Fabricating Large Area Electrospray Devices

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by
Jordi Vives Martorell

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Advisor:
Sandra Bermejo Broto

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Abstract

Nanofabrication is a developing field which covers applications such as optics, energy harvesting, biology, among others. The use of different nanofabrication techniques consequently becomes an emerging research field of interest. In this project we are working with a technology designed to control the deposition and layer formation of nanospheres called electrospray.

The electrospray technique is based on depositing an aqueous solution with nanospheres, which are pumped and conducted to a sample affected by an electric field. Electrospray appears as a novel fabrication down-up technique developed by the MNT group to work in areas of $2cm^2$, which is highly promising compared to the areas reached with other technologies found in the literature, such as Vertical deposit. In areas of these dimensions, we are capable of building high quality 3D ordered structures, such as colloidal crystals. However, these $cm^2$ area is not enough to be used in large area devices such as solar cells or other optic devices.

Thus, the aim of this project is to enlarge the area maintaining an acceptable time-quality trade-off while constructing 3D ordered devices. This work shows that modifying the traditional electrospray set-up by adding a guard or directly using a multineedle approach leads to a considerable increase in the area, obtaining more than 10 times its previous size. The materials used for the laboratory testing and characterization were 295nm diameter polystyrene nanospheres and off-the-shelf materials.

To analyse the quality of the colloidal crystal obtained, a Scanning Electron Microscope was used to visualise the 3D structure of the sample. More than 10 monolayers of thickness were observed as well as a ordered 3D structure, thus verifying the project’s new electrospray set-up viability.
Abstract

La nanofabricación es un campo de estudio que cubre aplicaciones como óptica, energías renovables, biología, entre otros. El uso de diferentes técnicas de nanofabricación se convierte entonces en un campo de investigación de interés. En este proyecto trabajamos con una tecnología diseñada para controlar el depósito y la formación de capas de nanoesferas llamada electrospray.

La técnica del electrospray se basa en depositar una solución acuosa con nanoesferas, las cuales son bombeadas y conducidas hacia la muestra viéndose afectadas por un campo eléctrico. El electrospray surge como una novedosa técnica de fabricación down-up desarrollada por el departamento MNT con áreas de trabajo de $2cm^2$, lo cual es muy prometedor en comparación con otras tecnologías encontradas en la literatura, como Vertical deposit. En áreas de estas dimensiones, somos capaces de construir estructuras ordenadas 3D de alta calidad, como colloidal crystals. Aún así, estos $cm^2$ de área no son suficientes para ser usados en dispositivos de gran área como células solares u otros dispositivos ópticos.

El objetivo de este proyecto es aumentar dicho área, manteniendo una relación tiempo-calidad aceptable, permitiendo la construcción de estructuras 3D ordenadas. En este trabajo mostramos cómo se modifica el electrospray tradicional añadiendo una guarda o directamente utilizando varias agujas, lo cual mejora considerablemente el área, multiplicando en más de 10 veces su tamaño anterior. Los materiales usados en el laboratorio para testeo y caracterización fueron nanoesferas de poliestireno de 295nm de diámetro y materiales off-the-shelf.

Por tal de analizar la calidad del colloidal crystal obtenido, un Microscopio de escaneo por electrones fue utilizado para visualizar la estructura 3D de las muestras. Se observaron más de 10 monocapas de ancho, así como una estructura 3D ordenada, verificándose así la viabilidad del nuevo tipo de electrospray.
Abstract

La nanofabricació és un camp d’estudi que cobreix aplicacions com l’òptica, energies renovables, biologia, entre d’altres. L’ús de diferents tècniques de nanofabricació és converteix llavors en un camp d’investigació d’interès. En aquest projecte treballem amb una tecnologia dissenyada per controlar el depòsit i la formació de capes de nanoesferes anomenada electrospray.

La tècnica de l’electrospray es basa a dipositar una solució aquosa amb nanoesferas, les quals són bombejades i conduïdes cap a la mostra veien-se afectades per un camp elèctric. L’electrospray apareix com una tècnica innovadora de fabricació down-up desenvolupada pel departament MNT amb àrees de treball de $2cm^2$, el qual promet un cop comparat amb altres tecnologies que es poden trobar a la literatura, com el Vertical deposit. En àrees d’aquestes dimensions, som capaços de construir estructures ordenades 3D d’alta qualitat, com colloidal crystals. Tot i així, aquests $cm^2$ d’àrea no són suficients per ser utilitzats en dispositius de gran àrea com cèl·lules solars o altres dispositius òptics.

Llavors, l’objectiu d’aquest projecte és augmentar l’àrea mantenint una relació temps-qualitat acceptable mentre es construeixen estructures 3D ordenades. En aquest treball mostrem com es modifica l’electrospray tradicional afegint una guarda o directament utilitzant més agulles, la qual millora considerablement l’àrea, multiplicant en més de 10 vegades la seva mida anterior. Els materials emprats en el laboratori per a realitzar tests i caracterització varen ser nanoesferes de poliestirè de 295nm de diàmetre i materials off-the-shelf.

Per analitzar la qualitat de colloidal crystal obtinguts, un Microscopi d’escaneig per electrons va ser utilitzat per visualitzar l’estructura 3D de les mostres. Més de 10 monocapes d’ample van ser observades així com una estructura 3D ordenada, verificant així la viabilitat del nou tipus d’electrospray.
I would like to dedicate this project to the brightest star in my world, who has always stayed by my side.
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# Contents

1 Introduction 1

2 Project goals 3
   2.1 Project’s Schedule 4

3 Electrospray 5
   3.1 Electrospray onset 6
   3.2 Droplet fission 6
   3.3 Gas-phase ion generation 6
   3.4 Procedure and applications 7

4 Theoretical study 8
   4.1 Needle plus guard 8
   4.2 Multi-needle 12
      4.2.1 4-needle device 12
      4.2.2 8-needle device 13

5 Technology development 15
   5.1 Sample fabrication 15
      5.1.1 Mask design 15
      5.1.2 Fabrication procedure 17
   5.2 Needle plus guard 18
   5.3 Multineedle 19
      5.3.1 4-needle set-up 19
      5.3.2 8-needle set-up 20

6 Results 21
   6.1 Technology’s viability study 21
      6.1.1 One needle plus guard: behaviour 22
      6.1.2 4-needle: behaviour 24
   6.2 SEM and FIB characterisation 27
      6.2.1 1 needle plus guard SEM 27
      6.2.2 4-needle FIB and SEM 27
7 Conclusions
List of Figures

1.1 Quality indicators for some of the most relevant colloidal crystal fabrication techniques .......................................................... 2
3.1 Taylor cone .................................................................................. 6
3.2 Electrospray machine drawing ...................................................... 7
4.1 3D representation of a needle plus guard ..................................... 9
4.2 Electrostatic simulation 6kV on needle and -3kV on sample, no guard .... 9
4.3 Electrostatic simulation 6kV on needle and -3kV on sample with guard on ground ................................................................. 10
4.4 Electrostatic simulation 6kV on needle, -3kV on sample and 3kV on guard . 10
4.5 Electrostatic simulation 6kV needle, ground on sample and -3kV guard .. 11
4.6 Electrostatic simulation 6kV needle, -3kV guard, sample and air on ground 11
4.7 4-needle electrostatic simulation 6kV on needle and 3kV on sample (top view) 12
4.8 4-needle electrostatic simulation 6kV on needle and 3kV on sample ....... 13
4.9 8-needle electrostatic simulation 6kV on needle and 3kV on sample (top view) 14
4.10 8-needle electrostatic sim 6kV on needle and 3kV on sample ............. 14
5.1 Multineedle mask from 1 to 4 needles ......................................... 16
5.2 Multineedle mask for 8 needles ..................................................... 16
5.3 Sample’s metallization process .................................................... 17
5.4 Metallized silicon wafer for 1 to 4 needles ................................. 18
5.5 Set-up with one needle plus guard ............................................. 19
5.6 3D drawing of the 4-needle support ......................................... 20
5.7 8-needle set-up parts ................................................................. 20
6.1 Test wafer one needle plus guard ............................................. 22
6.2 One needle plus guard digressed jet ......................................... 23
6.3 One needle plus guard liquid dispersed .................................... 23
6.4 One needle plus guard, sample not grounded ............................ 24
6.5 4-needle set-up ......................................................................... 25
6.6 4-needle set-up electrospraying ............................................... 25
6.7 4-needle samples result ............................................................. 26
6.8 1 needle plus guard SEM photo ............................................... 27
6.9  4-needle center sample’s SEM ................................. 27
6.10 4-needle SEM drop .............................................. 28
Chapter 1

Introduction

Within the last few decades nanotechnology has positioned itself as cutting-edge technology. It has shown quick evolution, with new developments spreading to multiple science fields, such as surface science, semiconductor physics, micro-fabrication, molecular engineering, among many others. Its main discipline involves precise material manipulation in order to fabricate macro-scale products. Working on such an atomic scale, quantum mechanics effects are predominant, so nanotechnology development is deeply bounded to various related physics research.

Nowadays, cost and energy saving are both crucial, and new applications demand devices of smaller area. Nanofabrication is positioned as a viable solution to such problems and arises as one of the most noteworthy nanotechnology sub-fields. New approaches to optimise this type of fabrication are being investigated. In the last decade, two main approaches were proposed: top-down, such as laser 3D or electron beam, and bottom-up techniques, such as spin-coating, Langmuir-Blodgett or vertical deposit [1] [2] [3] [4].

These techniques are used to construct three dimensional colloidal crystals, which are an ordered array of colloid particles. Nonetheless, it is difficult to obtain similar results in size and thickness on a macroscale device without maintaining long fabrication times. Therefore, range is limited to a few millimetres in area and dozens of monolayers in thickness, values that are certainly not enough for many applications.

One of the bottom-up approaches, electrospray, which is part of the vertical deposit branch, takes advantage of electrokinetic phenomena to control the pattern deposited over the desired materials, thus allowing numerous applications ranging from metamaterials to optics, among others. Electrokinetic phenomena are present in heterogeneous fluids, such as the solid nano-particles solutions used in this project, which in turn involve electric and mechanic components. Using this technique, particle deposit over a sample can be easily achieved by means of voltage that channels fluid to the desired area.
The electrospray technique is one of the fastest in terms of deposit time, being completed in just minutes, dispersing to few millimetres and thickness of dozens of monolayers, while obtaining a good quality [5]. For comparison, the Shear induced technique has a deposit time of minutes, with decimetres of area but low quality. Aside from those, the Wedge-cell technique has a longer deposit time, lasting up to various weeks, but leads to big areas, millimetres of thickness and an excellent quality. Electrospray would fall in between those two, but has a major strength in the small deposit time.

In this project we expect to further contribute to the electrospray technique development by working on different ways of enlarging the useful electrosprayed area, following the guidelines set by a novel way of electrospray [6] developed by the Micro- and Nano-Technology department at UPC. Starting with a single needle electrospray machine they were able to figure out the required conditions to obtain ordered structures.

Moreover, we have developed two different approaches in the electrospray method that will allow larger spread areas, such as solar cells or optics, to be constructed over them. A theoretical research by means of electrostatic simulations will determine the viability of each approach and experimental testing will decide the best ways to enlarge the area.

Upon looking at this project’s results, we can make an updated comparative graph of the most used techniques in the field and electrospray, as it can be seen in Figure 1.1. Through this project the area has been increased from $1cm^2$ up to multiple $dm^2$.

![Figure 1.1: Quality indicators for some of the most relevant colloidal crystal fabrication techniques](image-url)
Chapter 2

Project goals

The main objective of the project is to increase the area from the current $1cm^2$ up to $12cm^2$. The project does not cover applications of the increased area, which will be further studied once the project is finished.

Developing a microfluidic or electrostatic system able to increase the $1cm^2$ useful area as much as possible, taking as starting point the quantity that previous electrospray particle device was able to deposit on a single sample.

The procedure will be really similar to the one required for a regular needle electrospray. The particles will be contained in a liquid based solution, for instance, $0.295\mu m$ polystyrene particles in aqueous suspension. The liquid will be pumped to one or multiple needles connected to a bipolar high voltage supply. The electrostatic field will cause the particles within to disperse, thus incrementing the sample’s working area.

To achieve the main objective, certain steps have to be followed. Such steps will ensure the project is kept on track and will allow any difficulty that may arise to be overtaken as fast as possible. The milestones to be accomplished are listed below:

- Learn electrospray procedure (WP1.1)
- Decide the most viable liquid dispersion method (WP2)
- Design microfluidic set-up (WP2.1)
- Electrostatic simulations (WP2.2)
- Familiarise with Clean Room facilities (WP1.2 & WP1.3)
- Design masks (WP2.3)
- Produce substrates in Clean Room (WP2.4)
- Test deposit on substrates (WP2.4)
- Characterizing the nanoparticles with SEM (WP3)
2.1 Project’s Schedule

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<tr>
<td>Jul</td>
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Electrospray

Electrospray is a technique that employs electric forces to disperse liquid or produce a fine aerosol. High voltage is applied to a liquid that flows through an emitter. Using this process and controlling its parameters, such as the pumping rate or the electrical potential, it is possible to form small highly charged droplets of liquid. This charge allows to control the droplet’s motion by changing the electric field around it.

In the 16th century, William Gilbert detected that liquids reacted to magnetic fields. As he described in his book "De magnete" [7], a water drop degenerates into a cone when it is near the presence of a charged piece of amber.

One and a half century after Gilbert, Jean-Antoine Nollet noted that water flowing from a vessel would aerosolize if the container was charged and situated near electrical ground.

In the late 18th century, Lord Rayleigh also observed interaction between liquids and electrical fields [8]. He estimated the maximum amount of charge a droplet could carry.

In 1914, John Zeleny developed various experiments in order to study the behaviour of fluid droplets. [9]. In his report, Zeleny described droplet fission under electrospray techniques.

In 1964, Sir Geoffrey Ingram Taylor characterised the shape of a fluid droplet as a cone, formed as a result of the electric field’s effect. This phenomenon was named after him [10].

Today, the number of studies on the matter have increased and multiple applications keep on appearing. The electrospray process has been improved and divided in three main phases as stated in [11]:
3.1 Electrospray onset

In the first phase, the cone appears and is ready to eject liquid droplets. The physical process is regulated by equation 3.1.

\[
E_{\text{onset}} \approx \sqrt{\frac{2\gamma \cos \theta_0}{\varepsilon_0 r_c}}
\]  

(3.1)

Figure 3.1: Taylor cone

\( \gamma \) is the surface tension of the solution, \( \theta \) is half of the cone’s angle, as shown in Figure 3.1 and \( r_c \) is the capillarity radius.

3.2 Droplet fission

The droplet fission starts when the first droplets that were ejected from the Taylor cone subdivide. When the limit between the electric field and surface tension is exceeded, the droplet breaks into smaller pieces. This division behaves as predicted by the Rayleigh limit, defined in equation 3.2.

\[
Q = 8\pi \sqrt{\varepsilon_0 R^5}
\]  

(3.2)

\( Q \) is the droplet maximum charge and \( R \) is the droplet radius.

3.3 Gas-phase ion generation

Once the droplet fission has finalized, the nanospheres in the liquid become a foregather of gaseous ions. There are two theories that try to explain this phenomenon: Ion Evaporation Model (IEM) and Charge Residue Model (CRM). On the one hand, IEM takes for granted that in a small sphere radius (\( r < 10\text{nm} \)), the electric field can overcome solvation forces and extract an ion from the droplet surface. On the other hand, CRM model assumes fission will continue to happen until, after some cycles of the previous steps, there are only ions left.
3.4 Procedure and applications

In order to set up a testing environment, the components or parts that comprise an electrospray device must be defined. In this case, it is conformed by the three items listed below:

- Needle
- High voltage power supply
- Pumping machine

A schematic of a generic electrospray set-up is depicted in Figure 3.2

![Figure 3.2: Electrospray machine drawing](image)

Regardless of the main electrospray application being mass spectrometry, there are plenty of other usages that have been developed based on this technique, such as the deposit of ordered nanoparticles.
Chapter 4

Theoretical study

To properly address our goals, a certain theoretical basis has to be established first. Thus, before setting any experimental environments, various electrostatic field analysis have to be performed so we can cut down the possible solutions and tailor them to the problem we face.

Different settings have been proposed in order to vary the electrospray performance and ultimately lead to an increment in the deposit area. A study of viability taking into account both electrostatic has been carried out, from which its two main approaches will be further discussed within this section.

The simplest setting that would fulfil our requisites is keeping the one needle system, but adding a metallic guard to change the electrostatic field. The second setting takes a multiple equidistantly placed needles approach, instead of the basic way of doing electrospray with a single needle.

4.1 Needle plus guard

Let us study the first approach of the solution with a COMSOL\(^1\) [12] electrostatic simulation. It is easy to build up a physics simulation on COMSOL just by choosing the package you want to use, electrostatic in our case.

Once you choose the package you can build in-app the 3D bodies that will define the electrostatic voltages. For the first case, a working area of 6cm x 6cm x 6cm that will contain all the bodies and electric linestream solutions of the system is defined. Centred in the working area, we locate a cylinder with 1mm diameter that will represent the needle and, around it, a ring with 1cm inner and 2cm outer diameter is placed. Finally, we set a 1.5cm diameter sample in the lowest part of the working area, as it can be seen in Figure

\(^1\)COMSOL Multiphysics: A multiphysics finite element analysis, solver and simulation software/FEA software package for various physics and engineering applications.
4.1

Once the bodies are defined we can set voltages for each area. We want to get an increase of the electrosprayed area, which means that the field lines have to be as disperse as possible.

In order to proper characterise the method, we will first simulate a system with no potential in the guard like it is done for the usual electrospray. Then a positive high potential is applied to the needle (6kV) and a negative high voltage is applied to the sample (-3kV). The linestreams shape up as seen in Figure 4.2.

It can be observed that the field lines follow the expected path by going from the needle to the sample, but field lines open too much and the liquid will not be able to follow those lines. Next, we will observe what happens after changing the guard’s voltage to ground as seen in Figure 4.3.
We can see that the field lines are trying to reach the lowest voltage by evading the guard, but in the end they get clustered around the sample, but again field lines widen too much and liquid may not follow them. We determine that it would not work for our application. Now, we will set ground in the sample and set a middle voltage on the guard in Figure 4.4.

There is little change in the field lines in comparison to the simulation with guard on ground, but field lines from the needle widen evading the guard while the ring has its own lines to the sample. In this case, they linestreams still open too much for our application. Let us do one more simulation with a negative voltage set on guard and ground set to the sample. In this case, the needle will be located at the same level as the ring in order to obtain results able to test. This simulation can be seen in Figure 4.5.
CHAPTER 4. THEORETICAL STUDY

4.1. NEEDLE PLUS GUARD

We proved that with a negative voltage on the guard and ground set on the sample, field lines emerging from the needle expand through the sample. This will distribute liquid through the whole surface of the sample since field lines emerge from the tip of the needle, just as we could expect. Upon this result, we consider setting the sample’s voltage at a potential similar to the air around it, let us see the obtain solution in Figure 4.6.

![Figure 4.5: Electrostatic simulation 6kV needle, ground on sample and -3kV guard](image)

(a) Isometric view  
(b) Side view

Figure 4.5: Electrostatic simulation 6kV needle, ground on sample and -3kV guard

It can be observed that with this setting field lines expand to occupy a much wider area. However, it is important to note that field lines are not distributed evenly through the whole sample area, but keep spreading out the more you deviate from the needle axis. This way the electric field has a higher line density in the sample’s centre. But can get unstable pretty easily because field lines do not have a reference to follow.

![Figure 4.6: Electrostatic simulation 6kV needle, -3kV guard, sample and air on ground](image)

(a) Isometric view  
(b) Side view

Figure 4.6: Electrostatic simulation 6kV needle, -3kV guard, sample and air on ground
From these simulations we can extract that by keeping the high voltage on the needle, setting a negative voltage to the guard and ground to the sample we can spread out the field lines and disperse the liquid from one needle to all the sample’s area.

From the electrostatic point of view, this is a viable option to enlarge the total electrosprayed area. Another issue we might have to take into account is fluids physics. Knowing that we haven’t added needles and that it worked properly without guard, the most reasonable conclusion is to think it will work as expected with this configuration.

4.2 Multi-needle

The second approach we will study is adding needles and microfluidic flow splitters so we obtain a multineedle device. We will concentrate the study on 4 and 8 needles, since the microfluidic’s complexity increases as more needles are added. This study will include COMSOL electrostatic and microfluidics simulations, so we can determine their characteristics before trying the settings out.

4.2.1 4-needle device

Once characterization with a single needle is completed, we will perform simulations for a 4-needle case, as previously planned. The 3D setting will keep the same sample size as before, but now 3 needles will replace the guard. All of them will shape up a square, looked from the upside, separated 6cm from the sample.

We will increase the streamline number of the solution in order to get a clearer view of the electric field, as there are multiple field sources. We can see the solution from the upside in Figure 4.7.

![Figure 4.7: 4-needle electrostatic simulation 6kV on needle and 3kV on sample (top view)](image-url)
We can observe that the lines extend to more than the sample’s width, just as we wanted. Let us look at it from another side in Figure 4.8.

Looking from the side, we can observe that even though the lines extend outside the sample’s diameter, they shape an arc that returns to the sample going through it. Field lines are dispersed evenly in the samples wafer, with a higher concentration in the middle and more disperse on the edge.

This means, from an electrostatic point of view, that we can use 4 needles to perform large area electrospray, keeping a positive high voltage on the needles and a negative high voltage on the sample, which will lead to a dispersion of liquid an nanoparticles over the sample. With more liquid into the system we will achieve a better density of nanospheres resulting in wider and evenly dispersed monolayers.

### 4.2.2 8-needle device

Lastly, we simulate the most complex setting included in the project. This configuration will distribute up to 8 needles without guard, similar to the previous device.

As we did in the 4-needle simulation, we keep the same sample size and allocate 4 more needles, with equidistant separation arranged in a circular fashion, which will allow for a better distribution of the liquid.

Again, we keep a big streamline number so we get enough resolution to decipher the solution, as seen in Figure 4.9.
It can be observed that a symmetric pattern is followed by the field lines, even though not all the area is covered. This could be caused by a low simulation resolution, but is enough to determine that an 8-needle device would cover a wide sample, as it can be seen from another side in Figure 4.10.

This demonstrates that the wide sample will be fully covered with a 8-needle configuration, reaching more concentration of liquid than the previously achieved with 4 needles. This result lets us assume that as far as microfluidics allow us, we could increment the electrospayed area and density of liquid by adding needles to an electrospay machine.
Chapter 5

Technology development

In Chapter 5.2 we already performed a theoretical study, so we will now present the practical solution tested in the laboratory. First of all, we will explain the methodology for sample fabrication and then, following the previous chapter pattern, present each suggested approach, beginning with the single needle system.

Since the characterization section of the project requires a determined construction of a sample with silicon and aluminium to get more accurate results in SEM and FIB, we will first focus on obtaining them. In Chapter 6 results of each approach will be provided.

5.1 Sample fabrication

The sample fabrication process is split up in five main parts. Firstly, a mask is designed in order to define the silicon’s desired pattern. Then, once the silicon wafer is prepared in the Clean room, lithography, photoresistance removal, metal evaporation and lift-off will be performed.

5.1.1 Mask design

Two full 4” masks were designed for the different approaches, only differing in the main circle size, which is in turn connected by a line to another little circle used to connect the negative voltage to the sample.

Mask designs were printed in a soft transparent acetate paper that allows light to go through and hit the photoresist.

One of the samples was designed to fit the one needle plus guard and the 4-needle design approach. Since the useful area is little, we can divide a wafer in two parts and get two samples from a single silicon wafer, as it can be seen in Figure 5.1.
For the 8-needle taking a similar design with a bigger main circle was drawn. As it can be seen in Figure 5.2, a little pad that will conduct the voltage with a circular shape while a big circle domains the wafer, area in which electrospray will be applied.

Up to that moment we thought it would be approximately the maximum electrosprayed area that we would obtain from our approaches.

Once our masks are designed we just needed to print them in a soft plastic paper and head to the Clean room to fabricate our samples.
5.1.2 Fabrication procedure

The fabrication procedure will target the metallization of the desired area using the designed pattern printed in a mask. In order to accomplish that, we will follow five steps to be performed in the Clean room:

a) Cleaning and wafer preparation.

b) Lithography.

c) Photoresistance removal.

d) Metallization process.

e) Lift-off.

In Figure 5.3 it can be observe the sample’s evolution on each process from a side perspective.

![Sample's metallization process](image)

**Figure 5.3: Sample's metallization process**

**Clean and Preparation of the wafer** Clean the wafer and dry it. Afterwards, apply photosensitive resin using the spinning machine, which will evenly distribute the resin. Let it dry in the oven.

**Lithography** Use an aligning machine with a high intensity light, so the shape of the mask will be engraved in the wafer.
5.2 NEEDLE PLUS GUARD

Photoresistance removal Using revealing liquid, remove the enlightened resin on the wafer and clean it with isopropanol and acetone. Dry it again in the oven.

Metal evaporation Use an evaporator machine to perform the process. Insert your sample in the machine as well as a piece of the metal you want to evaporate, in our case, aluminium. Start the machine’s process in order to do a correct evaporation, following each step until the end.

Lift-off Put your metallized wafer into the isopropanol solution that will lift the photosensitive resin, leaving the original shape of the mask.

We could add an extra layer of photosensitive resin to better isolate aluminium from silicon, but we considered it was not necessary. After all those processes, we obtain a usable sample for our application, as it can be seen in Figure 5.4.

![Figure 5.4: Metallized silicon wafer for 1 to 4 needles](image)

With those samples done, let us develop each approach independently in the following sections.

5.2 Needle plus guard

In each one of the approaches we propose changing the basic set-up in order to get an increase in the electrosprayed area, which is the main goal of the project. Let us see how we change the parameters and geometry within the scope of each approach.

The first device uses a single needle plus guard approach. Which configuration we need to set in order to obtain good results can be derived from the simulations. We will also test the use of a 2cm diameter metallic ring, so the electrospray area is further increased. A high voltage needs to be connected to the needle and a low voltage is set to the ring and ground connected to the sample.

The test’s construction will be done as shown in Figure 5.5, where the needle tip is at the same level as the ring.
5.3 Multineedle

In the multineedle device, the physics involved are more complex. We have to change the set-up in order to hold the needles and provide them voltage. Another critical part are the microfluidics involved: since the solution is not 100% water, as it contains nanospheres, fluidics may become tricky.

Two supports will be designed, one support to hold 4 needles and the other one for 8 needles.

5.3.1 4-needle set-up

This set-up will resemble the one seen in Subsection 5.2 but able to feed all needles a 5-way splitter will be located between the syringe and each needle. This will allow to separate the liquid from one to four needles.

Besides this microfluidic adjustment, the needles must be held at the same level and at a constant height. For this reason, a 3D model of the support was designed using SolidWorks\textsuperscript{1} \cite{13}. One things to keep in mind is that we want to insert needles through the support, and to do so we will need to acknowledge each needle’s volume as well as their blockage occupation, so they do not overlap when assembled.

\textsuperscript{1}SolidWorks: A 3D design solution with multiple simulator tools. It enables quick design of pieces, assemblys and 2D drawings.
5.3. MULTINEEDLE

The 3D model takes into account the specific needle shape so each one of them can fit perfectly into the support. We have also designed a two-level support so needles can be placed in its thickest part and the thinnest section is used to grip the support with a grabber. The internal shape of the support can be seen in Figure 5.6.

![3D drawing of the 4-needle support](image)

Figure 5.6: 3D drawing of the 4-needle support

5.3.2 8-needle set-up

Regarding the 8-needle set-up, it behaves similarly to the 4-needle one, but deploying 4 additional needles in a circular fashion, as seen in Figure 5.7a.

![3D model of the 8-needle support](image)
![3D model of the whole 8-needle set-up](image)

Figure 5.7: 8-needle set-up parts

This allows us to build a 3D model of the whole system, including microtubes and the 9-way splitter. We have also distributed the 8 needles as described above. In Figure 5.7b it can be seen how it should end up looking in the real world.
Chapter 6

Results

In order to determine the best way to increase the electrospray area, we set-up each of the previously exposed approaches for in-lab testing and further characterization. We built the one needle plus guard and the 4-needle configurations successfully. However, the 8-needle setting could not be properly assembled due to technical problems and thus will be left out from this study, but proposed as future work.

First of all, we will discuss how each system performed, then compare the various outcomes to those theoretically expected and finally characterize each system’s physical behaviour within the project’s scope.

6.1 Technology’s viability study

In this section, we present the selected configuration behaviour and how the samples look like when they were electrosprayed.

I would like to point out the specific components used to perform the electrospray technique in our precise set-up. The system is kept in a glove box and is composed by an infusion pump Perfusor Space from B. Braun and a two channel high voltage source HV Rack from Ultravolt, which is able to output a voltage ranging from 0V to 15kV, delivered to one of the channels and from -15kV to 0V on the other, at a maximum of 2mA current.

A CCD camera with long optics is located outside the glove box. The consumables used for the electrospray are: syringes with normalized LEUER connector and KF needles from Hamilton, interconnected with 1/16” output diameter microtubes PEEK™. Two different types of microtubes were used, the first one being of 0.007” inner diameter, used on the one needle system, and a second one of 0.04”, which was used for the multineedle set-up. Finally, we used 295nm polystyrene nanospheres on a 5% concentration water solution.
6.1.1 One needle plus guard: behaviour

This set-up with just one needle was mounted by modifying the current UPC electrospray machine. The needle was fitted into a perforated plastic tube and kept connected to the positive high voltage supply. The guard was held on the air with a clamp connected to the negative high voltage supply and the wafer connected to ground.

The first test was performed over a whole metallized 4” wafer, before using clean samples. In that wafer the voltage was distributed along its surface, so the electric field was evenly spread and offered plenty of space for the liquid to be dispersed. As it can be seen in Figure 6.1, the electrosprayed area is large enough to be considered a success, with approximately 4cm of diameter. This sample was obtained with 2ml/h pump rate, 2665V in the needle and -1035V in the guard.

Figure 6.1: Test wafer one needle plus guard

Figure 6.1 shows a wafer test with different types of areas, metallized with aluminium (hydrophobic) and textured silicon (hydrophilic), and how liquid moves out of the aluminium and gets near the hydrophilic area. Although still some liquid remains in the aluminium side in form of little droplets.

Once the set-up had been proved to work, we performed the experiment on one of our samples. We tested it using the same conditions. Now we needed to be careful because the electric field coverage area is smaller than before.
We tweaked the voltage in order to obtain a stable Taylor cone. It stabilized at 2850V and -850V. At that point, the electrospray process started depositing nanospheres on the sample. To our surprise, we did not obtain the expected result. In Figure 6.2, it can be seen that the jet is digressing from the expected path. The stream follows a linear dispersion path, that is, a straight line, as opposed to the circular dispersion we expected in sight of our theoretical analysis.

![Figure 6.2: One needle plus guard digressed jet](image)

We tried to move the ring in order to change the pattern over this sample and, after successful nanosphere deposit over 10 minutes, the whole pad’s area was covered, as can be seen in Figure 6.3. What we could not obtain was the stable system we had on the previous test, that is, evenly liquid dispersion over the area. Afterwards, while keeping the voltage open, we let the samples dry for over an hour. The drying process took longer than expected due to high voltages being connected to the needle and ring, which prevents the electric field from hitting the sample.

![Figure 6.3: One needle plus guard liquid dispersed](image)

Another test was performed, this time disconnecting the sample’s voltage in order to determine if simulations were on track. With a new sample, we set the Taylor cone to be stable at 2500V (on the needle) and -900V (on the ring).
The jet follows a dispersion path that is similar to the previous one, but this time it can be observed that the Taylor cone is unstable and breaks with a little voltage variance. This instability causes liquid to flow from the wafer to the clamp. Water droplets have little mass and the electric field is thus strong enough to defeat gravity and push droplets towards the negative voltage. This can explain why we had linear dispersion in the previous experiment.

![Image of dispersion tests](image1)

(a) First test
(b) Second test

Figure 6.4: One needle plus guard, sample not grounded

In this approach, the result differs from simulations because they were simplified to obtain an easy to calculate approximation and did not take into account parameters modelling real world testing. We can not suspend a ring with a given voltage without causing some sort of disturbance to the whole system behaviour. In particular, the ring subjection affects the electric field when the grounded sample is small, but can work for larger area samples, as they seem to not be affected by the clamp’s field. It could be solved using adhesive tape in the clamp to isolate that source of voltage.

### 6.1.2 4-needle: behaviour

In the 4-needle set-up more changes were made on the UPC electrospray machine. A splitter was added between the syringe and needles, which caused a flow issue. We solved this issue by changing the first section microtube with the 0.04” inner diameter tube, which could handle more liquid volume. Therefore, the system had 0.04” inner diameter section followed by the 5-way splitter, and the 0.007” inner diameter connecting the splitter to the 4 needles.

Another piece of the equipment that changed is the needle’s support, designed for four needles. This support was printed with a 3D printer using white PLA material. PLA is a type of plastic, that is, an insulator material, but we needed all the needles to be connected with a single power supply and a plastic would not do it.

We tried to metallize the PLA support using a spattering process, but the high temperatures bent the piece and we could not achieve good results, so we redefined a more suitable solution. The problem was solved by wrapping the support’s bottom with a sheet of aluminium foil.
In this case, the needles were connected to the positive high voltage while the sample was connected to the negative high voltage, in a similar fashion to the regular one needle electrospray. The needles were interconnected through the aluminium foil where the voltage clamp was connected, as it can be seen in Figure 6.5.

![Figure 6.5: 4-needle set-up](image)

We set the flow rate at 4ml/h, four times higher than with a single needle. Our goal was to achieve stable Taylor cones for all four needles. To do so, we had to increase the differential voltage up to 13500kV, with 10000kV connected to the needles and -3500kV connected to the sample. In Figure 6.6 we can observe Taylor cones dispersing liquid over our sample.

![Figure 6.6: 4-needle set-up electrospraying](image)
The voltage used to achieve the Taylor cones is really high in comparison with the rest of the voltages seen in this project, that being due to the aluminium foil’s high resistance and the imperfect contact between the needles and the foil. We could improve the contact using conductive paint or conductive glue around the part of the needle that is in contact with the foil.

We can see the results of the deposit in Figure 6.7 after 15 minutes depositing liquid and then letting the wafer dry, with the voltage activated, for 30 minutes at a 40% relative humidity.

We can clearly see four circular marks of nanospheres with a definite distribution: highly concentrated in the center and dispersed in the surroundings. The surface covered by the nanoparticles is even bigger than the pads’ diameter, which is 5.5cm, providing a useful area of up to $25cm^2$.

Even with the multiple microfluidic and needle issues that arose, our approach has proven to be viable. By using just four needles, we have greatly increased the effective electrospray area. Further study on the matter could enable the usage of 8, 16 or even 24 needles at once, only limited by the physics of the microfluidics involved. With all the results obtained we can build a reference including the requirements for each approach with the results obtained at Table 6.1.

<table>
<thead>
<tr>
<th>Electrospray System</th>
<th>Deposition conditions</th>
<th>Area</th>
<th>Ordered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
<td>Flow Rate</td>
<td>% HR</td>
<td>Distance</td>
</tr>
<tr>
<td>1 needle plus guard</td>
<td>2850 V</td>
<td>2 ml/h</td>
<td>50</td>
</tr>
<tr>
<td>ground on sample</td>
<td>-850 V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 needle plus guard</td>
<td>2500 V</td>
<td>2 ml/h</td>
<td>50</td>
</tr>
<tr>
<td>without ground</td>
<td>-900 V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-needle</td>
<td>10000 V</td>
<td>4 ml/h</td>
<td>40</td>
</tr>
<tr>
<td>-3500 V</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1: Deposition conditions table of results

1This sample was not observed with the SEM.
6.2 SEM and FIB characterisation

We have performed Scanning Electron Microscope (SEM) and Focused Ion Beam (FIB) tests in order to see how the nanospheres were distributed in detail. Aside from enlarging the total electrospray area, the homogeneity and thickness of the deposit were also parameters we wanted to study.

The best sample from each of the configurations exposed in this document was selected for this process, obtaining good results as detailed below.

6.2.1 1 needle plus guard SEM

By simply looking at the sample with the naked eye, iridescence in the sample’s deposit could be observed, a characteristic confirmed by the SEM photographs obtained in the lab, in which we could see how the nanospheres formed an ordered structure, as shown in Figure 6.8.

![Figure 6.8: 1 needle plus guard SEM photo](image)

The sample’s surface presents an ordered pattern, even though it is not totally homogeneous due to some detached nanospheres spreading over the ordered layer. This behaviour should be further studied to determine if this effect has any noticeable impact on the electrospray technique application.

6.2.2 4-needle FIB and SEM

The second sample was selected from one of the more concentrated parts of 4-needle deposit. We performed a FIB in order to see the 3D pattern in the interior part of the sample, as shown in Figure 6.9.

![Figure 6.9: 4-needle center sample’s SEM](image)
We observe a nanoparticle deposit of more than $8\mu m$ thick, which in turn means there are more than 10 monolayers of 3D ordered structure. Beside the thickness, we notice there is a good quality colloidal structure, even though it shows some dislocations.

We noticed the fact that there was a scattered deposit between both needles, and decided to further analyse it with a SEM in order to determine if there was 3D ordered structure. Figure 6.10 shows a dry drop obtained by zooming in the scattered region, which presents a coffee stain formation, a phenomena already present in the literature [14]. The evaporation of colloidal structures drops leave behind ring-like solid residues, with disorganized nanospheres filling the internal part of the drop.

![Figure 6.10: 4-needle SEM drop](image)

(a) Nanosphere drop  
(b) Drop outer perimeter  
(c) Interior part of the drop  
(d) Zoom in the drop’s edge

Given this results, we conclude that a multineedle electrospray deposit will not have all nanospheres evenly distributed through the sample’s area, but present coffee stains between needles. Regions with coffee stains are mainly disorganized, as seen in Figure 6.10a, with the exception of the coffee stain’s edges, which will be ordered.
Chapter 7

Conclusions

The main objective of the project is to increase the electrospray area while maintaining a good time-quality ratio. In order to do so, two different approaches were taken, the first one was expanding the one needle electrospray concept and modify it with a guard able to change the electric field while the second approach was increasing the system’s needles to four.

The one needle plus guard configuration did not work as good as we expected for our prepared samples with clamp effects predominating over the system, but when using larger metallized wafers it worked as the simulations estimated. We have found the conditions to be met in order to obtain the desired results, and described the main issues that can occur in this type of electrospray. Taylor cones were observed, but that is not enough to ensure a stable deposit.

On the other hand, the multineedle approach is much more promising, being a success and even exceeding expectations: with just four needles, an electrospray area of 25cm² was obtained. By adjusting the liquid flow and using different inner diameter tubes we ensure the microfluidics do not prevent the set-up from its correct functioning. This system can allow both a large area device or a multidevice set-up, for deposit times of around 45 minutes and using samples properly designed.

Sample characterization determined that the guard and multineedle approaches presented in this project enable the production of large area ordered nanospheres structures, which can not be found in the field’s literature published to date.

It is important to note that all the required changes for this project’s set-up can be easily built over a regular electrospray machine, as adding a guard or a 3D printed support is always technically feasible.
However, the challenge lies in the ability to control the material’s organization, as well as the quantity of nanoparticles deposited.

Further work will produce an optical characterization of samples obtained using the multineedle technique. In order to improve the electric contact between the needles, thus reducing the voltage needed to perform multineedle electrospray, a better conductor material than the aluminium foil we used should also be implemented into the system. The system’s stability should be improved so each needle shapes a Taylor cone and is able to disperse liquid constantly.
Bibliography


[12] Inc COMSOL. COMSOL.
