CHAPTER I

Introduction & aims of the thesis

The introduction gives an insight of the context of the present study. A description of the major nanofabrication techniques brings to light the reasons why we opted for the Nanosphere Lithography (NSL) method. Some applications are briefly discussed. The scope and objectives of the research are then broached, followed by the thesis outline.
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“There’s plenty of room at the bottom”

More than 50 years have passed since the famous lecture ‘There's plenty of room at the bottom’ by Richard Feynman.\cite{1} In his talk, Feynman explored apparently simple and elegant possibilities of working at the atomic scale – possibilities that would have startling results. He touched upon ideas such as miniature writing, seeing and moving atoms, the prospect of designing molecules one atom at a time and the challenges involved in developing miniature machines.

Strictly speaking, a nanostructure is any structure with one or more dimensions measuring in the nanometer ($10^{-9}$m) range. Various definitions refine this further, stating that a nanostructure should have a characteristic dimension lying between 1nm and 100nm, putting nanostructures as intermediate in size between a molecule and a bacterium.\cite{2}

The advent of \textit{nanoscience} and \textit{nanotechnologies}\footnote{Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale. Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale.} has led to tremendous enthusiasm from researchers from different scientific disciplines who see an open door to the discovery of new properties due to nanostructuring of the material. Devices operating on this scale are expected to provide a number of breakthrough applications like more powerful computers and increased data storage due to more efficient and smaller components. Applications are also expected in fields like solar cells, (molecular) electronics, biosensors. The large expectations of nanotechnology have made nanotechnology into a \textit{buzzword} widening its definition to all research operating with at least one length scale in the nanometer level.

To cite Feynman, the question is now: “How do we write small?”...
Figure 1 - 1
Nanofabrication.[4]
1. The Art of Building Small

There are two major routes for nanofabrication, called the “TOP-DOWN” and the “BOTTOM-UP” approaches (Figure I - 1).\cite{3, 5-11}

1.1 Top-Down

In the Top-Down approach, thin films or bulk materials are scaled down to create nanodevices. This can be done by using various techniques such as precision engineering and lithography, and has been developed and refined by the semiconductor industry over the past 30 years. Indeed, the never-ending race towards miniaturization of devices (mobile, camera, etc.) induced an intense research in the manufacturing processes of the basic components of these devices.

The concept of lithography (from Greek λίθος - lithos, 'stone' and γράφω - grapho, 'to write') is central to nanofabrication and is one of several terms shared by both scientists and artists.

Lithography originally used an image drawn with wax or other oily substance applied to a porous stone as the medium to transfer ink to the printed sheet. The flat surface of the plate or stone is slightly roughened, or etched, and divided into hydrophilic regions that accept a film of water and thereby repel the greasy ink, and hydrophobic regions that repel water and accept ink.\cite{12} This method does not involve any engraving step.

In the semiconductor industry, lithography refers to the technique for structuring thin layers of materials to create transistors, tracks, and other components.

Lithography, the first part of the Top-Down process (Figure I - 2), is a collective term for several closely related processes:

1. A uniform layer of resist, dissolved in a certain organic liquid solvent, is spin-coated on a substrate or an unpatterned film. The resist thickness is typically a few thousand angstroms to a micron, depending on the spinning speed and the resist viscosity. A soft-bake of the resist is necessary to remove the resist solvent and promote adhesion.

2. Selected areas of the resist are then exposed to an electromagnetic radiation (Optical Lithography), ions (Ionic Lithography) or electrons\cite{13} (Electron Beam Lithography) that will modify the physicochemical properties of the resist (e.g. solubility). Upon sufficient exposure, the polymer chains are either broken (positive resist) or become cross-linked (negative resist). This step is subjected to special care and requires very sophisticated preparation methods to provide the most control over geometry of structures.

The lithographic tools are classified in two families: “parallel writing” (or replication) methods (e.g. optical lithography) and “sequential writing” (or patterning) methods (e.g. Focused-electron beam lithography).
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Figure 1 - 2
The Top-Down process.
(3) The development in a specific solvent will selectively remove the exposed (positive resist) or non-irradiated area of the resist (negative resist).

In parallel writing, the whole pattern is made simultaneously using a mask, which dictates the features to be reproduced. It is easy to understand that sequential lithography is slower as the pattern is written point by point on the resist surface and is therefore more expensive.

Optical lithographic processes are limited in final resolution by the wavelength of the light used to expose the photoresist.\(^\text{[14]}\) The use of short wavelengths and reduction optics between the mask and substrate has allowed a reduction in features size. Extending these processes to wavelengths in deep UV and soft X-ray brings increasing technical difficulty. Alternative techniques, such as electron beam lithography, have been developed to overcome the limitations of optical light. While optical lithography is mainly intended for patterns of a few micrometers to a few 100 microns, the electron beam lithography allows for its part to achieve sub-micron resolution far. Under ideal conditions, it is possible to reach a sub-10 nm resolution.

Each of these conventional fabrication tools, except for soft X-ray lithography, is commercially available (though expensive). These techniques are highly developed and optimized for semiconductor fabrication. The costs of purchasing, installing, and maintaining the tools they require limits their application in areas other than microelectronics. These tools are also often incompatible with nonstandard problems in fabrication (e.g. coatings on non-planar surfaces).

Over the years, many lithographic and patterning techniques have been proposed to overcome these disadvantages. The concept of soft lithography is introduced in 1988 by Whiteside's group at Harvard.\(^\text{[15]}\) It refers to a set of methods\(^\text{[8, 16, 17]}\) (MicroContact Printing, Replica Molding, MicroTransfer Molding, etc.) for generating or replicating structures by using a patterned elastomer (e.g. PolyDimethylSiloxane (PDMS)) as a mask, stamp or mold. These methods can be carried out by hand in an ordinary laboratory. Conventional photolithography must take place in clean-room facility devoid of dust and dirt; if a piece of dust lands on the mask, it will create an unwanted spot on the pattern. As a result, the device being fabricated may fail. Soft lithography is generally more forgiving because the PDMS stamp is elastic. If a piece of dust gets trapped between the stamp and the surface, the stamp will compress over the top of the particle but maintain contact with the surface. Thus, the pattern will be reproduced correctly except for where the contaminant is trapped.

Moreover, soft lithography can produce nanostructures in a wide range of materials, including the complex organic molecules needed for biological studies.\(^\text{[18]}\) The technique can print or mold pattern on curved as planar surfaces, but the technology is not ideal for making the structures required for complex nanoelectronics. Currently all integrated circuits consist of stacked layers of different materials. Deformations of the soft PDMS stamp can produce small errors in the replicated pattern and a misalignment of the pattern with any underlying patterns previously fabricated.
Therefore, soft lithography is not well suited for fabricating structures with multiple layers that must stack precisely on top of one another.

Researchers have found ways, however, to correct this shortcoming - at least in part - by employing a rigid stamp instead of elastic one. In a technique called step and flash imprint lithography,[17] photolithography is used to etch a pattern into a quartz plate, yielding a rigid bas-relief master. The master is then pressed against a thin film of liquid polymer, which fills masters recesses. Exposition to ultraviolet light solidifies the polymer to create the desired replica. A related technique called Nanoimprint Lithography[13] also employs a rigid master but uses a film of polymer that has been heated to a temperature near its melting point to facilitate the embossing process.

Scanning Probe techniques[19] are also potential tools for nanofabrication. Depending on the sharpness of the pen, the resolution of writing can vary from macroscopic feature sizes down to the atomic sale. These scanning probe techniques are based on the changes undergone by species present on the surface of a substrate. In practice, such changes can be induced by mechanical, electrical, magnetic or chemical means. One of the most striking examples of nanoscale fabrication by Scanning Probe Lithography has been the precise positioning of atoms with an STM tip.[20] Manipulations of atoms or particles by scanning probe lithography techniques will be rather classified in the bottom-up approach. These tools seem well suited for applications in research but will require substantial development (simultaneous writing patterns with multiple probes[21]) before they can be used for patterning large areas in manufacturing. The characteristics of all these lithography techniques are summarized in Table I - 1; where advantages are highlighted in green, while drawbacks are in red.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Minimum feature size</th>
<th>Pattern</th>
<th>Area</th>
<th>Cost</th>
<th>Time</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep UV L. [24]</td>
<td>50-100 nm</td>
<td>PW AP</td>
<td>Large</td>
<td>High</td>
<td>Short</td>
<td>Industry</td>
</tr>
<tr>
<td>Immersion Deep UV L. [25]</td>
<td>30 nm</td>
<td>PW AP</td>
<td>Large</td>
<td>High</td>
<td>Short</td>
<td>R&amp;D</td>
</tr>
<tr>
<td>Extreme UV L. [26]</td>
<td>&lt; 50 nm</td>
<td>PW AP</td>
<td>Large</td>
<td>High</td>
<td>Short</td>
<td>R&amp;D</td>
</tr>
<tr>
<td>X-Ray L.</td>
<td>20 nm</td>
<td>PW AP</td>
<td>Large</td>
<td>High</td>
<td>Short</td>
<td>R&amp;D</td>
</tr>
<tr>
<td>Electron Beam L.</td>
<td>nm</td>
<td>SW AP</td>
<td>Small</td>
<td>High</td>
<td>Long</td>
<td>R&amp;D (Industry)</td>
</tr>
<tr>
<td>Scanning Probe L. [19]</td>
<td>&lt; 1 nm</td>
<td>SW AP</td>
<td>Small</td>
<td>High</td>
<td>Long</td>
<td>R&amp;D</td>
</tr>
</tbody>
</table>

Table I - 1
Characteristics of most popular lithographic techniques,[10, 17, 22, 23] (L : Lithography; PW : Parallel Writing; SW : Sequential Writing; AP : Arbitrary Pattern)
Many reviews are focused on the evolution of these new “unconventional” approaches to nanofabrication.[17,22,23]

In the second part of the Top-Down process (Figure I - 2), the pattern is transferred into (subtractive transfer) or onto (additive transfer) the substrate/sample.[27]

In subtractive transfer, the resist film acts as a protective barrier for the substrate/sample surface, which is more easily accessible to an etching agent[28] (liquid, gas or plasma) in the previously developed nude areas. After pattern transfer, the resist can be removed for further process steps (e.g. stamp for nanoimprint lithography applications).

The second half of Figure I - 2 represents two additive transfers, in which the aim is to exploit the openings made in the resist film during lithography in such a way to deposit a new material on the sample surface. This material can be deposited by what are usually called physical methods, such as sputtering or vacuum vapor deposition (PVD), or by chemical methods (e.g. dewetting process explained in section 2.1). The technique used to locate this deposition precisely in the openings made in the resist is called lift-off. One can also use resist patterns as mask for growth via an electrochemical reaction in a liquid medium, which deposits electrolyte ions on the surface that remains unprotected by the resist. This is called electrolytic growth transfer.[29] The idea of using electrolytic growth was invented mainly to obtain thicker patterns than those obtained by lift-off.

Subtractive and additive transfers will lead to different nano-architectured materials (after removal of resist), which will be detailed in section 3.

1.2 Bottom-Up

Bottom-up approach uses small and simple building blocks (atoms, molecules, nanoparticles, etc.) that will self-assemble into larger, more complex structures (Figure I - 1). Compared with top-down route, this is more like a chemical or biological approach and it has the potential to make complex 3D structures cheaply and in large quantities. These methods can easily make the smallest nanostructures - easily reaching sub-10 nm dimensions - and do so inexpensively.

Self-assembly is defined as the spontaneous (without the assistance of external forces or spatial constraints) organization of two (or more) components into larger aggregates using covalent and/or non covalent bonds.[30]

Materials fabricated using this approach include self-assembled monolayers[31] or nanostructures that self-assemble from block-copolymers[26, 32-34] and that can be used as templates for the preparation of metallic or semiconducting nanostructures.[35] The main advantage of this technique is that nanoscale features can be achieved. Block-copolymer lithography is sometimes used together with a lithography prepatterned substrate for further specific assembly of copolymers.[26]
Recent advances in the fabrication of functional nanostructures using self-assembly include self-assembled magnetic nanoparticles. Crystalline areas of magnetic nanocrystals can store large amount of information. However, an annealing step is usually necessary to enhance the magnetic properties and may give rise to coalescence of the nanoparticles. Nontemplated self-assembly, while attractive for its minimalist use of materials and energy (compared to conventional lithography), is not widely used for nanofabrication. Indeed, self-assembly is prone to producing defects, and the perfect periodicity of self-assembled structures from nanoscale components is generally limited to micrometer-sized areas. Moreover, precise spatial positioning and nanostructure shape control are difficult to implement.

1.3 Top-Down, Bottom-Up or both?

The preferred nanostructuration technique should be able:

- to produce nanoobjects, exhibiting similar features in terms of size, shape and interface in order to exhibit similar (e.g. chemical, magnetic,...) properties;
- to manufacture long range ordered arrays of nanostructures: all nanostructures are equidistant and have the same environment;
- to control the density of these nanostructures in order to isolate or otherwise increase their number on a given surface;
- to offer a certain flexibility in the choice of materials, both for the substrate and the nanostructures;
- to fulfill the above conditions in a short time and at reasonable price.

Considering the previously described synthesis routes (1.1 Top-Down & 1.2 Bottom-Up), the following conclusions can be drawn. The complexity of the preparation process combined with high initial equipment costs makes the conventional lithographic techniques unfavorable for many researchers.

Most of the nonconventional lithographic techniques developed to date, however, require the assistance of conventional lithographic techniques, such as photolithography, to design and manufacture the masks or masters. Soft Lithography techniques, although they present many advantages, do require the production of a single mask (which will be used several times) by conventional lithographic techniques. Scanning probe lithography techniques are of course too slow for mass production. Bottom-up techniques, although they easily reach sub-10 nanometers may present some disadvantages. Self-assembly has its own problem of regularity and repeatability.

† Although the distinction is not always made in the literature, the terms self-assembly and self-organization should be used respectively to describe structures formed close-to-equilibrium and far-from-equilibrium dissipative processes involving energy/matter flow. In some cases, the words are used interchangeably and the confusion is still frequent in the literature. Therefore, it should be stressed that the term self-assembly will sometimes be mentioned by misuse of language throughout the manuscript.
Indeed, control of the density and shape of the nanostructures is difficult to achieve, which is rather annoying especially in case of magnetic data storage.

By the way, the dimensions that can now be controlled by either approach (Figure 1 - 3) are of similar order, and this leads to exciting new hybrid methods including nanosphere lithography towards which our choice was directed.

![Dimensional Scale](image)

**Figure 1 - 3**

The convergence of top-down and bottom-up approaches.[39]

### 2. Nanosphere Lithography (NSL)

Nanosphere lithography (NSL) is an ideal inexpensive fabrication tool for producing regular and homogenous arrays of nanoparticles with different sizes.

This process is divided in two steps (Figure 1 - 4), the first of which is mask preparation. After a chemical treatment to enhance its hydrophilic character, the flat substrate is coated with a suspension containing monodisperse spherical colloids (e.g. polystyrene). Upon drying, a hexagonal closed packed (HCP) monolayer or bilayer, called a colloidal crystal mask[40] (CCM), is formed.

This mask is then used to selectively pattern the substrate thanks to the deposition of the material of interest through the interstices of the ordered beads.

The subsequent removal of the mask by sonication in an adequate solvent or by stripping leaves an array of ordered nanodots on the surface of the substrate. An annealing step is sometimes necessary to crystallize the sample or/and induce a crystallographic phase change.

The NSL is often considered as a hybrid between the bottom-up approach (due to the self-organization of the colloidal spheres in a HCP lattice) and the top-down approach (due to the obtention of dots such as in a conventional lithography technique).
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Figure 1 - 4
Nanosphere Lithography process (NSL)
Nanosphere Lithography is also known as *Colloidal lithography*\(^{[41, 42]}\) or *Natural lithography*.

Fischer and Zingsheim\(^{[43]}\) are the first to report, in 1981, the formation of an ordered monolayer on a glass plate. They simply deposited a suspension of colloidal spheres with a diameter of 312 nm and allowed it to evaporate. They obtained small-area particle monolayers. The term of “naturally” assembled polystyrene (PS) latex nanospheres was then introduced. However, the focus of their work was the replication of submicroscopic patterns using visible light and not fabrication of lithographic colloidal masks.

A year later, Deckman and Dunsmuir\(^{[44]}\) extend the scope of the approach of Fischer showing that a monolayer of nanospheres can be used both as a ‘deposit material’ or as a lithographic mask. The deposition is either random or with ordered arrays over the entire surface of a macroscopic substrate.\(^{[45]}\) The coating procedure developed to produce microcrystalline arrays is based on a spin coating process. Several point defects or dislocations are present in the tens of micrometers scale. Because the mask preparation process is obtained by self-assembly phenomenon rather than by photolithography, they named this strategy “natural lithography”.

In the 90’s, the method is renamed by the group of Van Duyne\(^{[46]}\) and is still nowadays commonly called “Nanosphere Lithography”. Their work is not only focused on mono(single)-layers (SL) but extends to double-layers (DL) which leads to the formation of smaller dots corresponding to the small openings that remain in a closed packed structure (Figure I - 5).

![Figure I - 5](image)

Schematic diagrams of single-layer (SL) and double-layer (DL) nanosphere masks and the corresponding periodic particle array PPA surfaces (dotted line = unit cell).\(^{[46]}\)

Van Duyne's group\(^{[47, 48]}\) has also intensively investigated the plasmon resonance properties of metallic patterns with the ultimate goal of developing biosensors based on surface enhanced Raman spectroscopy.

Besides, several groups have studied experimentally and theoretically the behavior of colloidal suspensions in order to understand their stability as well as the mechanisms of formation of the mask.\(^{[49]}\)
Figure I - 6 highlights the increasing interest for NSL over the past 15 years.

2.1 Designing monolayers

In recent years, many groups have been working on different strategies to continually improve the quality of the crystal masks. The major methods will be briefly described below, focusing only on 2D polystyrene nanospheres lattices.

2.1.1 Self-assembly during solvent evaporation

Evaporation methods are based on solvent evaporation from a droplet of dilute colloidal nanosphere suspension deposited on a substrate. The evaporation of the solvent induces the formation of a meniscus between the particles and therefore attractive capillary forces give rise to the self-assembly of the particles.

Nagayama and his team[50] conducted pioneering work on self-ordering of colloidal particles by direct observation of colloids. They found that attractive capillary force and convective transport of the nanospheres are the main factors that dominate the self-assembly process, while the ordering and quality of the obtained arrays are considerably affected by the rates of solvent evaporation.[51]

By controlling the temperature and the humidity of the system, Micheletto et al.[52] prepared colloidal monolayers on a slightly tilted substrate. Since then, other tests were performed successfully.[53, 54] Low control over the process often yields mixed multilayers structures.
2.1.2 Dip coating

Based on their work on convective assembly of colloidal nanospheres during solvent evaporation, Nagayama et al. [55, 56] developed a dip-coating procedure for formation of 2D colloidal templates. Constant monitoring of the evaporation rate and the withdrawal speed of the substrate are key parameters to achieve large 2D ordered arrays (Figure I - 7). However, the particle layers are formed on both sides of the substrate, thereby increasing the amount of suspension used.

![Figure I - 7](image)

(a) SEM micrograph of a PS monolayer (480 nm diameter) containing defects of multilayers and voids [55]; (b) Tapping-mode atomic force microscopy micrograph of PS monolayer [56]

To overcome this drawback, Nagao et al. [57] engineered a hybrid method between evaporation and dip-coating. A drop of colloidal suspension is placed on the substrate, which is thereafter inclined vertically until the suspension is dried. However, many defects are still present in the network (Figure I - 8). Multilayers can be obtained by repeating the operation.

![Figure I - 8](image)

SEM micrograph of a PS nanoparticles (520 nm diameter) monolayer [57]
2.1.3 Spin coating

The spin coating of a colloidal suspension onto a substrate can accelerate the evaporation of the solvent.\textsuperscript{[44, 46]} The quality and thickness of colloidal templates are greatly affected by spin speed, size of the nanospheres, wettability...

Most of the literature on spin coating of colloidal suspension is experimentally based. Even if recent papers are more detailed, spin coating protocols described in the literature are varied and sometimes imprecise.\textsuperscript{[58, 59]} Therefore a major goal for further progress in NSL is the development of experimental protocols to control the ordering of particles on solid substrates and to get large well-ordered structures. This technique will be discussed in more detail in Chapter III.

However, the spin coating has a significant potential for mass production and scaling-up because of its rapid implementation and its compatibility with wafer-scale processes.

![Figure 1 - 9](image)

**Figure 1 - 9**

SEM micrographs of PS (500 nm diameter) colloidal template.\textsuperscript{[60]}

2.1.4 Self-assembly at interface of two media

- **Air-Liquid interface**

  **Langmuir-Blodgett coating**

Langmuir-Blodgett coating refers to the preparation and transfer of nanosphere monolayers from liquid-gas interface onto a solid substrate by controlled withdrawal of the substrate. Through use of surfactants\textsuperscript{[61]} or through surface modification of the nanospheres\textsuperscript{[62]} in order to enhance their hydrophobicity, a 2D crystal film is formed on the liquid surface. The resulting floating monolayer is compressed by a barrier that promotes the assembly of the nanospheres in close-packed lattices. This setup ensures that the pressure remains constant as the substrate is being withdrawn. Macroscopic areas can be patterned with nanospheres.

  **Controlled evaporation**

The first step of the process (colloidal monolayer formation) is similar to that of the Langmuir-Blodgett technique. However, the floating monolayer is left free without action of any barrier to modify its assembly, which greatly simplifies the apparatus.
Moreover, instead of being slowly withdrawn from the suspension, the substrate is left immersed during the liquid evaporation.\textsuperscript{[63, 64]} By slightly tilting the substrate, large HCP domains (Figure I - 10) with size greater than 150 μm\(^2\) (PS nanospheres with 200nm diameter) were manufactured.\textsuperscript{[65]}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image}
\caption{SEM micrograph showing large area of self-assembled PS (200 nm diameter) monolayer. The scale bar is 1μm.\textsuperscript{[65]}}
\end{figure}

- **Liquid-Liquid interface**

Self-assembly may also occur at the interface between two non-miscible liquids.\textsuperscript{[66]} Thanks to carefully prepared surface conditions, nanospheres assemble at the interface. Once they are trapped at the interface, they self-organize into a monolayer. Subsequently, the monolayer is deposited on the substrate by a removal procedure or evaporation of one phase.

### 2.1.5 Electrophoretic deposition

In electrophoretic deposition, a colloidal suspension is confined between two electrodes. An applied electric field induces the migration of the particles (Figure I - 11) and self-assembly occurs at electrode interfaces (Figure I - 12). This method is therefore limited to conductive substrates (e.g. indium tin oxide (ITO) glass). Two\textsuperscript{[67]} and three\textsuperscript{[68]} dimensional colloids crystals have been studied both in a DC field\textsuperscript{[69-71]} or AC field.\textsuperscript{[72, 73]}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image}
\caption{Scheme of electrophoretic deposition of colloids.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image}
\caption{SEM micrograph of PS pattern produced by DC electrophoretic deposition in the presence of an UV illumination motif. The inset shows the overall appearance of the pattern.\textsuperscript{[71]}}
\end{figure}
The use of AC field allows manipulation of almost any type of particle in any type of media and has the advantage of permitting high field strengths without causing water electrolysis.\cite{73}

### 2.1.6 Pre-patterned substrates

Template-assisted self-assembly of colloids is usually employed to fabricate types of arrangements which are difficult or impossible to fabricate with traditional self-assembly process.

Two fundamentally different strategies are available, namely the self-assembly on chemically or physically (Figure I - 13) patterned substrates. Both methods involve an additional preliminary step in the process and may consequently increase the time and the cost of preparation.

![Figure I - 13](image1.png)

Self-assembly on a physically patterned substrate.

Indeed, physically patterned substrates are produced by conventional lithographic techniques (optical lithography,\cite{74} electron beam lithography). By changing the shape of the patterned geometry and the ratio size to particle size (Figure I - 14 and Figure I - 15), it is possible to control the packing order of the colloidal crystals.\cite{75,76}

![Figure I - 14](image2.png)

SEM micrographs showing large area of polystyrene spheres on patterned photoresist template. Inset shows magnified image of the channel.\cite{77}

![Figure I - 15](image3.png)

SEM micrographs of some typical examples of polygonal aggregates that were formed by templating PS beads against 2D arrays of cylindrical holes. The cylindrical holes used in all experiments are \( \approx 2 \ \mu m \). (a) Dimers with 1.0 \( \mu m \) PS beads; (b) trimers with 0.9 \( \mu m \) PS beads; (c) Square tetramers with 0.8 \( \mu m \) PS beads and (d) Pentagons with 0.7 \( \mu m \) PS beads.\cite{78}
On the other side, a selective deposition of the colloids may occur on chemically patterned (Figure I - 16) substrates.\cite{79,80}
Depending on the nature of the interaction between the particles and the template surface, the assembly process is carried out by different methods (evaporation, spin coating or electrophoretic deposition (Figure I - 17)).

![Figure I - 16](image1)
SEM micrographs of a chemical patterned experiment by use of a square elastomer stamp as structure for printing. (a) Overview of the sample, (b) Zoom on one square. Dimensions of the pattern: squares [24 \textmu m].\cite{80}

![Figure I - 17](image2)
SEM micrographs of 2D colloidal crystals grown by electrophoretic deposition on (a) a patterned and on (b) an unpatterned ITO substrate. Scale bars are 5 \textmu m.\cite{76}

### 3. Applications of NSL

Assembling colloidal micro/nano particles into 2D ordered arrangements presents tremendous potential for applications in many different fields.

The 2D HCP monolayer is used as mask or template to generate patterns of functional materials on the substrate. The deposited materials can be chosen without almost any limitation and the feature size of obtained structures can be controlled by adjusting the particle diameters, ranging from less than ten nanometers\cite{81} to tens of micrometers.\cite{82}

Although the preparation of a colloidal mask is easy and cheap, the resulting pattern is limited to triangular structures, which can be a significant drawback, compared to conventional lithographic techniques. Indeed, in many applications, the material properties and target applications are highly dependent on the shape of the patterned species. To overcome this disadvantage and build new architectures, various strategies have been suggested and will be briefly discussed hereafter.

#### 3.1 Nanodots - Nanodisks - Nanorings

A huge variety of nanoparticle arrays can simply be generated by deposition on the substrate, which is usually positionned normal to the propagation direction of a material vapor.
Among all applications, Localized Surface Plasmon Resonance (LSPR)\textsuperscript{[83]} is one active area of great interest. Van Duyne and his co-workers\textsuperscript{[84]} investigated the relationship between particles sizes, shape, interparticle spacing and LSPR. They worked on hexagonally ordered triangular Ag dot arrays obtained with single-layered colloidal masks or Ag nanoparticle arrays obtained by double-layered colloidal masks (Figure I - 18). They demonstrated that the absorption band of the metallic nanostructures can be easily tuned from visible to near-IR. LSPR plays a major role in new developments of nanophotonics, such as surface enhanced Raman scattering\textsuperscript{[64, 85]} (SERS) substrates or bio-sensors.\textsuperscript{[86]}

In order to modify the interstitial structure of the colloidal mask, a number of post treatment methods (e.g. heating (Figure I - 19), etching) have been developed. The importance of the etching process will be highlighted and detailed in chapter III.

Van Duyne and co-workers\textsuperscript{[88]} also pioneered angle-resolved colloidal lithography, which consists in the deposition of materials at the non-zero incident angle (\(\theta\)) of the vapor beam with respect to the normal direction of the substrate. This technique not only reduced the dimension of the nanodots but also modified the shape from equilaterals to isosceles triangles (Figure I - 20). Recently, Wang and co-workers broadened the scope of angle-resolved colloidal lithography by developing a stepwise strategy to generate heterogeneous binary particles (Figure I - 21).
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Figure 1 - 20
SEM micrographs of gold nanodots fabricated by angle-resolved colloidal lithography with (a) θ = 20° and (b) θ = 40°. The scale bar is 1 µm.\(^{[88]}\)

Figure 1 - 21
(a) Schematic illustration of depositing gold and silver onto a hexagonally close-packed spheres monolayer at the incidence angles (θ) of 15 and -15°, respectively. The incident beam of gold, the incident beam of silver, and the normal direction of the colloidal template are highlighted by yellow, blue, and black arrows, respectively. (b) SEM image of the resulting heterogeneous binary array. The original location of PS spheres, gold nanoparticles (NPs), and silver NPs are highlighted by black circles, yellow triangles, and blue triangles, respectively. The scale bar is 2 µm.\(^{[89]}\)

A modified colloidal lithography (hole-mask colloidal lithography\(^{[90]}\)) enabled the preparation of metal nanodisk arrays after several deposition/etching steps. Kasemo and his group fabricated Pt\(^{[91]}\), Pd\(^{[91]}\), Ag\(^{[91]}\) and Al\(^{[92]}\) nanodisks (Figure 1 - 22) and studied their plasmonic properties. Aizpurua et al.\(^{[93]}\) investigated the optical properties of Au nanorings using another modified colloidal lithography. A red-shifted localized surface plasmon was observed compared to Au nanodisks of similar size. Those nanorings may also be used as ultrasensitive bio-sensors.\(^{[94]}\)

Figure 1 - 22
(a) SEM micrograph of Pt nanodisks. The scale bar is 500 nm.\(^{[91]}\) (b) AFM 3D micrograph of a Al nanodisk. Cross-section profile reveals a rather rough surface.\(^{[92]}\)

Figure 1 - 23
SEM micrographs of Au nanorings: (a) Top-view and (b) 80° tilted-view. Both scale bars are 100 nm.\(^{[94]}\)

A dewetting process also enables to synthesize nanorings of various materials (TiO\(_2\)\(^{[95]}\), CdSe Quantum Dots\(^{[96]}\), proteins\(^{[97]}\)). First, a solution containing the desired material is filled into a colloidal template on a substrate. During the evaporation of solvent at the nanosphere/substrate interface, the solvent molecules around the contact area usually evaporate last, because they are confined by capillary forces.
The materials dissolved or dispersed in the solvent move towards these areas and form ring-like structures under the nanospheres.

Finally another important area of the NSL is the design of ordered nanostructures for ultrahigh density magnetic recording. Compared with conventional techniques for fabricating magnetic ordered nanostructures, NSL is inexpensive and allows high-output fabrication. In general, reducing the feature dimensions to characteristic length scales has revealed novel magnetic properties.\textsuperscript{[35]} For example, nanoscale magnetic materials often exhibit superparamagnetic behavior, which hinders the miniaturization race. Some nanodots and nanodisks magnetic nanostructures are presented in Figure I - 24.

3.2 Nanoholes

The fabrication of nanoholes is based on the modification of colloidal masks by etching or heating treatment. It modulates the size of the interstitial pores between the particles, changing the arrangement from close packing to non-close packing. This technology allows considerable freedom to control both the feature dimensions and shape of nanoholes by changing the sizes of nanospheres. By filling the empty interspace between nanospheres with target materials, nanohole or nanopore arrays can be produced. Periodic metallic nanohole arrays (Figure I - 25 & Figure I - 26), as other metallic nanostructures, have attracted great interest because of their important technological applications in nanophotonic devices. Current challenge in this field lies in the fabrication of non-spherical nanohole arrays (Figure I - 26) due to the shape of the individual nanoholes offers an important handle to tune the plasmonic properties.
3.3 Nanorods - Nanowires - Nanopillars - Nanotips

By catalytic deposition or growth, 1D structured arrays can be fabricated using 2D colloidal crystals as templates.

Metal nanoparticle arrays can be used as catalysts to grow 1D nanowire arrays. Indeed, Ni nanoparticle arrays have been used to prepare carbon nanotube arrays (Figure I - 27) by plasma–enhanced chemical vapor deposition (PECVD). Wang and co-workers\textsuperscript{[102]} prepared aligned ZnO nanorods by vapor-liquid-solid growth guided by Au nanoparticles arrays.

Li and co-workers\textsuperscript{[103]} reported a new approach for manufacturing TiO\textsubscript{2} hcp nanocolumn arrays (Figure I - 28 (a)) by pulsed laser deposition (PLD) in oxygen on the top of PS nanospheres. The periodicity can be tuned by using different nanosphere sizes and the distance between neighboring columns could be controlled by experiment parameters (e.g. pressure) during process (Figure I - 28).

By changing the corresponding target in the PLD process, this strategy could be used to synthesize similar nanocolumns in different materials such as Co\textsubscript{3}O\textsubscript{4},\textsuperscript{[104]} ZnO,\textsuperscript{[105]} Fe\textsubscript{2}O\textsubscript{3},\textsuperscript{[105]} or CuO.\textsuperscript{[105]} These nanostructures, in addition to intrinsic properties of materials they are made of, may display interesting wettability properties.\textsuperscript{[104]}

![Figure I - 27](image1.png)

**Figure I - 27**
Tilted SEM micrograph of aligned carbon nanotubes (CNTs).\textsuperscript{[106]}

![Figure I - 28](image2.png)

**Figure I - 28**
TiO\textsubscript{2} nanocolumn array obtained by PLD using a PS colloidal monolayer as substrate.
(a) HR-SEM micrograph observed from the side (the dotted circle highlights the PS sphere); (b) & (c) Top-view HR-SEM micrograph of TiO\textsubscript{2} nanorods obtained under different background gas pressures ((b) 2.0 Pa for 200 min and (c) 26.8 Pa for 30 min) and subsequent annealing.\textsuperscript{[103, 107]}

Two-dimensional colloidal crystals can also be used as masks to prepare nanotip/nanopillar arrays by etching procedures such as dry etching by Reactive Ion Etching (RIE) or metal catalytic wet etching.\textsuperscript{[106, 109]} RIE steps of certain materials are realized by corresponding ions, e.g. polymer and carbon by oxygen ions, while silicon and silica by fluorine ions.\textsuperscript{[110]}
Nanotips and nanopillars are of great importance because of their unique potential in a wide variety of applications (Figure I - 29), such as antireflection coatings,[108, 111] highly hydrophobic surfaces,[108] mold for nanoimprint lithography,[112]

![Figure I - 29](image)

(a) SEM micrograph of a cross-section of the silicon tip arrays obtained by wet-etching. The inset is the profile of water droplet on the sample.[108]; (b) & (c) Respectively side and top SEM micrographs of RIE-etched silicon sample for antireflective applications.[111] The scale bar is 200 nm; (d) SEM micrograph of silicon nano-imprint lithography stamp obtained by RIE etching and (e) SEM micrograph of corresponding imprinted pattern on PMMA.[113]

4. Scope and objectives of the research

The present research is focused on both parts of the NSL process, with the aims to optimize PS colloidal masks prepared by spin coating for long range order/maximum density and to use these masks for the controlled growth of functional materials with various applications.

The extensive work undergone on the preparation of colloidal crystal masks (section 2.1) clearly highlights the growing interest owing to their potential in many important applications.

Compared with 'static evaporation', dip-coating or more sophisticated methods, spin coating presents some major assets in terms of implementation rapidity, low-waste production, scaling-up potentiality and low-cost. However, the preparation of colloidal crystal masks by spin coating may present some limitations. Indeed, dislocations, vacancies, other structural defects and small monolayer areas are numerous problems to which scientists are confronted. Therefore a major goal for further progress in NSL is the development of experimental protocols to control the ordering of particles on solid substrates and to get large well-ordered structures.

A set of experiments has been generated in an attempt to extract the influence of spincoating parameters (ramp, rotation speed) on the self-organization of PS nanospheres (490 nm diameter). In order to evaluate the quality of the mask, a computerized (MatLab®) image analysis procedure, based on SEM micrographs, has been completely developed. Indeed, most researchers give a rough idea of the size of the
monolayers area, ignoring most of the time the presence of small defects. The quality of the mask is described beyond reasonable doubt by the percentage of nanospheres in a hexagonal close-packed arrangement. The hcp percentage output data is subsequently used to perform a statistical study whose purpose is to link the sample quality to adequate spincoating parameters, highlighting which are determinants.

Some practical issues are also discussed like the hydrophilicity of the substrate, the tuning of the surfactant concentration usually added to the beads suspension or the use of reactive ion etching (RIE) process to tailor the size and interparticle distance of the PS nanospheres.

Those masks have then been used to design nanostructures for various applications.

The first of these consist in the deposition of magnetic nanodot (Co or FePt) arrays for magnetic information storage. Indeed, FePt has recently gained significant attraction as a candidiate for ultra high density magnetic recording due to its very high anisotropy constant and its high corrosion resistance. Currently, patterned FePt nanoparticle arrays can be produced either by self-assembly of chemically prepared FePt monodisperse nanoparticles or by EBL. However, a post-deposition annealing treatment is necessary to obtain the face-centered tetragonal (fct) phase (L1₀ phase with hard magnetic behavior), which may lead to agglomeration of the nanoparticles obtained by the self-assembly process. Moreover, as it was previously discussed (1.1 Top-Down), the electron beam lithography technique is a rather expensive and time-consuming process.

Therefore, large scale production of well-separated FePt nanodot arrays at low-cost is still a challenge and is in the reach of NSL. Morphology of the dots has been studied by SEM and AFM. The annealing temperature has been optimized and related to both the crystallographic structure and to the magnetic properties of the samples. Quantitative magnetic measurements have been performed by SQUID and focused-MOKE to highlight the magnetic stability of the designed nanostructures. Finally, the magnetic domain structure of the nanodots has been revealed by MFM.

In another area, we focused on the fabrication of template ZnO nanowire arrays.

PS monolayers on FTO glasses have been used to induce the hydrothermal growth of well-aligned ZnO nanowires for photovoltaic (PV) applications. Orientation of the nanowires has been checked by XRD and SEM. Nanosphere lithography is here clearly presented as a low-cost and powerful tool to manufacture wafer-scale, well-aligned, c-axis textured ZnO nanowire arrays with an increased accessible surface.

Moreover, controllable and reversible wetting properties (between superhydrophilicity and (super)hydrophobicity) are highly desirable for such metal oxide nanomaterials, particularly for the control of effective micro- or nano-fluid motion. Such a reversible surface wettability study has never been reported for templated ZnO nanowires and was therefore evaluated.
5. Thesis outline

The present thesis starts with this introduction (chapter I) and is then divided in two parts.

The first part is dedicated to the optimization of the colloidal mask. The development of the image analysis tool used for colloidal mask assessment is described in chapter II. The chapter III relates the preparation of the colloidal mask by spin coating. After a short overview of state of the art, a thorough description of the preparation of masks is discussed. Thanks to image analysis and statistical analysis, the key parameters affecting the quality of masks are highlighted.

The second part of the thesis is devoted to the description of the different nanostructures and their applications. Chapter IV deals with the magnetic nanostructures, which are morphologically, structurally and magnetically characterized.

The potentiality of using nanosphere lithography for the growth of well-aligned ZnO nanorod arrays is studied in chapter V.

Finally, some conclusions are drawn and some recommendations are made for future research works in chapter VI.
6. References

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