This chapter tends to predict the influence of the various spin coating parameters such as rotation speed or ramp time on the amount of defects in a colloidal crystal mask by a computerized image analysis tool of SEM micrographs from different samples.

The impact of surfactant concentration was also investigated as well as the use of an O$_2$ etching step to modify the masks.
CHAPTER III - Spin coating and experimental design ------------------------59

1. Introduction -------------------------------------------------------------61
   1.1 Static evaporation versus spin coating ------------------------------- 61
   1.2 Experimental design -------------------------------------------------- 65

2. Experimental part--------------------------------------------------------66
   2.1 Tuning of experimental set-up ---------------------------------------- 66
   2.2 Etching of the masks ------------------------------------------------- 68

3. Results and discussion -----------------------------------------------68
   3.1 Cleaning the substrate & composition of the suspension ------------- 68
   3.2 Experimental design ------------------------------------------------- 72
   3.3 Etching of the masks ------------------------------------------------- 82

4. Conclusions -------------------------------------------------------------86

5. Perspectives -------------------------------------------------------------87
   5.1 Increasing the coverage rate by increasing the deposited volume... --- 87
   5.2 Changing the nanosphere size ---------------------------------------- 87

6. References ---------------------------------------------------------------89
1. Introduction

In nanosphere lithography, self-assembled monolayers of colloidal spheres are either used as a masking layer for etching the substrate underneath the particle mask or for selective deposition/growth of additional structured layers, which is the configuration we opted for throughout this work.

Ever since the second half of the 20th century, the production of monodispersed colloidal spheres (e.g. polystyrene (PS) or poly(methyl methacrylate) (PMMA)) has been a major goal of colloid science and as it is already well established on the market,[1, 2] we focused our work on the preparation of the masks.

Three dimensional (3D) colloidal crystals have been extensively studied due to their potential applications as diffractive optical devices,[3] chemical and bio-sensors,[4] or photonic crystals.[5-9]

In general, the preparation of these multilayer PS beads is much more facile than that of a uniform monolayer, but is not in the scope of this study.

The first description of 2D arrays formation from colloidal particles was reported by Perrin[10] in his work on determining the Avogadro number. Hayahsi et al.[11] investigated imaging by particles of polystyrene latexes. Those studies present observation of the final result of ordering, without considering the forces governing the ordering.

We focused our work on the preparation of two-dimensional (2D) masks.

Several methods exist for the formation of the self-organized particles monolayers such as the Langmuir-Blodgett technique,[12, 13] controlled evaporation of solvent from a suspension containing latex particles,[14-17] floating-transferring technique,[18] convective self-assembly,[19, 20] dip coating[21, 22] or spin coating.[23] In chapter I, we briefly described these techniques highlighting their respective advantages and drawbacks as potential mass production tools. Thanks to its rapid implementation and its compatibility with wafer-scale processes, the spin coating appeared to be a technique of choice.

Before going into deeper details on spin coating, let’s take a closer look at processes occurring during evaporation of colloidal suspensions.

1.1 Static evaporation versus spin coating

A droplet of a colloidal suspension (e.g. coffee drop) on a solid substrate tends to form ring-shaped deposits if the liquid evaporates (Figure III - 1 (a)). The phenomenon is due to a convective flux of the liquid in the droplet that transports the solute to the rim of the droplet. Indeed, the probability of a liquid molecule to escape the droplet is higher at the rim of the droplet than in the center.

Two situations may arise during evaporation of the liquid.
First, if all the liquid is evaporated at the edge of the droplet the contact line is shifted toward to the center (Figure III - 1 (b)). In the second case, due to surface irregularities and later due to solute deposition the contact line is pinned to the substrate, i.e. it cannot move (Figure III - 1 (c)). Therefore the evaporated liquid has to be replaced by a flux from the center to the edge of the droplet. This flux is called convective flux and it is carrying the dispersed solutes to the rim where the ‘coffee ring’ forms.

Deegan et al.\textsuperscript{[24]} studied the formation of such ring-stain deposits in drying drops containing dispersed solids. They ascribed the characteristic pattern of the deposition to a form of capillary flow in which pinning of the contact line of the drying drop ensures that liquid evaporating from the edge is replenished by liquid from the interior.

![Figure III - 1](image)

\textbf{Figure III - 1}

\textit{Static evaporation of a drop}

(a) Micrograph of a coffee stain. The dark perimeter is due to an accumulation of coffee particles. The radius is approximately 5 cm.

(b) & (c) Schematic illustrations of an evaporating drop. The solid (resp. dashed) line represents the air-liquid interface before (resp. after) evaporation of the corresponding hashed layer. If the contact line is not pinned (b), uniform evaporation removes the hashed layer and the diameter of the drop decreases. However, if the contact line is pinned (c), the retreat of the drop is not possible. The length of the red arrows indicates the spatial variation in the evaporation rate, while the grey arrows represent the convective flux. The colloidal particles are then pushed toward the rim of the drop.\textsuperscript{[25]}

Nagayama and co-workers\textsuperscript{[26, 27]} focused their research on the understanding of interactions between colloidal nanospheres, which force them to organize into a 2D HCP array on a solid substrate or in thin films of liquids.

Following the self-organization process under evaporation by using an optical microscope, they proposed a two-step mechanism for the formation of the array.

First, a nucleus\textsuperscript{*} is formed when the thickness of the liquid layer approaches the diameter of the colloids. As theoretically shown by Krachelsky et al.\textsuperscript{[28]} interparticle capillary forces (F\textsubscript{c}) arise between spherical particles which are partially immersed in a liquid on a horizontal solid substrate.

\*A nucleus is an ordered region that consists of a small number of colloidal particles.
As the liquid film becomes thinner, the liquid surface deformation increases giving rise to increased capillary forces.

The second step begins with the motion of more colloids that are driven toward the nucleus. The horizontal component of the capillary was first thought to be a reason for this motion: the particles in the nucleus attract the nearest ones causing a driving flux. However, the particles in the ordered regions are surrounded by a concave liquid layer whose thickness is far larger than the particle diameter (Figure III - 2).

Hence, the particles totally immersed in this layer are not subjected to capillary forces. The particle motion was then attributed to a convective solvent flux \((J_S)\), which compensates the evaporated solvent in the already ordered array, hence dragging particles suspended in the thicker layers towards the thinner regions due to a hydrodynamic force \((F_d)\). The newcomers remain attached to the domains, pressed by the hydrodynamic pressure of the water and captured by capillary forces.

Those forces acting on the colloidal particles may be influenced by many factors such as the presence of surfactant, charge on the surface (i.e. type and surface density of functionalities on the particles).

Parameters such as temperature\(^{[19]}\) or concentration\(^{[29]}\) have been proved to have a significant impact on the evaporation rate for a given colloidal deposition process.

Dislocations, vacancies, other structural defects and small monolayer areas are numerous problems which scientists are confronted to in the formation of the 2D self-organized colloidal crystal mask.

The evaporation of solvent can be accelerated by carefully spin coating the colloidal suspension onto a solid substrate.

Spin coating is a well-established technique in microfabrication to form highly uniform thin films with adjustable thickness over large area.\(^{[8, 30]}\) Timescales that characterize spin coating of colloidal suspensions are shown to be quite different from those that characterize spin coating of polymer suspensions.\(^{[31]}\)
As for static evaporation, a flat, clean, and chemically homogeneous surface are of course necessary parameters to generate a highly ordered array with relatively large domain sizes.

A spin coating process is usually composed of four distinct stages. In the first one, a drop a colloidal suspension is deposited onto a fixed substrate. The substrate is then accelerated to a certain rotational speed in the second step and the liquid droplet spreads out to cover the whole substrate. In the third stage, the film thins due to equilibrium between centrifugal force and viscous shear force. Finally, evaporation dominates in the fourth stage, where the film thickness reduces to the same order as particle size, at which capillary forces have a significant impact on particle aggregation. The transition between the third and fourth stage depends notably on the volatility of the solvent.

Traditional spin coating is based on the use of volatile solvents (e.g. water or alcohol) to disperse colloidal particles, which may result in a rapid freezing of the system. In order to give enough time to the particles to organize into energetically favorable states, Jiang et al.[8, 32] recently reported the use of non volatile solvents (i.e. monomer), which led to a non-close-packed colloidal crystal embedded in a polymer matrix. The selective removal of the matrix can be performed by dry etching, without affecting the colloidal crystal. However, the non-close-packed structure of the mask is not suitable for the synthesis of isolated nanodot arrays.

A number of computational and theoretical studies exist for non particulate films of precise thickness during spin coating, starting with the classic work of Emslie et al.[35] However, for the spin coating of colloidal suspensions, so far empiricism mainly ruled the world of nanoparticles self-organization by spin coating and much of the literature is experimentally based.

Even if recent papers are more detailed,[36] spin coating protocols described in the literature are varied and most of the time imprecise.[37-39] Recent computational study by Zhao et al.[40] over spin coating of a colloidal suspension revealed that once the particles touched the substrate, they remained there due to the strong adhesive force and small radial velocity close to the bottom of the film. In order to obtain a uniform monolayer, it is therefore desirable that there exists an electrostatic repulsion between the colloidal spheres and the solid substrate.

Most researchers give a rough idea of the size of the monolayer areas, ignoring most of the time the presence of small defects and usually emphasizing on a perfect structure rather than on deviation. Moreover the wide diversity in the size of particles does not facilitate comparisons. For example, Spada et al.[41] announced homogeneous bidimensional colloidal mask (496 nm diameter PS nanosphere) reaching areas up to 0.5 cm². However, many defects were present in the monolayer and we estimated the defect-free area to ≈ 80 μm². For their part, Brown et al.[42] hardly reached defect-free areas of ≈ 30 μm² for particles of similar sizes.
The development of experimental protocols to control the ordering of particles on solid substrates and to get large well-ordered structures is therefore a major goal for further progress in NSL.

Moreover, as it was shown in chapter I (Figure I - 4 & Figure I - 19), the control of the interstitial structure of the colloidal masks is a key factor in NSL manufacturing, as the void areas between the self-organized nanospheres act as channels for material deposition.

Reduction of the PS nanospheres diameters\textsuperscript{[43]} or correction of the deformation of ‘soft’ PS nanospheres\textsuperscript{[44]} has been reported in the literature through the use of an oxygen plasma etching treatment. Depending on the degree of etching, various nanostructures, such as discrete nanodots or anti-hole patterns\textsuperscript{[45]}, were synthesized after the deposition of a desired material through the etched colloidal masks. Simultaneous etching of the substrate (glass, silicon) has also been studied by combining oxygen with fluorinated gazes.\textsuperscript{[13]}

In our study, the use of an O\textsubscript{2} etching step was necessary to remove excess of surfactant closing the void areas.

### 1.2 Experimental design

As shown in Figure III - 3, no less than ten parameters (RPM\textsubscript{i}, TIME\textsubscript{i} and RAMP\textsubscript{j}) are required to set a spin coating protocol with our equipment. Moreover, the inherent parameters of the colloidal suspension (concentration, surfactant etc.) are added to the list.

![Figure III - 3](image)

A typical spin coating cycle composed of three plates.

Since a detailed study is difficult to carry out due to the large number of parameters, we turned to experimental design in an attempt to extract the influence of the spin coating parameters on the amount of defects in the prepared colloidal masks.

Indeed, experimental design is traditionally used to plan experiments in order to extract the maximum of information from the collected data in the presence of noise, in the fewest number of experimental runs. The basic idea is to vary all relevant factors.
(inputs) simultaneously over a set of planned experiments and then measure the responses (outputs). Experimental data are used to derive an empirical (approximation) model linking the outputs and inputs. This mathematical model is then used for interpretation, predictions and optimization.

To our knowledge, no experience of this type has yet been reported in the literature.

2. Experimental part

2.1 Tuning of experimental set-up

All manipulations were performed in a Class-100 clean room at constant temperature and humidity (50 % RH) so as to minimize external contaminations or physical perturbation.

Monodisperse PS nanospheres with a mean diameter of 490 nm (polydispersity less than 5 %) were purchased from Bangs Laboratory as suspensions in water (concentration of about 10 % wt). We checked their diameter by dynamic light scattering.

Previous to spheres deposition, circular quartz substrates (Crystal Gmbh) were cleaned following procedure described in many papers.[46, 47] The aim is to obtain a hydrophilic surface. Each substrate was separately cleaned by immersing in a piranha solution† (1:3 30% H₂O₂/H₂SO₄) and sonicated for 1h.

† Piranha solution can be explosive. Mixing the solution is exothermic. The resultant heat can bring solution temperatures up to 120°C. The sudden increase in temperature can also lead to violent boiling, or even splashing of the extremely acidic solution. Also, explosions may occur if the peroxide solution concentration is more than 50%.
We rinsed the substrates repeatedly with ultrapure water (18.2 MΩ, Millipore simplicity) and then sonicated for 1h in 5:1:1 H₂O (MilliQ)/NH₄OH/30% H₂O₂. Finally, the substrates were copiously rinsed with water and stored in water (no longer than one week) until used. Before deposition of the colloidal suspension, the substrates were flash-air dried at room temperature. We studied the wettability by contact angle measurements of the colloidal suspensions on the quartz substrates. We performed the measurements in the GRASP laboratory (University of Liege) using a CAM 200 Optical Contact Angle (KSV Instruments Ltd.) and the CAM 200 software provided with the instrument.

We first tried to use the as-received commercial suspensions but due to lack of wettability we diluted them in a surfactant Triton X-100/methanol mixture (1:400 by volume). We also investigated the impact of surfactant concentration.

The spin coating of the beads suspension onto the substrate was performed on Spin-coater P-6708 (SCS) following a three-steps scheme (Figure III - 3): RAMP_i stands for the time to reach the required speed RPM_i with i = 1 to 3. Those parameters have to be set according to the conditions RPM_3 > RPM_2 > RPM_1 and in the ranges RPM_1 < 2000 rpm, RPM_2 < 4000 rpm and RPM_3 < 8000 rpm.

A set of twenty experiments was generated by MODDE software (Umetrics), which is commonly used for experimental design. In this study, all ramp times (RAMP_i) were taken equal to each other within an experiment, and spinning rates RPM_i were maintained for 2 seconds. The discrete parameter values of each experiment will be detailed in section 3.2.

Before deposition, the suspension was filtered through centrifugal filter units (porosity 0.65 μm) in order to eliminate aggregates of higher dimension, which would definitely disturb the formation of the monolayer. A defined volume (17 μL), determined by preliminary calculations, was delivered using an Eppendorf pipette. We paid careful attention in the preparation of the samples by designing specific substrate holder in order to center the deposition of drop.

We analyzed the samples by scanning electron microscopy (SEM) analyses on a FEG-ESEM XL30 (FEI) with an accelerating voltage of 15 kV under high vacuum. All samples were gold-coated (60 s) before observation.

To improve sampling, fourteen SEM pictures were taken on each sample, starting from center and moving towards the edge of the substrate. The SEM pictures were taken at 4000 x magnification (cfr. Chapter II).

Thanks to our program developed in chapter II, we then quantified the order in the colloidal masks. As a quantification index of order in hexagonal compact packing (HCP), the image analysis consisted in measuring the percentage of beads in contact with six close neighboring beads. This digital output value is unambiguously the rate of HCP order in the PS layer and allowed a classification of samples in a less subjective way than a visual assessment.
The HCP percentage output data was subsequently used to perform a statistical study (Statistica) whose purpose is to link the sample quality to adequate spin coating parameters, highlighting which are determinants.

The twenty samples were synthesized in the same day. Repetitions were carried out on other days with freshly prepared suspensions to check repeatability.

2.2 Etching of the masks

To modify the shape and feature spacing of the PS latex nanospheres, we submitted the as-obtained masks to an oxygen plasma etching. The process was performed at the Liege Space Center (CSL).

The etching steps were performed under 300 W with a 50 sccm O₂ flow. We tested eight different etching times (0.5, 1, 1.5, 2, 3, 5, 7 & 9 min) on the masks prepared with the 490 nm diameter nanospheres, while the PS 250 nm masks were only etched during 0.5 min.

We measured the nanosphere diameters by scanning electron microscopy (SEM) on a FEG-ESEM XL30 (FEI) with an accelerating voltage of 15 kV under high vacuum. All samples were gold coated (60s) before observation.

We also studied the topography of the masks by atomic force microscopy (AFM) under ambient conditions using a Digital Instruments Nanoscope III microscope (Veeco). The image acquisition was performed in tapping mode with a high-aspect ratio probe.

3. Results and discussion

3.1 Cleaning the substrate & composition of the suspension

Based on our first deposits, we concluded that the complete wetting of the substrate surface by the colloidal suspension is a key point to obtain uniform and repeatable coatings (Figure III - 5).

![Figure III - 5](image)

**Importance of the complete wetting of the suspension**

Optical images of PS nanosphere (490 nm diameter) layers synthesized by spin coating on circular quartz substrates (15 mm diameter). Both samples were obtained by depositing an equal volume of suspension. On the left image, the drop did not wet the whole surface before starting the spin coating process. The arrow indicates the pinning line of the drop. On the right image, surface treatment of the substrate and various additives in the suspension allowed the drop to wet the substrate before the spin coating process. The iridescence of materials is due to interference between the incident light and the periodic arrangement of the PS nanospheres within the monolayer.
Indeed, we observed that the way the drop spreads on the substrate already tells us about the macroscopic final shape of the deposit. This is attributed to a competition between the hydrodynamic flow due to the drop velocity and the drying: drying accounts for particle agglomeration that pins the contact line whereas the liquid flow dilutes the agglomerated particles and allows the contact line to move forward continuously. Drying often occurs while the contact line of the liquid is advancing on the solid surface, causing the contact line to be temporarily pinned on the substrate, leading to a non-homogeneous deposition of colloid layer.

This behavior was also reported by Lima et al.\cite{48} who studied moving contact lines of drying colloidal suspension. They concluded to the appearance of two regimes. At high rotation speed and low colloid concentration, the contact line advances continuously with a contact angle very close to the one observed on a drop of pure water. At low rotation speed or large concentration, the contact line is pinned from time to time, and a stick-slip motion appears.

We therefore measured the contact angles of the commercial suspension on as-received and treated substrates (Figure III - 6).

![Figure III - 6](image_url)

**Figure III - 6**

*Influence of piranha-treatment on the wettability of colloidal suspension*

Contact angle measurements of the commercial colloidal suspension (PS nanospheres with 490 nm diameters) on (a) an as-received quartz substrate and on (b) a piranha-treated quartz substrate.

The cleaning treatment of the substrate obviously increased its hydrophilic character, resulting in the decrease of contact angle. Piranha solution is known as a strong oxidizer, which removes most organic matter and also hydroxylates most surfaces, thus increasing the number of silanol groups on the surface of quartz wafer.\cite{49}

However, even with the highest rotation speed, we didn’t manage to cover the whole substrate surface with the commercial suspension due to the previously described stick-slip motion of the drop. For repeatability reasons, we decided to improve the wetting by adding a surfactant instead of manually forcing the drop to spread.

We therefore diluted the aqueous PS suspension with a mixture of the non-ionic Triton X-100 surfactant in methanol (1/400 by volume). Triton X-100 is a nonionic surfactant with a hydrophilic polyethylene oxide group and a hydrophobic hydrocarbon group (para-(1,1,3,3-tetramethylbutyl)-phenyl group).
The surfactant Triton X-100 adsorbs at the latex surface; the hydrophobic part adsorbs on the PS bead and the hydrophilic PEO part extends into the aqueous phase, which leads to a steric stabilization of the suspension. The presence of methanol in the diluting mixture increases the evaporation rate of the suspension.

The contact angles measurements of the commercial colloidal suspension diluted in various amounts of the mixture Triton X-100/methanol are presented in Figure III - 7. The increasing concentration in surfactant resulted in increasing wettability of the suspension.

When the volume fraction of the commercial suspension was lower than 0.5, the drop almost instantly covered the substrate and hence the contact angles were impossible to measure. We assimilated those values to a contact angle of zero degree.

To ensure a complete wetting of the colloidal suspension, we decided to work far beyond this critical threshold and diluted the commercial suspension by a factor of 10 (volumic fraction = 0.1).

![Contact angle measurements of the commercial colloidal suspension for various dilutions in a Triton X-100/methanol mixture (1:400 by volume) on piranha-treated quartz substrates.]

We then studied the influence of the concentration of the surfactant in the diluting mixture. The micrographs, presented in Figure III - 8, show that the addition of surfactant is very important to increase the size of the HCP domains.

Those results indicate that the adsorption of surfactant molecules on the surface of the PS beads improve the self-organization of the system. On the contrary, the lack of surfactant in the diluting mixture leads to a lack of organization and to low density of spheres deposited on the substrate (Figure III - 8 (a)).
Figure III - 8

Influence of the concentration of surfactant in the diluting mixture
(a) No surfactant, (b) Surfactant: MeOH (V/V) 1:800, (c) Surfactant : MeOH (v/v) 1:400. The inset is a magnified view. Main scale bars and inset scale bars are respectively 5 μm and 500 nm.
According to Pillai and al.,\cite{52} the neutrally charged Triton X-100 adsorbed to the particle surface moderates particle-particle interactions and particle-substrate surface interaction which is necessary to obtain a uniform monolayer.\cite{2} However, when observed at higher magnification (see insets), the monolayers prepared at high concentration of surfactant (Figure III - 8 (c)) are not suitable for the sputtering step since the voids between the beads are filled by a continuous smooth phase.

We attributed it to an excess of surfactant that fills the empty spaces between the beads upon evaporation of the solvent. Nevertheless, a compromise has to be found between the organization degree of the monolayer and the accessibility of the voids when used as a mask.

An alternative is to submit the well-ordered mask prepared at high surfactant concentration to an etching step by reactive O₂ plasma etching, in order to remove the excess surfactant and free the access to the substrate. This step will be discussed in section 3.3.

### 3.2 Experimental design

The spin coating parameters of each experiment and the corresponding output values (total number of nanospheres, % HCP and % occupied surface) calculated with our program are summarized in Table III-1.

We tested twice the repeatability of our process on experiments 2 and 10, which gave the highest percentage of HCP packing. We obtained less than one percent deviation on the percentage of hexacoordinated nanospheres. However, the total number of nanospheres presented a significant deviation, which of course affected the proportion of occupied surface in the analyzed area.

The samples with the highest hcp order (2 & 10) are characterized by low covering percentage. According to Zhao et al.,\cite{40} this could be due to the strong adhesive force between the particles and the substrate, which therefore remain trapped to the substrate when they touched it. It is tempting to consider the selected spin coating parameters applied to suspensions with higher concentrations to increase coverage.

However, as described by Prevo et al.,\cite{29} the evaporation rate must be increased accordingly to avoid the formation of multilayers. Moreover, the modification of suspension composition is known to impact significantly the wetting of the substrate, which is a key point in early stages of the process.\cite{2,52} Consequently, such modification of solution would imply a complete revision of spin coating parameters.

We therefore decided to choose the % HCP as the output value to find out any correlation with the spin coating parameters.
### Table III - 1

Spin coating parameters of the experiments generated by the experimental design program and the corresponding HCP percentage given by our program. Monolayer samples were obtained in the experiments circled in red.

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<th>RPM2 (rpm)</th>
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Regarding the organization of the nanospheres in the different experiments, we obtained many different results such as multilayers or monolayers with small or large HCP well-ordered domain sizes. Typical SEM pictures are presented in Figure III - 9. We only obtained monolayer in six of the twenty samples (circled in red in Table III - 1).

For multilayer samples, square lattices were systematically observed in the nanospheres arrangements. According to Prevo et al.,\cite{20, 29} the packing of the PS nanospheres in a hexagonal or square lattice is due to a balance between thermodynamics (which aims to reduce the surface energy by packing the beads in a way to maximize the contacts between them) and the geometric arrangement of PS beads in the drying liquid film. Square lattices, considered as metastable transition states to the hexagonal lattices, could result from a quick drying step.\cite{53}

The highest percentage of HCP order (73 %) was observed for experiments 2 and 10. In these experiments, we obtained large totally defect-free HCP areas of $\approx 200 \mu m^2$, which is very good compared with literature.

Looking closer at Table III - 1, all parameters are similar except the rotation speed of the third step (RPM3). Ramp time and RPM1 have a respectively low (3 s) and high ($\sim 2000$ rpm) value, which means that the high rotation speed is reached in a short time. The RPM2 value is slightly higher than RPM1. On the opposite, the smallest percentage of HCP (10 %) is obtained for experiment 14, characterized by a median value of Ramp time (12 s), a rather low value of RPM1 (580 rpm) and an equal value of RPM2 and RPM3 (2500 rpm).

From this point of view, it is tempting to conclude that an increase of Ramp Time and a sharp decrease of RPM1 lead to a decrease in the order. However, regarding experiment 7 with a high Ramp Time (30 s) and low value of RPM1 (760 rpm), the percentage of HCP is not that bad (56 %). Therefore, a combination of a small Ramp Time and high RPM1 is not sufficient to explain a high percentage of hcp order in the sample.
Figure III - 9
2D or 3D organization of PS nanospheres
Typical SEM micrographs of organized PS nanospheres showing in (a) Large HCP area, (b) Small HCP area and (c) multilayers. Scale bars are 5 µm.
By plotting the acceleration of the three steps in each experiment (Figure III - 10), experiments 2 and 10 clearly stand out, presenting very high acceleration times in steps 1 & 3 compared with the other experiments. This could be a reason to explain the large difference with the other experiments.

![Acceleration profile of the three spin coating steps in each experiment](image)

As it was rather difficult to draw general conclusions on how the spin coating parameters influence the percentage of HCP order by just taking a look at the table, we subjected the set of data to a statistical analysis.

First, we tried to identify separately any linear correlation between the % HCP and each factor (RAMP, RPM1, RPM2 & RPM3). Unfortunately, as seen from the low $R^2$ values in the linear regressions (Figure III - 11), we didn’t evidence any obvious correlation between the output value and any of the inputs.

Traditionally, multiple linear regression (MLR) is used to predict some response properties from a set of independent variables, but the multiple linear regression methodology yields imprecise predictions when the independent variables are correlated.

We therefore selected the partial least square regression (PLS) method, which overcomes some of these numeric problems since it first extracts uncorrelated factors, and works from there.
Is there a linear correlation between the % HCP and the various inputs?

PLS regression replaces the initial space of the (many) regressors by a low-dimensionality space spanned by a small number of variables called "factors". Factors are built iteratively. They will then be the new regressors of classical linear regression model. Factors are orthogonal (uncorrelated), and are linear combinations of the original regressors. In this respect, they are therefore similar to Principal Components (PC) of Principal Component Analysis (PCA). But while PCs are determined by regressors only (with no reference to the response variable $y$), identifying the factors of PLS involves taking into consideration each factor’s individual usefulness in predicting % HCP by maximizing its correlation with % HCP while maintaining the constraint of being orthogonal to the previously determined factors.

Based on the PLS regression on all experiments, the program generated predicted values for the parameters of our twenty experiments.

Unfortunately, the measured (observed) % HCP values did not agree with the predicted ones (Figure III - 12) and a large deviation was observed.

We have been looking for reasons to explain those results and we concluded that the presence of multilayered samples in the twenty experiments could disrupt the modeling procedure.

Hence, we performed another PLS regression analysis only on the monolayer samples. This time, the predicted and measured values agree (Figure III - 13).
**Figure III - 12**

**PLS regression on all experiments**

Comparison between measured (observed) % HCP values and the values predicted by the PLS regression.

**Figure III - 13**

**PLS regression on monolayer samples**

Comparison between measured (observed) % HCP values and the values predicted by the PLS regression.
In order to judge the predictive power of our model, we generated five new experiments (with equal ramp times) and asked to the model the expected % HCP values. Although all samples were composed of monolayers, a quite large deviation (up to 20 %) was observed between predicted and measured values (Table III - 2).

<table>
<thead>
<tr>
<th>Experiment N°</th>
<th>RAMP (s)</th>
<th>RPM1 (rpm)</th>
<th>RPM2 (rpm)</th>
<th>RPM3 (rpm)</th>
<th>% HCP PREDICTED</th>
<th>% HCP MEASURED</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>3</td>
<td>1930</td>
<td>4000</td>
<td>6900</td>
<td>59</td>
<td>61</td>
</tr>
<tr>
<td>P2</td>
<td>3</td>
<td>1200</td>
<td>1770</td>
<td>6170</td>
<td>74</td>
<td>54</td>
</tr>
<tr>
<td>P3</td>
<td>3</td>
<td>1200</td>
<td>3270</td>
<td>6170</td>
<td>70</td>
<td>49</td>
</tr>
<tr>
<td>P4</td>
<td>3</td>
<td>1930</td>
<td>3130</td>
<td>7530</td>
<td>71</td>
<td>61</td>
</tr>
<tr>
<td>P5</td>
<td>3</td>
<td>1930</td>
<td>3130</td>
<td>6030</td>
<td>69</td>
<td>51</td>
</tr>
</tbody>
</table>

This could be due to the fact that our model is based on a very small amount of experiments.

In order to improve the model, we would suggest making many more experiments and to directly remove the multilayer samples from the regression. Moreover, the acquisition of high-resolution micrographs could also allow increasing the size of the analyzed area. Finally, the fact that the RPM values are in a way linked to each other due to the inherent constraints of the apparatus may annihilate any chance of modeling their impact on the organization of the nanospheres.

Still in an attempt to find out any relation between the % HCP and the spin coating parameters, we submitted the results to the Principal Component Analysis\(^{[54]}\) (PCA). PCA is recommended as an exploratory tool to uncover unknown trends in the data.

Basically, the PCA is based on a mathematical process that aims to reduce the dimensionality of a problem while trying to minimize the loss of information (maximize the explained variance). The analysis seeks to replace a family of variables by new variables (principal components) of maximum variance, which are linear combinations of original variables.

The number of components extracted in a principal component analysis is equal to the number of observed variables being analyzed.

The first component extracted in a PCA accounts for a maximal amount of total variance in the observed variables. Under typical conditions, this means that the first component will be correlated with at least some of the observed variables. It may be correlated with many.
The second component extracted will account for a maximal amount of variance in the data set that was not accounted for by the first component. Again under typical conditions, this means that the second component will be correlated with some of the observed variables that did not display strong correlations with component 1.

In general, you expect that only the first few components will account for meaningful amounts of variance, and that the later components will tend to account for only trivial variance.

The choice to retain only the first two components is based on the Kaiser criterion. An eigenvalue represents the amount of variance that is accounted for by a given component. The rationale for this criterion is straightforward. Each observed variable contributes one unit of variance to the total variance in the data set. Any component that displays an eigenvalue greater than 1.00 is accounting for a greater amount of variance than had been contributed by one variable. Such a component is therefore accounting for a meaningful amount of variance, and is worthy of being retained.

First, we performed PCA on all the experiments and then we repeated the operation on the monolayer samples.

Figure III - 14 & Figure III - 15 represent the projections of the different parameters in the plane of the two first components.

The angle between two variables, measured by its cosine, is equal to the linear correlation coefficient between 2 variables. Therefore, the variables that are pointing in the same (opposite) direction are correlated positively (negatively), while perpendicular oriented variables are uncorrelated. Moreover, the closer a variable is to the circle of correlations, the more weight it has to explain the variability described by the first two PC's.

As expected, the cumulated variance explained by the two first components is higher when the analysis is performed on the monolayer samples (≅ 91 %) than on all samples (≅ 60 %).

The analysis of the first component in Figure III - 14 shows that the weight is well distributed on all variables.

We noticed that the variable RAMP is diametrically opposed to the % HCP, which means that a low value of RAMP is required to achieve high values of hcp organization.

As the percentage of HCP and RPM1 are pointing in the same direction (with a cosine near from 1), it can be concluded that they are strongly positively correlated, which means that a high value of RPM1 leads to a high percentage of organization. The fact that the parameter RPM2 is orthogonally oriented relative to % HCP suggests that it has no impact on the HCP order. These results correspond to the observations made in Figure III - 10 about the influence of RPM1 & & 3 on the % HCP.
In the PCA performed on monolayer samples (Figure III - 15), the first component is mainly composed of contributions due to RPM1 and RAMP variables, while most of the weight in the second PC is distributed on RPM2 and RPM3.
The strong positive (resp. negative) correlation between RPM1 (resp. RAMP), already suspected in Figure III - 14, is here confirmed.

These results agree with studies on spin coating of colloidal suspensions\cite{31,32} and are highly valuable as the conclusion is here reached through a statistical analysis.

The onset of ordering process coincides with the moment when the thickness of the liquid layer becomes smaller than the particle diameter.\cite{56}

As theoretically shown by Kralchevsky et al.,\cite{28} interparticle capillary forces arise between spherical particles, which are partially immersed in a liquid on a horizontal solid substrate. As the liquid becomes thinner, the liquid surface deformation increases giving rise to increased capillary forces. The next step begins with the motion of more colloids that are driven toward the nucleus and is attributed to a convective flux, which compensates the evaporated solvent in the already ordered array, hence dragging particles suspended in the thicker layers towards the thinner regions. The newcomers remain attached to the domains, pressed by a hydrodynamic pressure and captured by capillary forces.

The ordering is therefore highly related to the thickness of the evaporating film. The film thickness has been demonstrated to be inversely proportional to the spin speed,\cite{32,57} which corroborates our results. Moreover, Rehg et al.,\cite{31} and Dushkin et al.,\cite{58} both concluded that rapid evaporation rates is better at assembling more uniform monolayers and colloidal crystals. Our results confirm that the first acceleration in the spin coating process is the critical parameter to reach high % hcp.

### 3.3 Etching of the masks

In order to free the access to substrate, we subjected the polystyrene masks to an oxygen plasma etching during different times. The process affected the diameter of the nanospheres but not their 2D organization.

We observed a linear decrease of the nanosphere diameter versus the etching time (Figure III - 16).

SEM and AFM micrographs (Figure III - 17) show the evolution of the topography of the PS nanospheres.

Half a minute etching was enough to remove the surfactant while keeping not connected voids, which is crucial to use the masks to synthesize well-defined nanodots.

After 7 min, the shape of the nanospheres was no longer spherical but had changed to a hexagonal structure. The contrast in the SEM micrograph and the 3D AFM view highlighted a larger amount of material at the edges of the particles.

Only a ring-like structure persisted on the substrate after 9 min etching.
We would like to attract the reader’s attention on the shape evolution depicted on the AFM views. Indeed, from 0.5 to 3 min etching times, we cannot observe any significant difference between the 2D views.

On the other hand, the 3D views suggest an erosion of the nanopsheres due to a darker contrast around the particles.

For longer etching times, we did not observe any difference between the SEM and AFM micrographs. This was attributed to a convolution between the shape of the tip and the topography of the sample, which affects the apparent topography of the sample. This is clearly an artifact due to finite size of the tip.

After 1.5 min, some links persisted between the nanospheres but they were no longer present after 3 min. Those isolated nanospheres could therefore be used for the production of hole patterned films.

![Graph](image)

**Figure III - 16**

**O₂ plasma etching of PS colloidal masks**

Decrease of the diameter of PS nanospheres under O₂ plasma etching during various times.
CHAPTER III
Spin coating and experimental design
Figure III - 17

O$_2$ plasma etching of polystyrene masks (original diameter 490 nm)
SEM and AFM (2D & 3D) of the nanospheres. SEM and AFM scale bars are 500 nm. The z-scale of the 3D AFM view is 500 nm.
4. Conclusions

First of all, we evidenced the importance of the wetting properties (chemical treatment of the substrate as well as the addition of a surfactant in the suspension) to get homogeneous deposits.

The tuning of the surfactant concentration allowed to increase the size of HCP domains but resulted in closing the voids between the nanospheres.

However, we succeeded in creating a controlled O\textsubscript{2} etching process so that the surfactant in excess could be sputtered away, while keeping the nanospheres in close contact. This is of critical importance to use the masks for the synthesis of separated nanodots.

Moreover by increasing the etching times, we obtained isolated nanospheres that could be used to synthesize connected architectures.

In an attempt to model the influence of the various spin coating parameters (RAMP, RPM\textsubscript{1}, RPM\textsubscript{2} and RPM\textsubscript{3}) on the 2D HCP order, twenty experiments were generated by experimental design.

Thanks to our homemade image analysis program tuned in chapter II, we calculated the percentage of hexacoordinated nanospheres and very small deviation (1 %) in the repetition experiments.

As no direct linear correlation was found between the % HCP and the spin coating parameters, we proceeded to a PLS regression on the results.

However, the predicted % HCP values did not agree with the measured ones (deviation up to 20 %). We therefore decided to run another PLS regression but only on the experiments, which gave monolayers (6 out of the 20). Predicted and measured did agree pretty well. Unfortunately, the predictability of our model proved to be unsatisfactory.

Nevertheless, in an attempt to find out any trend, we performed a principal component analysis on the results.

The explained variance reached 91 % (resp. 60 %) when the analysis was performed on the monolayer samples (resp. on all samples). In both cases, PCA highlighted that the percentage of HCP order was respectively positively and negatively correlated to the ramp time and RPM\textsubscript{1}. That means that to get large HCP well-ordered areas, we had to quickly spincoat the suspension at high rotation speed. These results agree with studies on spin coating of colloidal suspensions\textsuperscript{[31, 32]} and are highly valuable as the conclusion is here reached through a statistical analysis.

Finally, we identified adequate spin coating parameters to synthesize large HCP domains. We obtained large defect-free areas reaching up to 200 \SI{}{\mu m^2}, which is the largest defect-free area reported so far for samples prepared by spin coating.
5. Perspectives

The colloidal crystal masks developed in this study present very interesting features for various applications. At this point, they present the following characteristics:

- Deposition technique: spin coating on quartz substrate;
- Substrate coverage: around 40 %;
- Maximum size of defect-free hexagonal domain: \( \sim 200 \ \mu m^2 \).

While already fairly optimized, we consider that new sets of experimental conditions are worth testing. Some of them are presented hereafter.

5.1 Increasing the coverage rate by increasing the deposited volume...

As we noticed in Table III - 1, the proportion of occupied surface in experiments 2 and 10 is not quite large and it would be interesting to increase it.

For this purpose, we decided to increase the deposited volume (from 30 to 100 \( \mu \)L) without modifying the others parameters. The resulting coatings show no apparent modification of the size of HCP domains, but we did not submit them to quantification by image analysis.

Besides this one-step procedure, we also tested sequential procedure by depositing twice 50 \( \mu \)L onto the substrate. Surprisingly, the nanospheres preferably assembled in the non-covered areas and hence monolayers were predominant in the sample. We do not observe any increase of the multilayering phenomenon.

Another route consists in increasing the nanospheres concentration in the colloidal suspension. We prepared such colloidal masks from suspensions exhibiting the requested wettability (Figure III-7). Those templates will be used and described in chapter V, which is dedicated to the synthesis of ZnO nanowire arrays.

5.2 Changing the nanosphere size

The size of the nanodots synthesized by NSL is directly dependent of the size of the PS nanospheres in the colloidal masks.

In order to study the magnetic properties (Chapter IV) of different sized dots, we synthesized colloidal masks with 250 nm diameter PS nanospheres. We selected the spin coating parameters of experiment 2 in Table III - 1, which gave the highest HCP order for the 490 nm PS nanospheres.

We didn't proceed to quantification of order in theses samples. This would require the acquisition of high magnification SEM micrographs in order to ensure that enough pixels account for the nanospheres. This would also need some fine-tuning in our program.
However, the SEM micrographs revealed that the domain size of the ordered region decreased with the dimension of colloidal spheres (Figure III - 18). We also proceeded to an O₂ etching step (0.5 min) on these templates to remove the surfactant present in the voids between the nanospheres. The nanostructures obtained with these templates will be presented in chapter IV.

![Figure III - 18](image)

SEM micrograph of colloidal mask with (a) 490 nm and (b) 250 nm diameter PS nanospheres obtained by spin coating. The scale bars are 5 μm.
6. References


