, R. A.; Moreno, F.; Maier, S. A. Electric and Magnetic Field Enhancement with Ultralow Heat Radiation Dielectric Nanoantennas: Considerations for Surface-Enhanced Spectroscopies. *ACS Photonics* **2014**, *1* (6), 524–529.
- (169) Miroshnichenko, A. E.; Evlyukhin, A. B.; Yu, Y. F.; Bakker, R. M.; Chipouline, A.; Kuznetsov, A. I.; Luk'yanchuk, B.; Chichkov, B. N.; Kivshar, Y. S. Nonradiating Anapole Modes in Dielectric Nanoparticles. *Nat. Commun.* **2015**, *6*, 8069.
- (170) Shcherbakov, M. R.; Shorokhov, A. S.; Neshev, D. N.; Hopkins, B.; Staude, I.; Melik-Gaykazyan, E. V.; Ezhov, A. A.; Miroshnichenko, A. E.; Brener, I.; Fedyanin, A. A.; Kivshar, Y. S. Nonlinear Interference and Tailorable Third-Harmonic Generation from Dielectric Oligomers. *ACS Photonics* 2015, *2* (5), 578–582.
- (171) Yang, Y.; Wang, W.; Moitra, P.; Kravchenko, I. I.; Briggs, D. P.; Valentine, J. Dielectric Meta-Re Fl Ectarray for Broadband Linear Polarization Conversion and Optical Vortex Generation. *Nano Lett.* **2014**, *14*, 1394–1399.
- (172) Gutruf, P.; Zou, C.; Withayachumnankul, W.; Bhaskaran, M.; Sriram, S.; Fumeaux, C. Mechanically Tunable Dielectric Resonator Metasurfaces at Visible Frequencies. ACS Nano 2016, 10, 133–141.
- (173) Spinelli, P.; Macco, B.; Verschuuren, M. A.; Kessels, W. M. M.; Polman, A. Al2O3/TiO2 Nano-Pattern Antireflection Coating with Ultralow Surface Recombination. *Appl. Phys. Lett.* 2013, 102 (23), 2011–2015.
- (174) Khorasaninejad, M.; Chen, W. T.; Devlin, R. C.; Oh, J.; Zhu, A. Y.; Capasso, F. Metalenses at Visible Wavelengths: Diffraction-Limited Focusing and Subwavelength Resolution Imaging. *Science* **2016**, *352* (6290), 1190–1194.
- (175) Devlin, R. C.; Khorasaninejad, M.; Chen, W.-T.; Oh, J.; Capasso, F. High Efficiency Dielectric Metasurfaces at Visible Wavelengths. **2016**, *113* (38), 10473–10478.
- (176) Fu, Y. H.; Kuznetsov, A. I.; Miroshnichenko, A. E.; Yu, Y. F.; Luk'yanchuk, B. Directional Visible Light Scattering by Silicon Nanoparticles. *Nat. Commun.* **2013**, *4*, 1–6.
- (177) Krasnok, A. E.; Maloshtan, A.; Chigrin, D. N.; Kivshar, Y. S.; Belov, P. A. Enhanced Emission Extraction and Selective Excitation of NV Centers with All-Dielectric Nanoantennas. *Laser Photonics Rev.* **2015**, *9* (4), 385–391.
- (178) Andres-Arroyo, A.; Gupta, B.; Wang, F.; Gooding, J. J.; Reece, P. J. Optical Manipulation and Spectroscopy of Silicon Nanoparticles Exhibiting Dielectric Resonances. *Nano Lett.* **2016**, *16* (3), 1903–1910.
- (179) Groep, J. Van De; Polman, a. Designing Dielectric Resonators on Substrates : Combining Magnetic and Electric Resonances. *Opt. Express* **2013**, *21* (22), 1253–1257.
- (180) Ding, L.; Lee, T.; Wang, C. H. Fabrication of Monodispersed Taxol-Loaded Particles Using Electrohydrodynamic Atomization. *J. Control. Release* **2005**, *102* (2), 395–413.
- (181) Smith, T.; Guild, J. The C.I.E. Colorimetric Standards And Their Use. Trans. Opt. Soc. 1931, 73 (3).
- (182) Zhu, X.; Yan, W.; Levy, U.; Mortensen, N. A.; Kristensen, A. Resonant Laser Printing of Structural

Colors on High-Index Dielectric Metasurfaces. Sci. Adv 2017, 1–9.

- (183) Bass, J. D.; Grosso, D.; Boissiere, C.; Sanchez, C. Pyrolysis, Crystallization, and Sintering of Mesostructured Titania Thin Films Assessed by in Situ Thermal Ellipsometry. J. Am. Chem. Soc. 2008, 130 (25), 7882–7897.
- (184) Louis, B.; Krins, N.; Faustini, M.; Grosso, D. Understanding Crystallization of Anatase into Binary SiO2/TiO2 Sol- Gel Optical Thin Films: An in Situ Thermal Ellipsometry Analysis. J. Phys. Chem. C 2011, 115, 3115–3122.
- (185) Zhou, W.; Zhang, J.; Liu, Y.; Li, X.; Niu, X.; Song, Z.; Min, G.; Wan, Y. Z.; Shi, L.; Feng, S. Characterization of Anti-Adhesive Self-Assembled Monolayer for Nanoimprint Lithography. *Appl. Surf. Sci.* **2008**, *255* (5), 2885–2889.
- (186) Bottein, T.; Grosso, D.; Favre, L. Process for Forming an Organized Network of Semi-Conducting Nanoparticles or Nanowires onto a Silicon Substrate. EP 18153070.0, 2018.
- (187) Jaccodine, R. J. Surface Energy of Germanium and Silicon. *J. Electrochem. Soc.* **1963**, *110* (6), 524.
- (188) Zhang, H.; Banfield, J. F. Thermodynamic Analysis of Phase Stability of Nanocrystalline Titania. *J. Mater. Chem.* **1998**, *8* (9), 2073–2076.
- (189) Benkouider, A.; Ronda, A.; David, T.; Favre, L.; Abbarchi, M.; Naffouti, M.; Osmond, J.; Delobbe,
 A.; Sudraud, P.; Berbezier, I. Ordered Arrays of Au Catalysts by FIB Assisted Heterogeneous Dewetting. *Nanotechnology* 2015, *26* (50), 505602.
- (190) Choi, W. K.; Liew, T. H.; Chew, H. G.; Zheng, F.; Thompson, C. V.; Wang, Y.; Hong, M. H.; Wang, X. D.; Li, L.; Yun, J. A Combined Top-down and Bottom-up Approach for Precise Placement of Metal Nanoparticles on Silicon. *Small* **2008**, *4* (3), 330–333.
- (191) Zhang, X.; Qiao, Y.; Xu, L.; Buriak, J. M. Constructing Metal-Based Structures on Nanopatterned Etched Silicon. *ACS Nano* **2011**, *5* (6), 5015–5024.
- (192) Boissiere, C.; Grosso, D.; Lepoutre, S.; Nicole, L.; Bruneau, A. B.; Sanchez, C. Porosity and Mechanical Properties of Mesoporous Thin Films Assessed by Environmental Ellipsometric Porosimetry. *Langmuir* **2005**, *21* (26), 12362–12371.

Publications and patents

Scientific publications

- A Full Investigation of Angle Dependence in Dip-Coating Sol-Gel Films. Bottein, T.; Loizillon, J.; Grosso, D. J. Phys. Chem. B 2017, 121 (25), 6620–6625.
- Environment-Controlled Sol-gel Soft-NIL Processing for Optimized Titania, Alumina, Silica and Yttria-Zirconia Imprinting at Sub-Micron Dimensions Bottein, T.; Dalstein, O.; Putero, M.; Cattoni, A.; Faustini, M.; Abbarchi, M.; Grosso, D. Nanoscale 2018, 10, 1420–1431.
- "Black" Titania Coatings Composed of Sol-Gel Imprinted Mie Resonators Arrays. Bottein, T.; Wood, T.; David, T.; Claude, J. B.; Favre, L.; Berbézier, I.; Ronda, A.; Abbarchi, M.; Grosso, D. Adv. Funct. Mater. 2016, 27 (2), 1604924.
- Complex Dewetting Scenarios of Ultrathin Silicon Films for Large-Scale Nanoarchitectures.

Naffouti, M.; Backofen, R.; Salvalaglio, M.; Bottein, T.; Lodari, M.; Voigt, A.; David, T.; Benkouider, A.; Fraj, I.; Favre, L.; Ronda, A.; Berbezier, I.; Grosso, D.; Abbarchi, M.; Bollani, M. *Sci. Adv.* **2017**, *3* (11), 1472–1482.

Solid-State Dewetting of Single-Crystal Silicon on Insulator: Effect of Annealing Temperature and Patch Size.

Abbarchi, M.; Naffouti, M.; Lodari, M.; Salvalaglio, M.; Backofen, R.; Bottein, T.; Voigt, A.; David, T.; Claude, J.-B.; Bouabdellaoui, M.; Benkouider, A.; Fraj, I.; Favre, L.; Ronda, A.; Berbezier, I.; Grosso, D.; Bollani, M. *Microelectron. Eng.* **2018**, *190*, 1–6.

Large surfaces of 2D hexagonal metallic and semiconductor nanodots by double self-assembly.

Bottein T., Bouabdelaoui M., Claude J.B., David T., Putero M., Ronda A., Abbarchi M., Favre L., Berbezier I. and Grosso D. **2018** Nanoscale. Submitted.

Titania-based spherical Mie resonators elaborated by high-throughput aerosol spray; single object investigation.

Checcucci S., Bottein T., Claude J.B., Wood T., Putero M., Favre L., Gurioli M., Abbarchi M., Grosso D. **2018** Adv. Func. Mat. Submitted

Patents

Nanoimprint Lithography Process and Patterned Substrate Obtainable Therefrom.
Patterned De Exercición Ma Deleteira O a Cattaria A ED17205286 1 2017.

Bottein, T.; Grosso, D.; Faustini, M.; Dalstein, O.; Cattoni, A. EP17305286.1, 2017.

- Microtransfer Molding Process and Patterned Substrate Obtainable Therefrom. Bottein, T.; Grosso, D. EP 17305823.1, 2017.
- Process for Forming an Organized Network of Semi-Conducting Nanoparticles or Nanowires onto a Silicon Substrate. Bottein, T.; Grosso, D.; Favre, L. EP 18153070.0, 2018.