

École polytechnique de Louvain

Development of pulsing surfaces for underwater motion

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Abstract

Biomedical devices, such as catheters or implants, are always sterilized before use to prevent patients from getting an infection. However, during placement, they may inadvertently be contaminated by microorganisms, resulting in infections once in the body. The goal of this work is to develop a dynamic surface, using a thermoresponsive polymer brush, that will allow to better understand the interaction of bacteria with a dynamic surface and thereby provide new elements to ultimately combat such infections. Although it will not be possible to incorporate the device in the human body as it is, the new understanding of the interaction of bacteria could lead to novel designs of antifouling dynamic surfaces.

The surface is covered with a thermoresponsive polymer brush, immersed in water for reproducing physiological conditions, that will be locally heated and thus actuated by an array of electrodes buried just below. Therefore, this master thesis starts by performing finite element simulations for determining the thermal profile in water above the surface. The knowledge of this profile will allow to determine the optimal dimensions, such as the thickness of the different thin films, as well as the current that needs to pass through the electrodes for collapsing locally the thermoresponsive polymer brush. Afterwards, the optimal design determined with the simulations will be fabricated using microfabrication techniques such as photolithography, reactive ion etching, electron beam evaporation, or reactive sputtering. Metrology using ellipsometry, profilometry, and scanning electron microscopy will be regularly used along the process. Finally, it will be shown that spectroscopic and imaging modes of ellipsometry allow to characterize the fabricated dynamic surface in real-time.

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Chapter 1

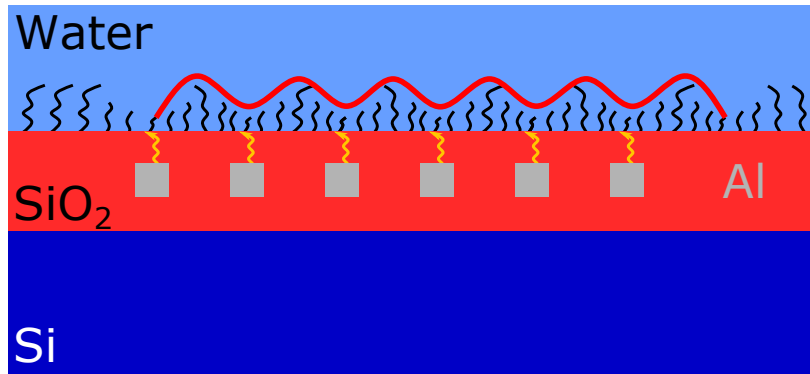
Introduction

During the last decades, several antibacterial surfaces were imagined to solve the problem of infections related to biomedical devices and implants. One of these attempts is a surface covered with a polymer brush which is able to prevent the adsorption of cells at the surface, thereby preventing the creation of a biofilm which could subsequently lead to an infection [1, 2]. Another attempt was made by Glinel *et al.* (2009) [3] where this polymer brush was further functionalized to kill the bacteria coming close to the surface.

Despite these efforts, the problem persists because biomedical implants require an antibacterial surface remaining active for at least several months, which has not yet been demonstrated [4]. Indeed, bacteria always find a way to adsorb somewhere on the surface, ultimately leading to the creation of a biofilm. The existing surfaces have the common point that they are static.

The goal of this work is to design, develop and characterize a dynamic surface, which will be used in the future to check whether such surfaces might not be a better solution for fighting bacteria adhesion. The cross-sectional view of the device to be created is illustrated by the following schematic. An array of aluminum electrodes will be incorporated inside silica with a polymer brush grown on it. This polymer brush is said to be thermoresponsive because it has the particularity to be swollen below a critical temperature and collapsed above it. More precisely, this polymer brush is swollen when it is placed in water at room temperature. This same brush will collapse if the temperature of water around it is raised above its critical temperature. Interestingly, it is possible to heat very locally water by passing a current through the array of aluminum electrodes, which are only a few microns wide. Doing so, it is possible to heat locally above the critical temperature, thereby creating a spatial wave at the surface of the device with the polymer brush. A dynamic surface is obtained by alternatively turning on and off the current in the electrodes.

These dynamic surfaces will serve several purposes. The first of them is to prevent the creation of a biofilm at the surface of the device by controlling the interaction of bacteria with the surface. Indeed, it is expected that some “resonant” frequencies will particularly interact with bacteria, which will eventually lead to the complete prevention of biofilm creation. This device is a prototype and it is difficult to imagine its insertion inside the human body. If these surfaces are successful, it can be imagined that an intensive



research will allow the creation of dynamic surfaces without resorting to an array of metal electrodes.

In addition, studying the interaction of bacteria at several oscillation frequencies should allow to better understand their dynamical behavior at the surface, opening the door to new solutions for antifouling surfaces.

Finally, the creation of this device also aims at determining whether it is possible to move microscopic objects, especially colloidal particles and bacteria, with such a dynamic surface for applications in microfluidic devices.

This master thesis begins with Chapter 2 which presents the state of the art of the research field, containing among others an introduction to polymers in solution. This prerequisite is absolutely required for understanding how a polymer brush can be thermoresponsive. Chapter 3 performs finite element simulations that will allow to design a device able to create a dynamic surface. Chapter 4 explains how the previously designed device is fabricated in practice. Microfabrication techniques in the *Winfab* facility were used. Finally, Chapter 5 aims to find characterization techniques that will allow to study the interaction of the surface with colloidal particles or bacteria.

Chapter 2

State of the art

In order to have in mind the interactions of polymers with a solvent as well as their growth, properties, and applications, this master thesis starts with a state of the art about free and tethered polymers chains in a solvent.

In this chapter, polymer brushes are first defined. The interactions of polymers in a solution along with their dependence on parameters such as the temperature are expressed using a thermodynamical approach. The growth method of the polymer brushes used in this work, which is able to achieve a high surface coverage, is detailed step by step. The choice of this method of growth is motivated by the importance of having a high grafting density. The possibility to tune the transition temperature, above which the polymer brush becomes dehydrated, is addressed. As an application, the possibility to make antifouling surfaces by covering a surface with polymer brushes is presented. Finally, the motivation of this work justifies how the creation of a dynamic surface could eventually lead to more reliable antifouling surfaces.

2.1 Definition of polymer brushes

From a structural point of view, a polymer brush can be simply defined as a tethered polymer layer with a high grafting density of polymer chains. The conformational dimensions of individual polymer chains are altered due to the proximity between the end-grafted polymer chains, leading to a high stretching of the polymer chains and to novel properties compared to chains in solution [5].

The grafting density is defined as the number of tethered polymer chains per unit area of the surface to which they are attached.

2.2 Introduction to polymers in solution

Thermoresponsive brushes are able to transit from a hydrophilic to a hydrophobic behavior, which is the key property for the conception of dynamic and antifouling surfaces. Due to the fundamental importance of this property, and because it is essential to grasp the interactions of a brush with the solvent they are in, this section presents an introduction

to polymers in solution. Although polymers in solution are not attached at one end, their interaction with a solvent remains the same and they also exhibit a well described thermoresponsive behavior that will be used to understand the one of polymer brushes.

A polymer chain, generally found in a solvent with the shape of a random coil, is a macromolecule made of many repeating units, which can be of different types. The polymers with one type of repeat unit are called homopolymers (see Figure 2.1(a)) while the ones with two or more types of repeat units are called *copolymers* (see Figure 2.1(b)), and are of tremendous importance in polymer science as well as in this master thesis.

This section is an introduction to polymer science and is inspired by the courses *LMAPR2019A - Science et ingénierie des polymères-Physique* [6] and *LCHM2261B - Polymer Chemistry and Physical Chemistry* [7].

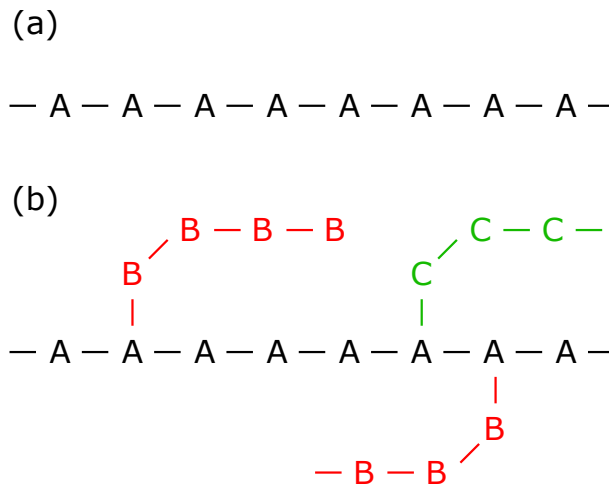


Figure 2.1: Two different types of polymers **(a)** Homopolymer with only 1 type of repeat unit. **(b)** Graft copolymer with 3 different types of repeat units.

2.2.1 Model of ideal chain : the freely-jointed chain

A polymer chain can adopt many conformations. A conformation is the shape of a chain at a given time. The conformations of the polymers vary continuously in time making their study complex. Therefore the simple model of the freely-jointed chain is used, which supposes that the polymer chain is made of n_s rigid segments, the Kuhn segments, which are attached but do not interact with each other. For this hypothesis to be valid, the length of the Kuhn segments, b , is fixed to $2L_p$, where L_p is the persistence length which evaluates the length over which the chain loses the memory of its local orientation. This model is schematically presented in Figure 2.2.

Average end-to-end distance R_{EE}

The end-to-end vector of the conformation presented in Figure 2.2 is equal to

$$\vec{R} = \sum_{i=1}^{n_s} \Delta \vec{r}_i. \quad (2.1)$$

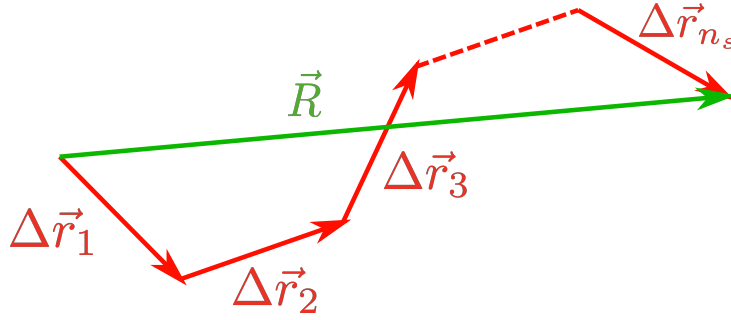


Figure 2.2: Schematic of the freely-jointed chain model. The end-to-end vector $\vec{R}$ is defined in the frame of the freely jointed chain model.

However, the conformation of the polymer chain varies over time and so does the end-to-end distance. The root-mean-square average end-to-end distance, R_{EE} , can be demonstrated to be equal to

$$R_{EE}^2 = \langle |\vec{R}|^2 \rangle = n_s b^2, \quad (2.2)$$

where $\langle \rangle$ designates an average over all the possible conformations. Equation 2.2 is the most important result of this model. It is relevant to define the contour length, L_c , as the length of the chain in its fully extended state. For a freely-jointed chain, the contour length is simply equal to $n_s b$. Equation 2.2 can thus be written as

$$R_{EE}^2 = b L_c. \quad (2.3)$$

Interestingly, one can notice that the average end-to-end distance is proportional to the square root of the contour length (i.e. $R_{EE} \propto \sqrt{L_c}$).

Radius of gyration R_G

Another relevant way to measure the size of the random coil formed by macromolecules is the radius of gyration, defined as

$$R_G^2 \triangleq \left\langle \frac{1}{n_m} \sum_{i=1}^{n_m} |\vec{r}_i - \vec{r}_M|^2 \right\rangle, \quad (2.4)$$

where n_m is the degree of polymerization, $\vec{r}_i$ is the position of a repeat unit in the chain, and $\vec{r}_M$ is the position of the center of mass of the macromolecule in a given conformation. This radius of gyration is a measure of the locations where the repeat units of the macromolecule reside on average, knowing that the probability to find a repeat unit can be described by a bell-shaped Gaussian 3D function [7]. The graphical meaning of R_G is provided in Figure 2.3. It can be shown for an ideal freely-jointed chain that

$$R_G^2 = \frac{R_{EE}^2}{6} = \frac{n_s b^2}{6}. \quad (2.5)$$

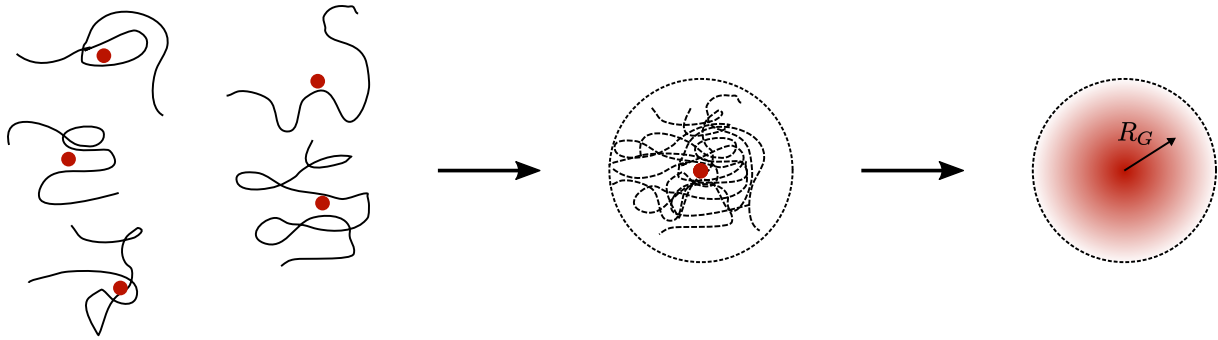


Figure 2.3: The different possible conformations for a chain (left) are superimposed by bringing their centers of mass in coincidence, thereby creating a random coil (middle). The average of all conformations gives access to the probability to find a repeat unit at a given position in space (right), leading to the definition of the radius of gyration R_G . Reproduced from Jonas (2018) [7].

2.2.2 Quality of a solvent and swelling coefficient

The model of the ideal chain (i.e. freely-jointed chain) supposes that the segments do not interact with each other, which is obviously wrong. However, in specific conditions called the theta conditions, the segments of a real polymer chain act *as if* they were not interacting. These conditions are reached at the theta temperature T_θ which depends on the potential of interaction between the segments. For these Θ conditions, the average end-to-end distance $R_{EE\Theta}$ and the radius of gyration $R_{G\Theta}$ are respectively given by Equation 2.2 and Equation 2.5. Out of these Θ conditions, the radius of gyration is computed as

$$R_G \triangleq \alpha R_{G\Theta}, \quad (2.6)$$

where the *swelling coefficient* α has been defined. If the attraction between the segments of the macromolecules is stronger than the attraction between the segments and the solvent, then the polymer will adopt the shape of a compact coil for maximizing the contact between the segments. In this case, the solvent is said to be a poor or even a bad solvent and $\alpha < 1$. In the opposite case where the interaction between the segments and the solvent molecules is stronger, the polymer will swell in order to maximize the contact with the solvent. In this case, the solvent is said to be a good solvent and $\alpha > 1$.

2.2.3 Flory-Huggins theory

The previous subsection was focused on a single chain and its interaction with a solvent. In practice, there are many polymer chains in a solvent. If the concentration of macromolecules exceeds a critical concentration

$$C^* = \frac{M/\mathcal{N}_A}{(4/3)\pi R_G^3}, \quad (2.7)$$

where M is the molar mass of the macromolecule, and $\mathcal{N}_A$ is the Avogadro's number, then the chains will on average interpenetrate each other. Paul Flory and Maurice Huggins proposed a theory which allows to determine the variation of the Helmholtz free energy

upon mixing of the macromolecules in a solvent with a concentration above C^* , written ΔF_m . By considering that the temperature does not vary upon mixing and using the definition of the free energy¹,

$$\Delta F_m = \Delta U_m - T\Delta S_m, \quad (2.8)$$

where ΔU_m and ΔS_m are respectively the variation of internal energy and entropy upon mixing, and T is the temperature during mixing². The lattice and the hypotheses considered within the frame of the model of Flory & Huggins are presented in Figure 2.4.

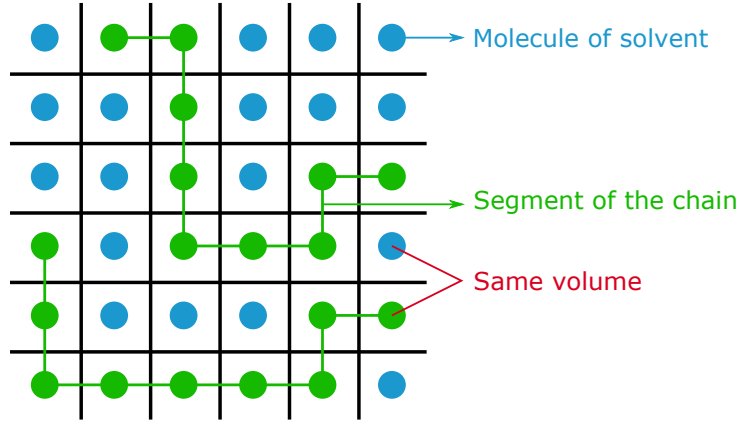


Figure 2.4: Schematic lattice of macromolecules in a solvent, forming a solution. In the frame of the model of Flory & Huggins, the macromolecules have the same molar mass (i.e. same number of Kuhn segments n_s) and a segment of the polymer solute occupies the same volume as a molecule of solvent. In addition, only linear chains are considered in this model.

Entropy of mixing ΔS_m

The variation of configurational entropy upon mixing is

$$\Delta S_m = k_B \ln \left(\frac{\Omega_{\text{after mixing}}}{\Omega_{\text{before mixing}}} \right), \quad (2.9)$$

where k_B is the Boltzmann's constant, $\Omega_{\text{before mixing}} = \Omega_{\text{solvent}} \Omega_{\text{macromolecules}}$ is the number of states before mixing, and $\Omega_{\text{after mixing}}$ is the number of states after mixing (i.e. the number of possibilities to place $n_{\text{macromolecules}}$ chains in a lattice such as the one in Figure 2.4). Using the model of Flory-Huggins, the variation of entropy is found to be

$$\Delta S_m = -k_B n_{\text{cell}} \left(\phi_1 \underbrace{\ln \phi_1}_{<0} + \frac{\phi_2}{n_s} \underbrace{\ln \phi_2}_{<0} \right) \Rightarrow \boxed{\Delta S_m > 0}, \quad (2.10)$$

¹ $F \triangleq U - TS$

²If the temperature significantly varies upon mixing, one should integrate the differential of the free energy, $dF = dU - TdS - SdT$.

where n_{cell} is the total number of cells in the lattice, and ϕ_1 and ϕ_2 are the volume fractions of the solvent and of the polymer, respectively. Since $\phi_1, \phi_2 \in [0, 1]$, it can be deduced from Equation 2.10 that the entropy will always increase upon mixing.

Internal energy of mixing ΔU_m

When the macromolecules are placed in the solvent, contacts between the macromolecules and the solvent are formed while contacts between solvent/solvent and segment/segment of the macromolecules are destroyed, as illustrated in Figure 2.5. In this figure, ω_{11} (resp. ω_{22}) is the energy required to form a contact between two molecules of solvent (resp. segments of the polymer chain) starting from two infinitely distant identical molecules (see Figure 2.5 before mixing). ω_{12} is defined in the same way but for the formation of a contact between a molecule of solvent and a segment of the polymer chain (see Figure 2.5 after mixing).

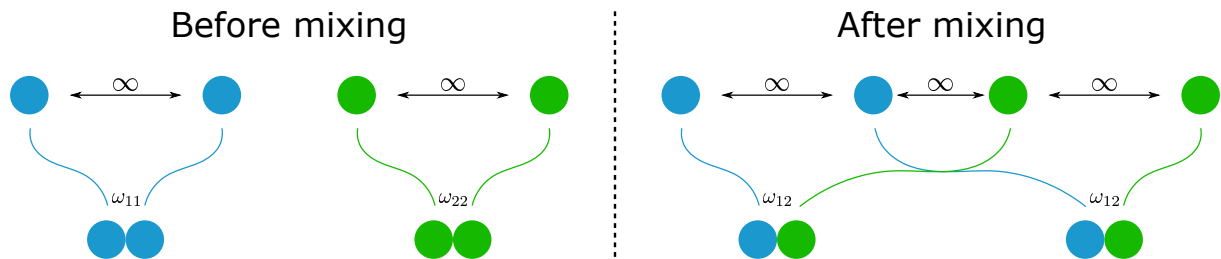


Figure 2.5: Scheme illustrating that the energy needed to create 2 contacts segment/solvent starting from the pure solvent and the polymer melt is equal to $2\omega_{12} - (\omega_{11} + \omega_{22})$.

Therefore, the energy needed to create a single contact segment/solvent starting from the pure solvent and the polymer melt, written $\Delta\omega_{12}$, is equal to

$$\Delta\omega_{12} \triangleq \omega_{12} - \frac{1}{2}(\omega_{11} + \omega_{22}). \quad (2.11)$$

If n_{12} contacts are formed, then the variation of the internal energy is equal to $\Delta U_m = n_{12}\Delta\omega_{12}$. Considering that a cell of the lattice is surrounded by z neighboring cells, the variation of the internal energy reads

$$\Delta U_m = (z - 2)n_{\text{solv}}\phi_2\Delta\omega_{12} = k_B T \chi_{12} n_{\text{solv}}\phi_2, \quad (2.12)$$

where n_{solv} is the number of cells occupied by the molecules of solvent, and where the interaction parameter has been defined as

$$\chi_{12} \triangleq \frac{(z - 2)\Delta\omega_{12}}{k_B T}, \quad (2.13)$$

which is a dimensionless number related to the needed energy to create a contact between the solvent and the solute compared to the thermal energy. If this interaction parameter is negative (resp. positive), then mixing the polymer in the solvent is an exothermic (resp. endothermic) process. The solution is called an athermal solution in the case of a null variation of the energy of mixing.

Helmholtz free energy of mixing ΔF_m

By combining Equations (2.8), (2.10), and (2.12), one can obtain

$$\Delta F_m = n_{\text{cell}} k_B T \left(\chi_{12} \phi_1 \phi_2 + \phi_1 \ln \phi_1 + \frac{\phi_2}{n_s} \ln \phi_2 \right), \quad (2.14)$$

which governs the phase diagrams of polymer solutions. By remembering that $\phi_1 = 1 - \phi_2$ and $R \triangleq k_B \mathcal{N}_A$, Equation 2.14 becomes

$$\Delta F_m = N_{\text{cell}} R T \left(\chi_{12} (1 - \phi_2) \phi_2 + (1 - \phi_2) \ln(1 - \phi_2) + \frac{\phi_2}{n_s} \ln \phi_2 \right), \quad (2.15)$$

where N_{cell} is the number of moles of cells in the lattice. From this equation, it is possible to plot $\Delta F_m(\phi_2, \chi_{12})$ as done in Figure 2.6 where $n_s = 10$ was fixed.

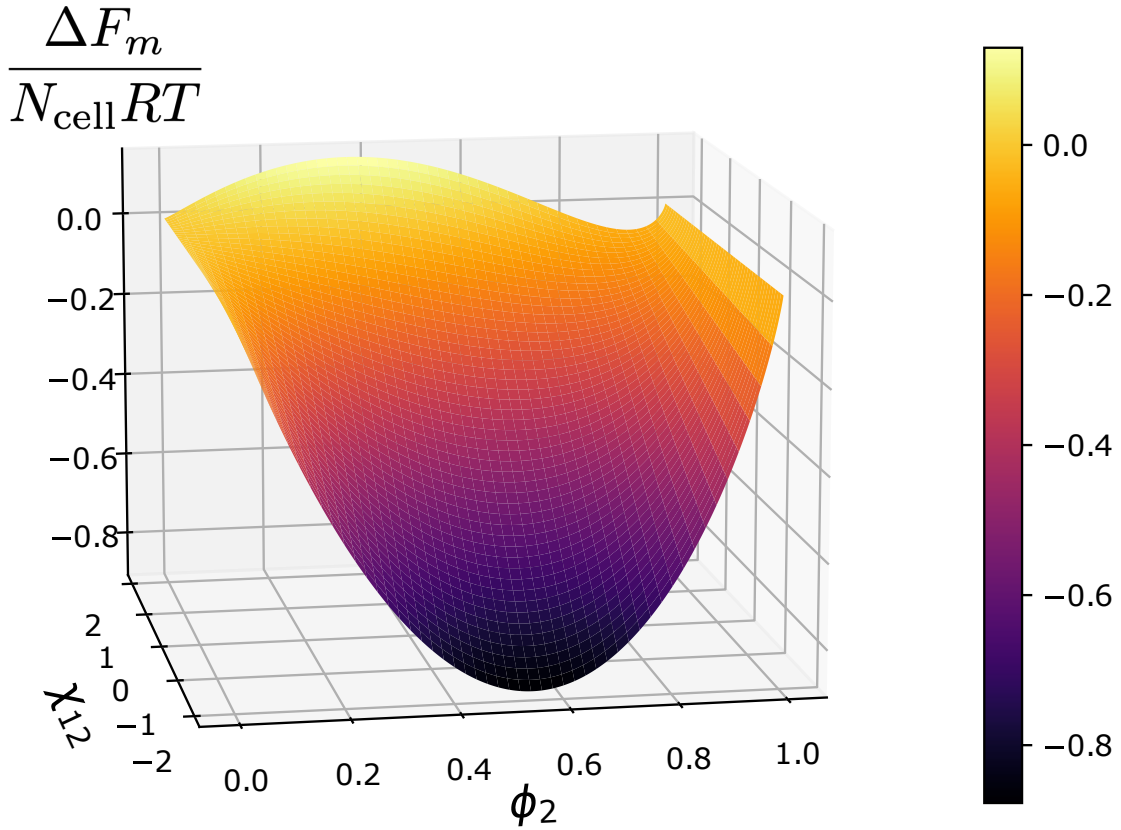


Figure 2.6: Three-dimensional graph of the free energy (divided by a constant factor) versus the interaction parameter χ_{12} and the fraction volume of macromolecules in the solution ϕ_2 . The number of Kuhn segments of each chain in the solution n_s is fixed to 10, as was selected in Jonas (2018) [7].

2.2.4 Phase diagram

There are two distinct cases when the macromolecules are placed in the solvent. The first possibility is that they form a stable solution, in which case the macromolecules are said to be soluble and form only one phase with the solvent. The second possibility is that they form an unstable solution and therefore separate in two different phases. One phase will be more concentrated in macromolecules and the other phase will be more diluted. The three factors determining whether or not the macromolecules are soluble in the solvent are the interaction parameter χ_{12} , the volume fraction of macromolecules ϕ_2 , and the number of Kuhn segments constituting a macromolecule n_s (taken as a parameter instead of a variable here, since 4-dimensional graphs are outside the scope of this master thesis).

The criterion for having an unstable solution with a fraction volume ϕ_{2P} of macromolecules is mathematically expressed as

$$\frac{\partial^2 \Delta F_m}{\partial \phi_2^2}(\phi_{2P}) < 0. \quad (2.16)$$

By differentiating twice the expression of ΔF_m in Equation 2.15, the criterion for finding the concentrations at the limit of an unstable solution becomes

$$2n_s\chi_{12}\phi_2^2 - (2n_s\chi_{12} - n_s + 1)\phi_2 + 1 = 0. \quad (2.17)$$

which is a second order polynomial in ϕ_2 . The discriminant of this polynomial only depends on χ_{12} and n_s . If the discriminant is negative, Equation 2.17 does not have any real root and the solution is stable for all concentrations. However, if the discriminant is positive, the polynomial has two real roots given by

$$\phi_2^\pm(\chi_{12}, n_s) = \frac{2n_s\chi_{12} - n_s + 1 \pm \sqrt{(-2n_s\chi_{12} + n_s - 1)^2 - 8n_s\chi_{12}}}{4n_s\chi_{12}} \quad (2.18)$$

and the solution will be unstable for the concentrations between these two roots. The two roots are plotted in Figure 2.7 for $n_s = 10$, along with a contour plot of the free energy of mixing ΔF_m . If the discriminant is equal to 0, a single concentration ϕ_2^c is unstable corresponding to an interaction parameter χ_{12}^c . These two critical values are given by

$$\phi_2^c = \frac{1}{\sqrt{n_s} + 1} \simeq \frac{1}{\sqrt{n_s}}, \quad (2.19)$$

$$\chi_{12}^c = \frac{1}{2} + \frac{1}{\sqrt{n_s}} + \frac{1}{2n_s} \simeq \frac{1}{2} + \frac{1}{\sqrt{n_s}}. \quad (2.20)$$

and are also plotted in Figure 2.7. It can be noticed that $\chi_{12}^c \rightarrow 1/2$ when $n_s \rightarrow \infty$.

2.2.5 Lower and upper critical solution temperatures

It would be more convenient to draw a phase diagram depending on the temperature instead of the interaction parameter, as it is the case in Figure 2.7. It is noticed in the definition of the interaction parameter (see Equation 2.13) that $\chi_{12} \propto T^{-1}$. However, the

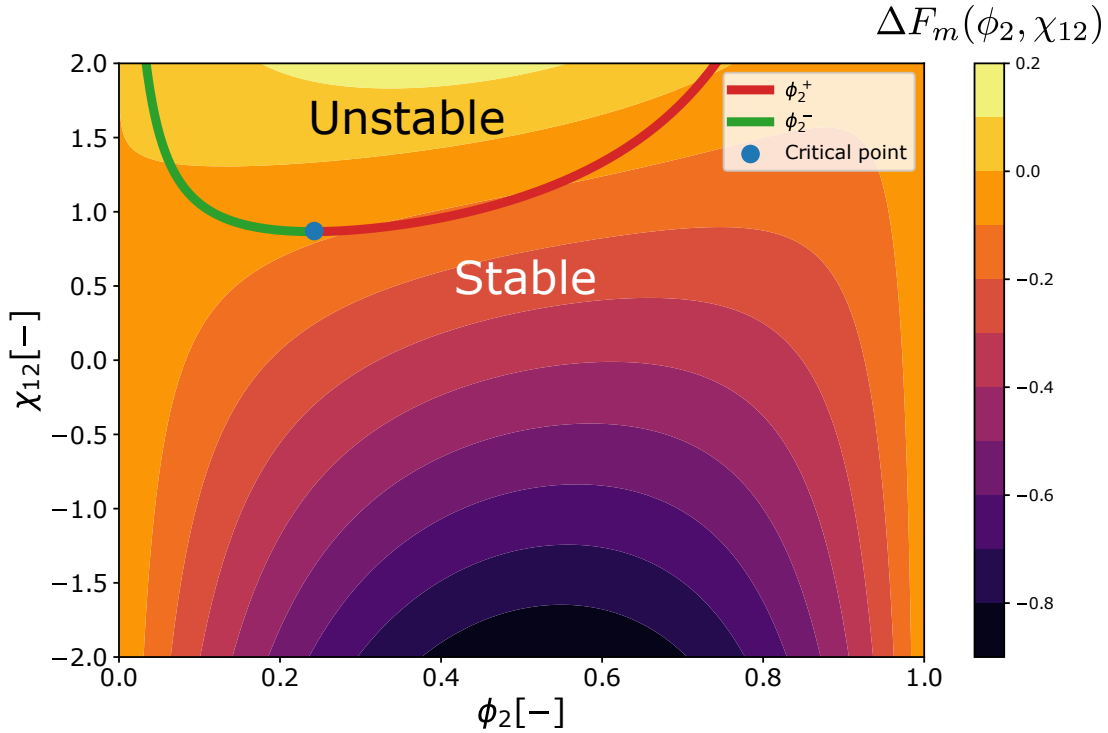


Figure 2.7: Contour plot of ΔF_m for $n_s = 10$. The two roots of Equation 2.17 are plotted as a function $\chi_{12}(\phi_2)$, determined from Equation 2.18.

interaction parameter has been defined using the model of Flory & Huggins which makes strong hypotheses. The interaction parameter can be measured experimentally³ and it has been found [8] that the interaction parameter is better expressed as

$$\chi_{12} = \chi_s + \frac{\chi_U}{T} \quad (2.21)$$

where χ_s and χ_U are admitted to arise from entropic and energetic contributions, respectively. The sign of χ_U is the same as the one of $\Delta\omega_{12}$. If χ_U is positive (resp. negative), the interaction parameter decreases (resp. increases) with temperature so that increasing (resp. decreasing) the temperature above (resp. below) a critical temperature, called the upper (resp. lower) critical solution temperature and shortened as UCST (resp. LCST), makes the macromolecules soluble in the solvent.

These two critical temperatures are indicated on the phase diagrams in Figure 2.8. If $\chi_U > 0$, as in Figure 2.8(a), then the contact between a solvent molecule and a chain segment is unfavorable. By increasing temperature, the system acquires the energy needed for forming these contacts and the macromolecules become soluble in the solvent. In the opposite case $\chi_U < 0$, as in Figure 2.8(b), the contact between a solvent molecule and a chain segment is favorable. The macromolecules are therefore soluble below the LCST but become insoluble when the temperature is raised above the LCST because the bonds (e.g. hydrogen bonds) between the solvent and the macromolecules are broken.

³With osmometry and static light scattering, as explained in [7].

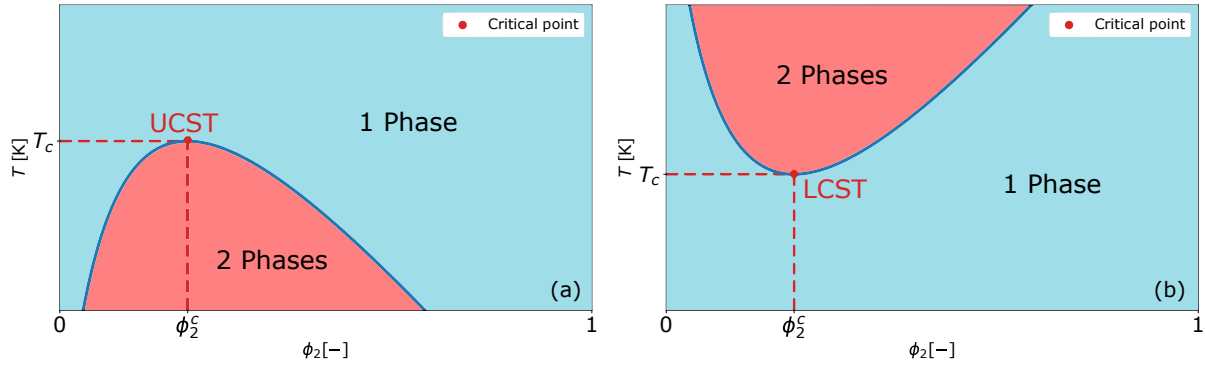


Figure 2.8: Phase diagram for **(a)** $\chi_U > 0$ exhibiting a UCST and for **(b)** $\chi_U < 0$ exhibiting a LCST. The blue region maps the solutions for which the macromolecules are soluble in solvent (only one phase) whereas the red region maps the solutions where the macromolecules are not soluble in solvent and thus separate into two distinguishable phases.

2.2.6 Thermoresponsive polymers

Firstly, it has been stressed in Section 2.2.2 that the swelling coefficient α depends on the interaction between the segments of the macromolecules and the molecules of solvent. Secondly, it has been demonstrated in Section 2.2.4 that the phase diagram depends on the interaction parameter χ_{12} , which in turn depends on the energy of formation of a contact between a segment of the macromolecule and a molecule of the solvent (see Equation 2.13). Therefore, it is not surprising to learn that the swelling coefficient varies when the interaction parameter is varied, which can be performed experimentally by *changing the temperature*.

More quantitatively, it can be shown that the Θ conditions are reached when

$$\chi_{12} = \frac{1}{2} = \lim_{n_s \rightarrow \infty} \chi_{12}^c, \quad (2.22)$$

which builds the bridge between the quality of a solvent and the associated phase diagram. As a reminder, χ_{12}^c is the critical value of the interaction parameter above which the solution is not soluble at every concentrations. Thus, “*This also defines Θ conditions as the ones for which a polymer of infinite molar mass reaches its critical point*” [7]. Since the critical value is always above 1/2 for macromolecules with a finite molar mass, a polymer in Θ conditions is always soluble.

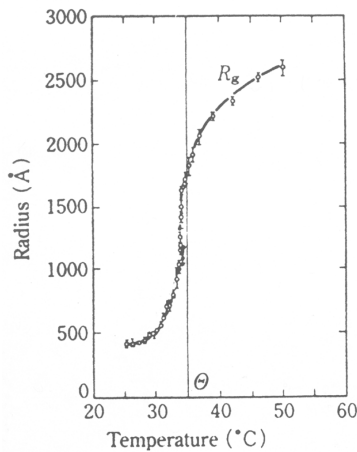


Figure 2.9: Variation of the radius of gyration of polystyrene in cyclohexane, depending on temperature. Taken from Sun *et al.* (1980) [9].

More important is the variation of the radius of gyration around T_θ ($\simeq T_c$ if n_s is sufficiently large) given in Figure 2.9. It is observed that the slope of R_G drastically increases when Θ conditions are reached. Since the swelling of the polymers has an important impact on their interaction with their surroundings, this critical temperature will be of great importance in what follows.

2.3 Chemistry of polymer brushes

This section focuses on the polymerization technique that allows to reach the physical properties that are desired for the polymer brushes in this work. Indeed, parameters like the LCST, the grafting density, the thickness, and the swelling coefficient of polymer brushes are controlled by numerous factors such as the polymerization technique, the choice of monomers and their proportions, or the time of polymerization. The ideal polymerization technique should achieve a high grafting density (the reasons will be explained in Section 2.4), control accurately the thickness of the brush, and lead to an homogeneous brush thickness in order to not create a profile at the surface. This technique exists and is called *surface-initiated atom transfer radical polymerization* (SI-ATRP).

2.3.1 Free radical polymerization

SI-ATRP is a complex process, such that it is easier to start by explaining fundamental principles of polymerization. The first step in this explanation is *free radical polymerization* (FRP), a type of chain-growth polymerization⁴ in which the active center is a free radical. An active center is the position of the growing macromolecule that will react with monomers for increasing the degree of polymerization. FRP is composed of three steps: initiation, propagation, and termination, hereunder described.

Initiation

The first step of initiation is shown in Figure 2.10(1). A molecule is dissociated into two radicals, which are the active centers on which the polymer will grow. This radical initiator molecule can be dissociated for example by heat or light [10]. The second step is shown in Figure 2.10(2), in which a first monomer is added onto the radical. The monomer just added then becomes the active center.

Propagation

In propagation, as shown in Figure 2.10(3), monomers are added one by one onto the active site of the growing chain.

Termination

In termination, as shown in Figure 2.10(4), the active site is deactivated and the chain is no longer able to grow. This deactivation can occur either through radical coupling (reaction of two active sites, cancelling each other) or disproportionation (transfer of hydrogen from one chain to the other) [10].

⁴In chain-reaction polymerization, monomers are added one by one to a long polymer chain by reacting with the active center.



Figure 2.10: Reactions occurring during FRP. **(1)** Formation of the initiator radical. **(2)** Addition of the initiator radical to monomer. **(3)** Addition of a monomer onto the active center of the growing molecule, repeated n times. **(4)** Termination of chain propagation. I = initiator, R = radical, M = monomer, P = polymer.

2.3.2 Controlled radical polymerization

Controlled radical polymerization (CRP) is an FRP in which the termination is reversible, so that the reaction (4) in Figure 2.10 should be replaced by an equilibrium. This equilibrium favors the dormant species, P_n in Figure 2.10, which are terminated polymers that still have a small probability to become active and thus to propagate the chain growth. This strong equilibrium towards the dormant species implies that there are not a lot of growing brushes with an active center $(\text{R}(\text{M})_n\text{M}\cdot$ in Figure 2.10). Therefore, the initiation step is much faster than propagation (the free radical does not react into dormant species) and all the chains can be considered as initiated before starting to grow. This reversibility hence leads to a very low dispersity in the growing polymers [11, 12].

2.3.3 Surface-initiated atom transfer radical polymerization

There are a few reactions that can lead to a reversible termination. One of them is *atom transfer radical polymerization* (ATRP), in which the active center of the growing chain is neutralized by reacting with an atom, thereby becoming temporarily inactive. For such polymerization to occur, one can use an alkyl halide R-X as an initiator (with for example $\text{X}=\text{Cl}$) and a transition metal as a catalyst (for example $\text{Cu}^{\text{I}}\text{Cl}$) [11, 13, 14].

Two approaches exist for growing polymer brushes on a surface:

1. The first of them is the “grafting to” approach where an end-functionalized polymer is grown in solution and then chemisorbed on a previously treated surface (see Figure 2.11(a)). Due to steric hindrance, polymer chains cannot easily reach the anchor points on the surface and only low grafting densities can be achieved [15–17].
2. The second one is the “grafting from” approach where the initiator is grafted onto the surface and the brushes are progressively grown from this initiator (see Figure 2.11(b)). Since the chains are growing at similar rates, the monomers can easily reach the active centers. Hence, the problem of steric hindrance from the “grafting to” approach does not occur and high density brushes can be produced. In addition, this technique allows an accurate control over composition, architecture, and brush thickness [15–17] and larger values can be achieved for the latter compared to the “grafting to” approach [18–21]. For all these properties, this second approach will be used in this master thesis

There are several ways to produce polymer brushes by controlled surface-initiated polymerization. These techniques are reviewed by Edmondson *et al.* (2004) [22], but only SI-ATRP is of interest here because it is experimentally accessible and chemically extremely versatile and robust [16, 22]. SI-ATRP follows the same scheme as ATRP with the difference that initiators are anchored onto the substrate. To summarize in one sentence, SI-ATRP produces polymer brushes with a very low dispersity (SI-ATRP $\in$ CRP), with a high grafting density, allows an accurate control over brush thickness, composition, architecture (SI-ATRP $\in$ “grafting from” approach), and is an efficient and robust technique.

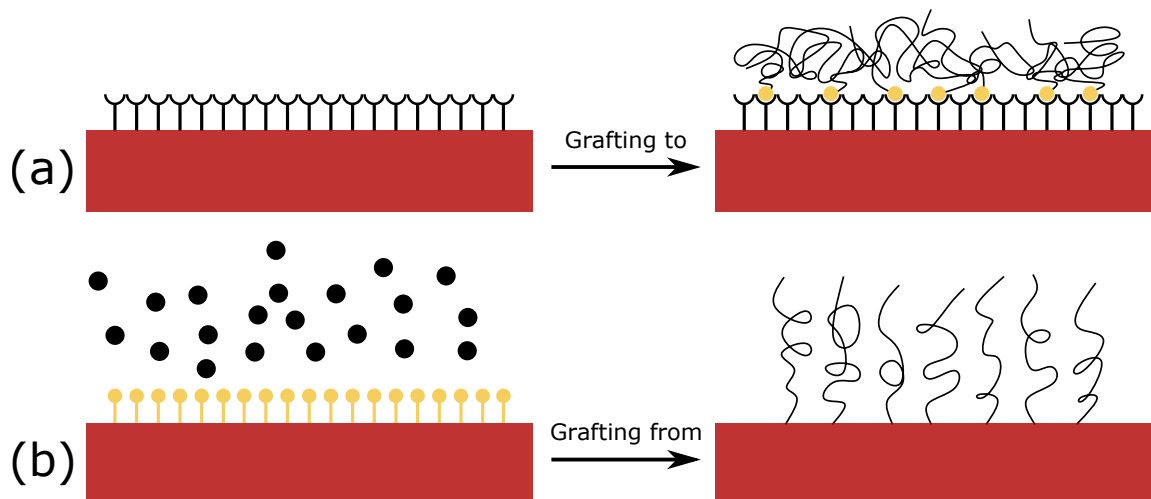


Figure 2.11: Schematics of the two approaches for growing polymer brushes. **(a)** “Grafting to” approach. The surface is treated for creating anchor points. The already grown polymer chains are then chemisorbed at the surface via a covalent bond between the anchor point and a functional group on the macromolecule (orange sphere). Many anchor points are virtually inactive because of the steric crowding of the already grafted chains. **(b)** “Grafting from” approach. The surface is treated for covering the surface with initiator molecules (orange spheres). The monomers in solution (black spheres) react with the initiator and are then added one by one during the propagation step.

2.4 Importance of the grafting density

SI-ATRP yields brushes with a high grafting density. Therefore, it is important to understand the impact of this density on the grown polymer layer in order to modify it for reaching the desired properties.

2.4.1 Effect on brush thickness

The grafting density (i.e. the number of tethered chains per unit of surface) defines how close are the polymer chains constituting the brushes, and therefore determines how the chains are interacting. If the grafting density is low (e.g. in Figure 2.11(a) with the “grafting to” approach), the chains will be far from each other and not significantly interact. In a similar way to a polymer in solution, this tethered polymer chain will adopt

the conformation of a coil, even if slightly different because the chain is anchored to the substrate at one end. Having such a coil is not desired in this work.

On the contrary, a high grafting density (e.g. in Figure 2.11(b) with the “grafting from” approach) means that the tethered chains are close to each other and that a chain will feel the presence of the other chains in its neighborhood. Due to the strong interaction arising from this proximity, the polymer chains are forced to stretch perpendicularly to the surface [15, 23]. It has been shown that the average brush thickness, L_e , evolves as

$$L_e \propto L_c \sigma^n, \quad (2.23)$$

where L_e is the equilibrium thickness of the swollen brush, L_c is the full length of the chain in the all-trans conformation, σ is the grafting density, and $n = 0.3 - 0.5$ (see Figure 2.12) for values of σ between 0.07 and 0.7 chains/nm², i.e in the high grafting density regime [24, 25]. This exponent is reduced to 1/3 in the “moderate density” regime [26], emphasizing the fact that the tethered chains are forced to stretch more and more when σ increases.

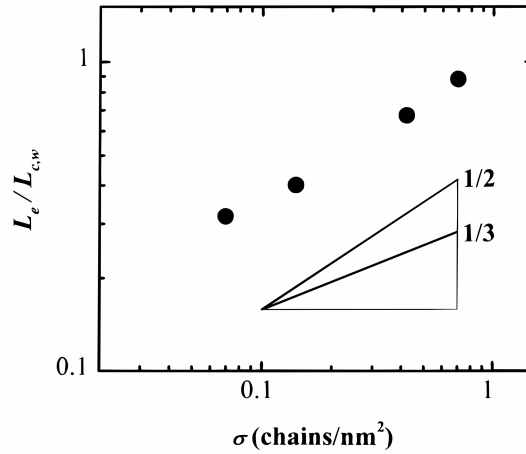


Figure 2.12: Log-log graph in the high grafting density regime plotting the ratio between the equilibrium thickness of the swollen brush L_e and the full length of the grafted chain in the all-trans conformation $L_{c,w} = (M_w/M_0)l_0$ with M_w and M_0 being the molecular weight of the chain and monomer respectively, and l_0 the length per monomer unit, versus the grafting density σ . The two continuous lines emphasize that L_e follows a power law with an exponent between 1/3 (case of moderate regime) and 1/2. Taken from Yamamoto *et al.* (2000) [25].

2.4.2 Effect on adsorption

When particles are placed in a solution with the polymer brush, three modes of adsorption are possible at the surface covered with the brush (see Figure 2.13). From the schematic presented in Figure 2.13, it is already intuitive that the active mode will depend both on the distance between the grafted chains and the size of the adsorbing particles. A high grafting density is likely to prevent primary and ternary adsorptions because of the very small distance between grafted chains [27, 28].

During secondary adsorption, the brush is compressed due to steric repulsion and is

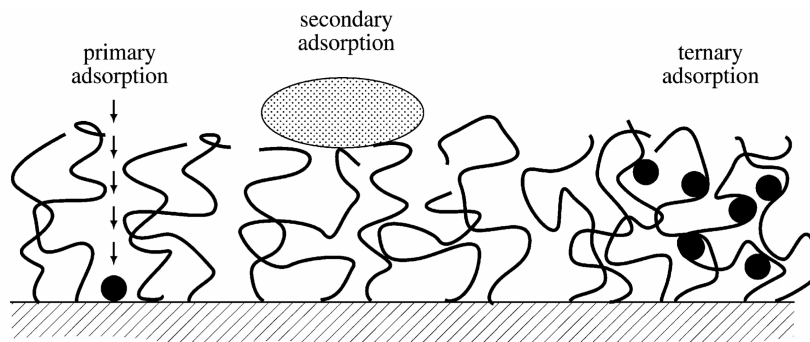


Figure 2.13: Three generic modes of adsorption of a particle on a polymeric layer grafted to a substrate. Primary adsorption: Particles are able to diffuse through the brush and adsorb on the substrate. Secondary adsorption: Particles are *not* able to diffuse through the brush and adsorb at the brush-solvent interface. Ternary adsorption: Particles are adsorbed within the brush layer. Taken from Currie *et al.* (2003) [27].

deformed away from its equilibrium structure. Upon compression, the increase in osmotic interactions⁵ (osmotic contribution in Figure 2.14(a)) in the grafted layer promotes separation to the equilibrium thickness of the layer, thus exerting a restoring force on the adsorbed particle [27]. Although much smaller than the osmotic contribution, the conformation entropy contribution⁶ to free energy in Figure 2.14(a) decreases upon compression and goes against stretching.

If the restoring force exerted on the adsorbed particle (osmotic repulsion contribution in Figure 2.14(b)) is larger than the attractive forces (van der Waals interaction contribution in Figure 2.14(b)), the particle could be desorbed from the brush-solvent interface. The attractive forces on the particle can come from the interaction with either the brush or the substrate. Indeed, the brush is only a few tens of nanometers, thus leaving the possibility to have long-range attractive interaction between the solute particle and the substrate. The total potential in Figure 2.14(b) highlights the fact that the polymer brush is seen as a potential barrier from the point of view of the particle. If the particle overcomes this barrier, it will be adsorbed on the substrate at a distance where van der Waals interaction and steric repulsion are balanced.

A theoretical study assuming that van der Waals forces are exerted on the particle, coming from the interaction with both the brush and the substrate, suggests that these attractive interactions can be mitigated by increasing the brush thickness. As a reminder from the previous section, increasing the grafting density increases the brush thickness and therefore also decreases the attractive interactions. On top of that, the grafting density must be increased for preventing primary adsorption [29–31]. In addition, it has been

⁵Osmotic interactions arise from the interaction between the chains and the solvent. For a good solvent, the chains tend to stretch to maximize this interaction. In short, this contribution is unfavorable to compression because it would decrease the attractive interaction between the solvent and the polymer brush.

⁶The conformation entropy contribution decreases when the chain is compressed because the number of states in the phase space increases, thereby increasing the entropy. In short, this contribution is favorable to compression because it increases the entropy of the brush.

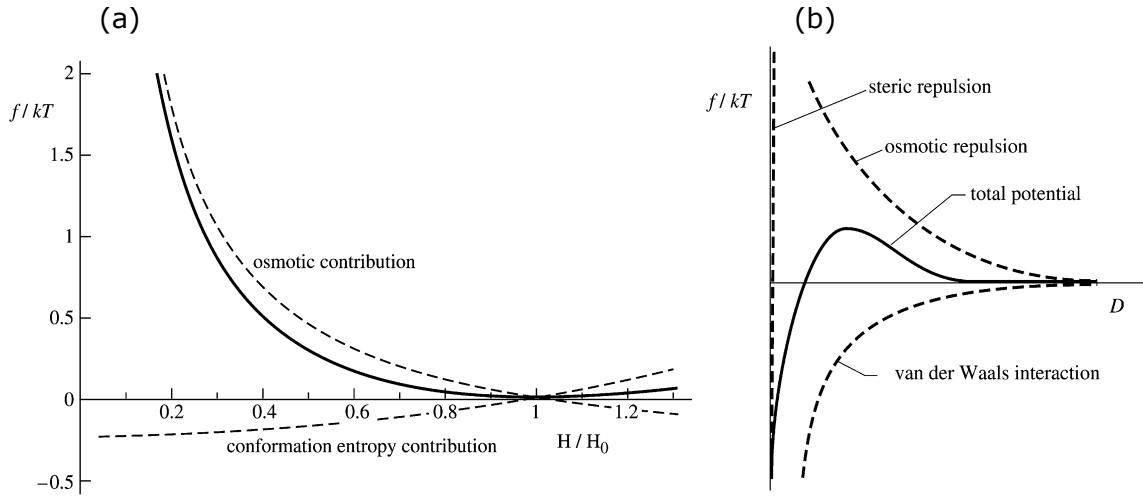


Figure 2.14: **(a)** Osmotic and conformation entropy contributions to the free energy of a *brush* stretched to a distance H (dashed lines). The sum of these two contributions gives the total free energy per unit area (solid line) in the mean field box approach. H_0 is the equilibrium distance. **(b)** The three interactions acting on a *particle* in close contact with a grafted layer (dashed lines) together with the total interaction potential (solid line). Taken from Currie *et al.* (2003) [27].

demonstrated experimentally that dense and long polymer brushes are more resistant to compression [24, 25], hence keeping the greatest possible distance between the particle and the substrate even when the particle compresses the brush.

Despite these encouraging results and due to all the possible attractive interactions, keeping surfaces and solute particles apart over nanometric scales remains challenging [27].

2.4.3 Effect on swelling coefficient

As discussed in Section 2.2.2, the swelling coefficient progressively decreases when the temperature is raised across the LCST. However, this coefficient does not only depend on temperature.

Both computational modeling [32] and experimental evidences [33–35] agree on the fact that the swelling ratio, representing the thickness variation between the swollen and the collapsed state, depend on both the molecular weight of the chains and on the surface coverage, at least for the thermoresponsive polymer Poly(N-isopropylacrylamide) (PNIPAM). The latter has been extensively studied because it exhibits an LCST in water around 32 °C close to physiological temperatures, and also because its LCST is relatively insensitive to environmental conditions (variation of pH, concentration, and chemical environment), which opens the road to biological applications [36].

At low molecular weight and density, PNIPAM remains swollen above the LCST and thus loses the expected temperature-responsive behavior [34, 37]. It is possible to increase the collapse of the chain by increasing both the grafting density and the molecular weight [33, 37]. In addition to this loss of thermoresponsive behavior, the reduced interchain interaction at low grafting density results in a less collective behavior of the PNIPAM

chains, leading to the broadening of the temperature range over which the collapse of the brush occurs [38].

At high grafting density, an opposite trend to the previous one is observed, as theoretically predicted by Mendez *et al.* (2005) [32]. Indeed, the collapse of the brush becomes weaker when the molecular weight [39] and the surface coverage [40] are increased (see Figure 2.15). Due to the high density and nonuniformity of the chains, the transition is broadened when increasing the grafting density [40, 41].

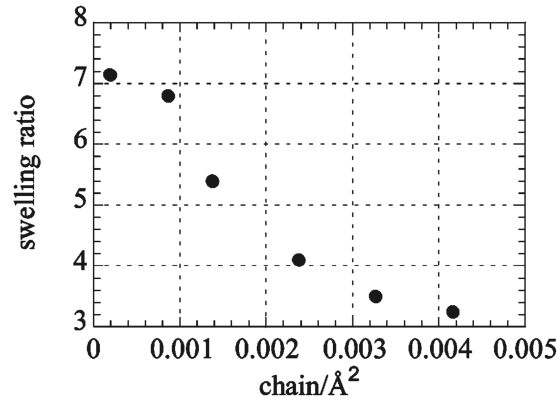


Figure 2.15: Graph for PNIPAM in water. Swelling coefficient α as a function of brush density. The swelling ratio of the brushes decreases from 7 to 3 when the number of grafted chains per unit area increases. Taken from Malham & Bureau (2010) [40].

Two opposite trends are observed at low and high grafting densities. Therefore, one can expect to find a maximal swelling ratio for an intermediate regime. Indeed, Figure 2.16 shows that PNIPAM brushes with intermediate grafting densities and high molecular weights display the largest conformational change with temperature [35].

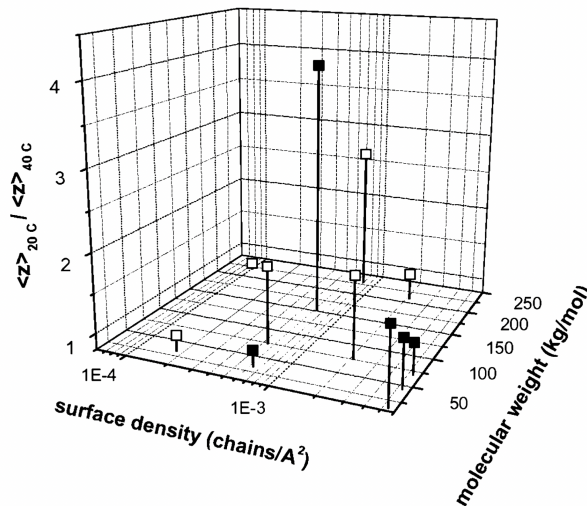


Figure 2.16: Graph for PNIPAM in D₂O. Ratio of the first moments of the segment concentration profile at 20 and 40 °C as a function of molecular weight and surface density, as determined with neutron reflection. This ratio provides an estimation of the swelling coefficient. Open (filled) symbols indicate samples grafted from silicon oxide (gold). Taken from Yim *et al.* (2006) [35].

2.5 Tunability of the transition temperature

As mentioned in Section 2.4.3, PNIPAM has been the “gold standard” of thermoresponsive polymers because its LCST does not depend on environmental conditions. However, it would be interesting to be able to tune the transition temperature of a new type of polymer brush during the polymerization step. Ideally, this new polymer should keep the properties of PNIPAM that made it so popular among thermoresponsive polymers.

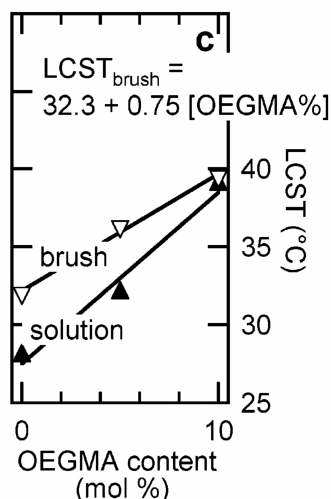


Figure 2.17: LCST of P(MEO₂MA-*co*-OEGMA) as a function of the OEGMA content. A comparison is made between the LCST in solution (data from Lutz (2006) [42]) and the one of the brush. Taken from Jonas *et al.* (2007) [43].

The random copolymers made of 2-(2-methoxyethoxy)ethyl methacrylate (MEO₂MA) and oligo(ethylene glycol) methacrylate (OEGMA) exhibit LCST values between 26 (MEO₂MA) and 90 °C (OEGMA) that can be finely tuned by adjusting the content in OEGMA [42, 44]. Figure 2.17 is a graph of the collapse temperature illustrating the ability to tune the LCST in the physiological range [43]. Figure 2.18 highlights the fact that the copolymer P(MEO₂MA-*co*-OEGMA) constituted in average of 5% of OEGMA displays a thermoresponsive behavior comparable or even superior to PNIPAM. Indeed, the LCST of these polymer brushes is less sensitive to the environmental conditions than the one of PNIPAM. In addition, PNIPAM was shown to be moderately cytotoxic at 37 °C, which is not the case of poly(ethylene glycol)-based copolymers that are expected to be nontoxic and non-immunogenic [45].

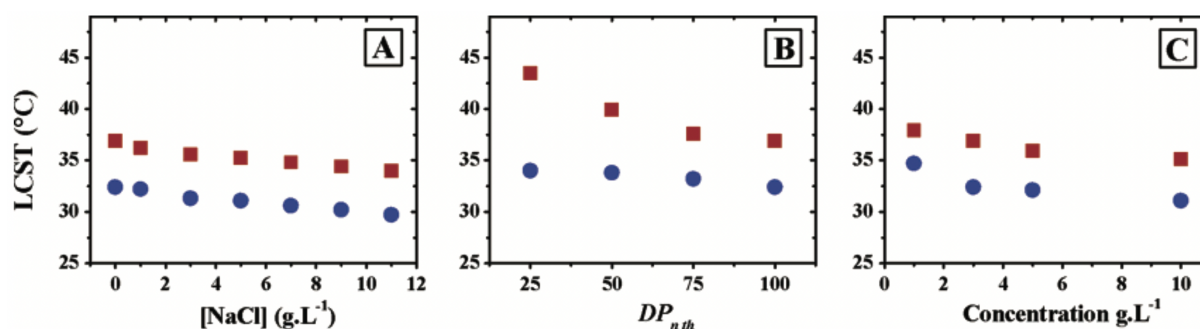


Figure 2.18: LCST as a function of the (A) NaCl concentration (B) theoretical degree of polymerization (C) polymer concentration in DI water. In all figures, cloud points of P(MEO₂MA-*co*-OEGMA) (5% in molar mass of OEGMA) and PNIPAM are represented by blue dots and red squares, respectively. Taken from Lutz *et al.* (2006) [46].

2.6 Tuning cell-surface interactions for antifouling

Biological implants such as catheters, pacemakers, mechanical heart valves, or prostheses, may, if not fully sterile, be covered by microorganisms that produce extracellular polysaccharides, resulting in the formation of a biofilm. The matrix of this biofilm is known to decrease the diffusion of antibiotics with physical and chemical barriers [47], making bacteria more resistant to antimicrobial agents and leading to infections [48, 49]. These infections have clinical and economical consequences [50] and can even lead to death [51, 52]. A solution is to control the interactions between the cell and the surface in order to prevent the creation of this biofilm.

2.6.1 Interaction of bacteria with a substrate

To control the adsorption of bacteria, it is important to understand how they interact with a surface. Busscher & Weerkamp (1987) [53] suggested that a mechanism constituted of three steps leads to the adhesion of bacteria on a substrate. If the separation distance is written as d ,

1. $d > 50$ nm: Only van der Waals forces operate. Therefore, the bacterium is attracted towards the surface. At this stage, the interaction between the bacterium and the substrate is non-specific.
2. $10 \text{ nm} < d < 20 \text{ nm}$: Attractive van der Waals forces and electrostatic repulsion are both operating so that an equilibrium position exists in this range of distances. The adhesion of the bacterium at this position is initially reversible, but can become irreversible due to a rearrangement of the bacteria on the surface, leading to specific short-range interactions. This rearrangement can occur in the presence of an hydrophobic substrate with a dehydrated surface, thus enabling specific short-range interactions to occur.
3. $d < 1.5$ nm: Attractive and specific interactions such as hydrogen bonding can take place, at the condition of having an hydrophobic surface for facilitating direct contact between bacteria. This contact is important because it allows to overcome the electrostatic potential barrier from step 2.

The importance of this hydrophobic surface for the adhesion of bacteria was further emphasized by Cerca *et al.* (2005) [54], who found that *Staphylococcus epidermidis* is adhering better onto hydrophobic surfaces than onto hydrophilic surfaces.

2.6.2 Tunable interaction of bacteria with a polymer brush

The solubility of polymers in solution was discussed in Section 2.2.5. The same principles apply for hydrophilic polymer brushes. Below the LCST, the brush is soluble so that it is in a swollen and hydrated state. When this hydrophilicity is added to the osmotic

repulsion coming from the compression of the brush, nothing at the surface is favorable for the adsorption of bacteria. When the temperature is raised above the LCST, the brush collapses and becomes dehydrated, allowing bacteria to adsorb at the surface.

Tang & Eaton (1993) [55, 56] found evidences that the adsorption of serum proteins on the substrate, occurring within seconds [57, 58], was also playing a role in the interaction between the cells and the surface. The schematic in Figure 2.19 illustrates that the adsorption of these proteins as well as the adhesion of cells can be tuned by controlling the temperature of the brush [59].

The resistance of brushes based on oligo(ethylene glycol), grown using SI-ATRP, against adsorption of proteins and cells has been demonstrated by Ma *et al.* (2004, 2006) [1, 2].

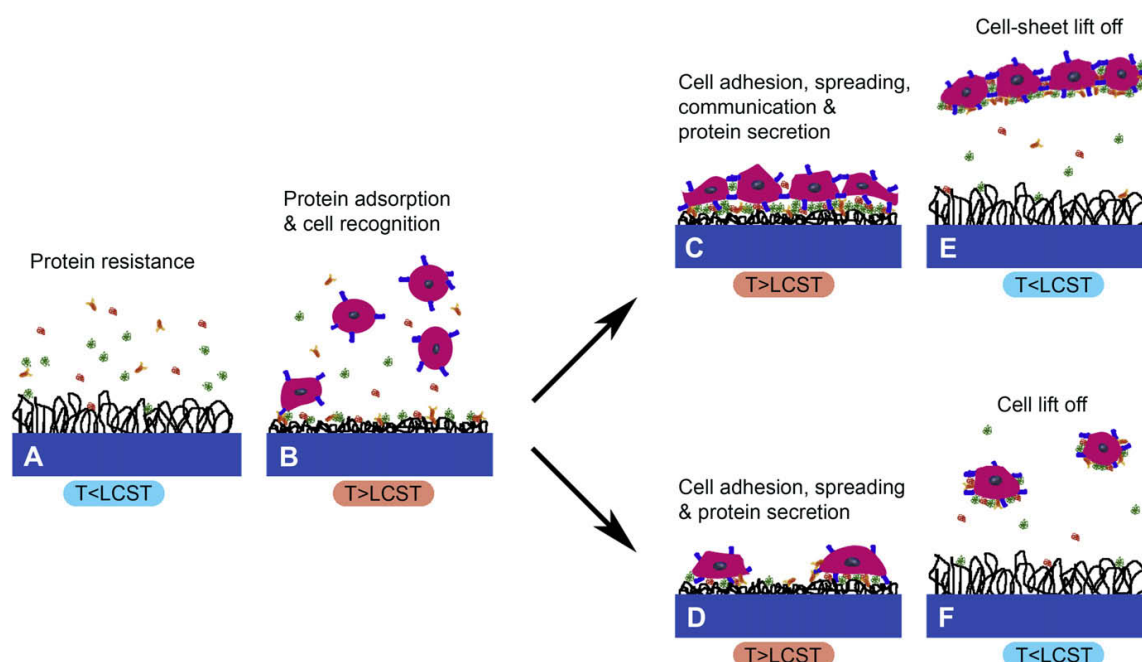


Figure 2.19: A model for thermosensitive cell attachment. **(A)** Below the transition temperature the surface resists protein adsorption and cell attachment. **(B)** Raising the temperature above the LCST allows adsorption of serum proteins and cell attachment. **(C)** During extended cell culture, secretion of extracellular proteins along with cell proliferation and communication results in confluent cell sheets. **(D)** Low seeding density or short cell incubation times results in adherent cells without extensive cell–cell junction formation. **(E & F)** Cooling to below the LCST allows release of intact cells or cell sheets along with associated extracellular matrix proteins. Taken from Cole *et al.* (2009) [59].

2.6.3 Antifouling surface with antimicrobial peptide

Glinel *et al.* (2009) [3] combined the nonadhesive properties of P(MEO₂MA-*co*-HOEGMA) with biocidal properties by grafting a natural defense peptide on the hydroxyl groups of the brush. Figure 2.20 shows that the selected peptide, magainin I, successfully kills *Listeria ivanovii* [3]. Once the bacteria are dead, they cover the surface and thus slowly deactivate the biocidal behavior of the surface.

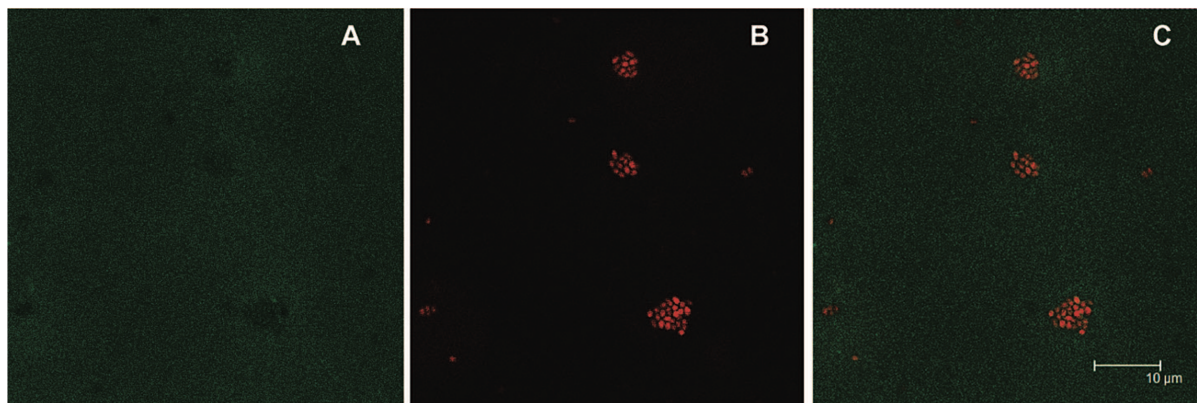


Figure 2.20: Confocal Laser Scanning Fluorescence Microscopy images of P(MEO₂MA-*co*-HOEGMA) brush functionalized with magainin I incubated in the presence of *L. ivanovii* and subsequently stained with the LIVE/DEAD viability kit. **(A)** green channel image corresponding to alive stained bacteria; **(B)** red channel image corresponding to dead bacteria; **(C)** overlay image built from (A) and (B). Taken from Glinel *et al.* (2009) [3].

2.7 Motivations of this work

The previous solutions for preventing the creation of a biofilm still have drawbacks for long term applications of biofouling surfaces. To this day, bacteria has always found a way to adsorb somewhere on the surface in spite of the nonadhesive behavior of the brush described in Section 2.6.2 [60–63]. This preliminary adsorption enables more bacteria to adsorb and ultimately leads to the creation of a biofilm.

The functionalization of the brush with an antimicrobial peptide, as discussed in Section 2.6.3, allows to kill the adsorbed bacteria. However, the dead bacteria progressively covers the polymer brush, thus deactivating this protective layer. Again, a biofilm will inevitably form.

All the antifouling surfaces studied until here have the common feature to be static. This master thesis aims at designing and characterizing a surface able to create some dynamics in the polymer brush. Ultimately, the goal will be to create an oscillating wave along the substrate, using the thermoresponsive behavior of P(MEO₂MA- *co*-HOEGMA), that will enter in resonance with the movement of bacteria at its surface. Doing so, the adsorption of bacteria, and thus the creation of a biofilm, could be completely removed. In addition, such surface would allow to better understand the dynamical behavior of bacteria at the surface, opening the door to new solutions for antifouling surfaces.

As mentioned in Chapter 1, the wave will be induced by an array of equally spaced electrodes that will heat locally the polymer brush. By alternatively turning on and off a current that will pass through the electrodes, this wave at the surface will oscillate in time and thus create the intended dynamic surface.

Chapter 3

Finite element simulations

The first step in the creation of a device is to design it. However, it can be expensive and time-consuming to fabricate and characterize several designs in reality. In this case, simulations are of great help because they are faster and cheaper, but still provide reliable results. In this section, simulations using finite element methods are developed to better understand the parameters that influence the temperature field in the system, especially around the polymer brush. The parameters of interest are the thicknesses of the two silica layers, the current passing through the electrodes that dissipates heat, the heating time, and the distance between adjacent electrodes.

This chapter is accompanied by Appendix A which gives the physical parameters of the material, the equations used for the simulations, and justifies the finite element mesh selected for the system.

3.1 Real system to simulate

In a first time, the geometry of the device must be created in *Comsol Multiphysics*. The simulations will need to acquire some information from the real system through calibration measurements. Therefore, the system implemented in the simulations needs to reproduce the experimental setup used for extracting this information from the real system, made of the sample placed between a Peltier cell and a liquid cell.

The geometry of the system in *Comsol Multiphysics* is presented in Figure 3.1. The silicon wafer with water on top of it is presented in Figure 3.1(a). This water is contained in a liquid cell (see Figure 3.2) and aims to reproduce physiological conditions. These physiological conditions are an important aspect of the experiment since it affects the solubility of the thermoresponsive polymers which is an essential property for creating a pulsing surface or standing waves at the surface. Figure 3.1(b) shows 2 out of the 32 electrodes that are making the heating network. Finally, Figure 3.1(c) highlights an electrode surrounded by SiO_2 with its dimensions. These dimensions are very likely to change because of the influence they have on the temperature profile.

It is important to take advantage of the device symmetry because it opens the possibility to simulate the real system made of 3 dimensions with a system made of only 2 dimensions.

This dimensional reduction is a huge advantage because it drastically reduces the computing time.

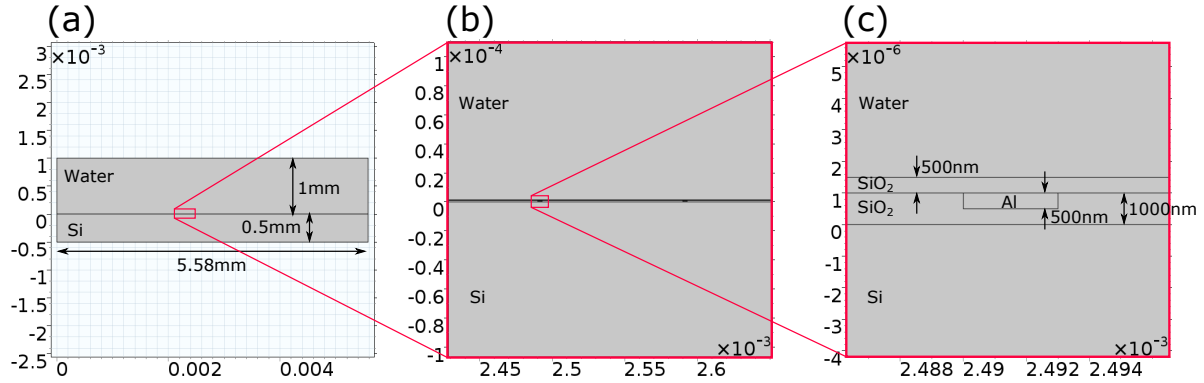


Figure 3.1: Geometry of the simulated system in *Comsol Multiphysics*. (a) Overview of the sample with the dimensions of the water-filled cell and Si. (b) Magnified view of (a) where the SiO₂ layers and the Al electrodes start to be visible. (c) Magnified view of (b) where the SiO₂ layers and one out of the 32 electrodes are clearly visible with their associated dimensions. The units of both axes are in meters.

3.2 Calibration of the simulated system

In order to run a simulation providing quantitative results, one must carefully set the physical parameters of the system that determine the heat transfers inside and outwards the system. These parameters are the heat transfer coefficients between the device and the air surrounding it, as well as the thickness of the layer of air between the device and the Peltier cell. This thin layer of air is there to represent a non-ideal thermal contact. These three degrees of freedom will be fixed in order to reproduce experimental results. Additionally, these heat transfer coefficients are needed in order to provide Neumann boundary conditions which are mandatory to run simulations.

3.2.1 Experimental measurements

To keep the system as simple as possible, the electrodes are turned off during the experiment that calibrates the simulations. The parameter that is varied is the temperature of the Peltier cell while the parameter that is measured and used for calibration is the temperature at the top of water. A type K thermocouple is used to measure the temperature of water. These thermocouples are provided with tables allowing the conversion of a finite number of voltage values into temperatures. In order to convert any voltage into its associated temperature, a linear approximation can be used to fit the data provided in Ref. [64], as shown in Figure 3.3(a). The graph of the temperature of water as a function of the temperature of the Peltier cell is in Figure 3.3(b), which is obtained after the conversion of the measured thermoelectric voltage into the temperature of water. It can be observed that the experimental data are well fitted with a line.

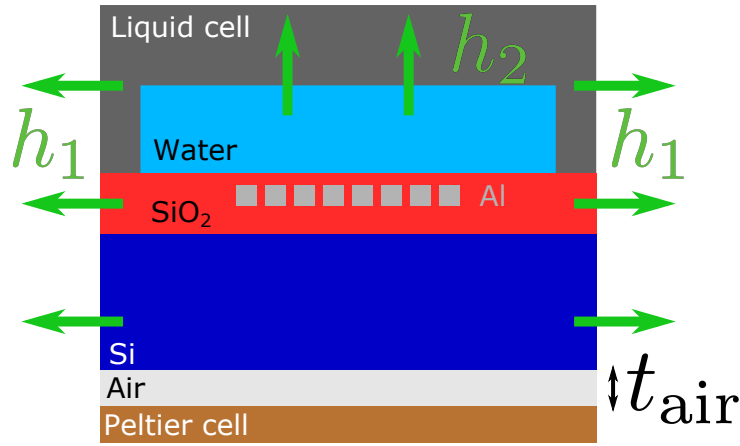


Figure 3.2: Schematics of the simulated system, reproducing the setup of ellipsometry that provides the experimental results. The three parameters that can be controlled are represented with arrows: the heat transfer from the device to air h_1 , the heat transfer from water to the liquid cell h_2 , and the thickness of the layer of air between the device and the Peltier cell t_{air} . The two heat transfer coefficients h_1 and h_2 include the transfer of heat through conduction, convection, and radiation.

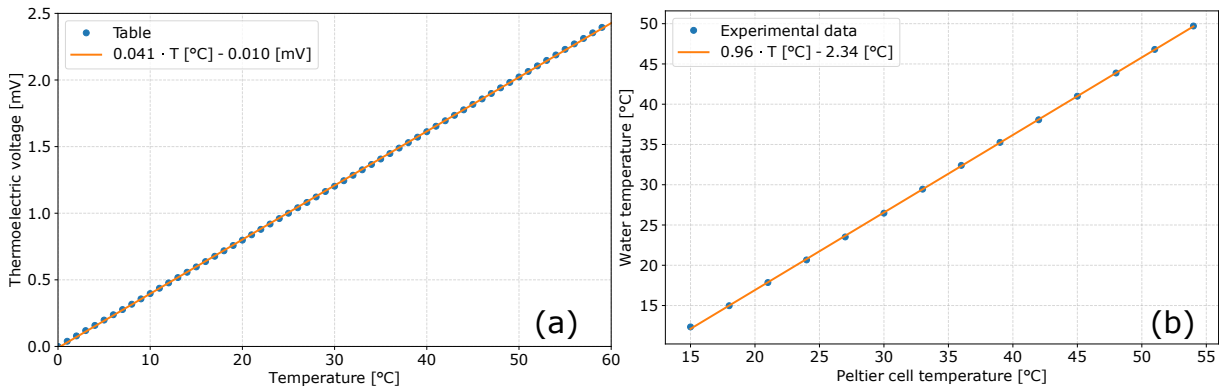


Figure 3.3: **(a)** Calibration graph of the thermocouple in a temperature range going from 0°C to 60°C . The orange straight line is fitting the blue markers which are values that can be found in a table. **(b)** Graph of the water temperature, measured with a type K thermocouple, against the temperature of the Peltier cell, set by the user.

3.2.2 Simulated system

The physical parameters of the system that are used in the simulations are calibrated by reproducing the fit obtained in Figure 3.3(b) with *Comsol Multiphysics*. Since the temperature of water (at the top of the system) is directly affected by the heat coming from the Peltier cell (at the bottom of the system), the heat transfers in the simulations should reproduce well the heat transfers in real system if they are able to reproduce the line in Figure 3.3(b). Several points will be fitted for different Peltier cell temperatures because it is more reliable than just trying to reproduce the same temperature of water for a single Peltier cell temperature. Indeed, the study of the system at a single temperature would give an unreasonable importance to the external temperature, which should be irrelevant for setting the value heat transfer coefficients. For example, if the exterior and Peltier cell temperatures are fixed to 15°C , the temperature of water will always be 15°C .

too. With this example, it is clear that better results would be obtained by using other Peltier cell temperatures. The exterior temperature will be here fixed to 10°C ¹.

The parameters shown in Figure 3.2 can be tuned in order to obtain the values that will yield the best fit. It is expected that increasing h_1 and h_2 will increase the heat transfers towards the external air at a temperature of 10°C . Since the water will always be at a higher temperature, its temperature will decrease if h_1 and h_2 are increased. In a similar way, increasing the thickness of the layer of air t_{air} will decrease the heat transfer from the Peltier cell (supposed to be at a higher temperature) towards water and will thus reduce the temperature of the latter.

As depicted in Figure 3.4(a), the temperature of water is evaluated in the top part of water, at the center of the system. This position has been chosen because it is the approximate location of the thermocouple junction during the experiments. The evolution of the temperature of water using a first estimation of the parameters is presented in Figure 3.4(b). Since the system was at equilibrium during the experimental measurements, the *stationary* solution is calculated during the calibration of the simulations. In a similar way to the experimental data, the temperature of water is increasing linearly with the temperature of the Peltier cell. This linearity already highlights that the geometry of the device depicted in Figure 3.1 is able to reproduce the experimental data. However, the parameters need to be adjusted in order to enhance the correspondence between the simulations and the data measured in reality.

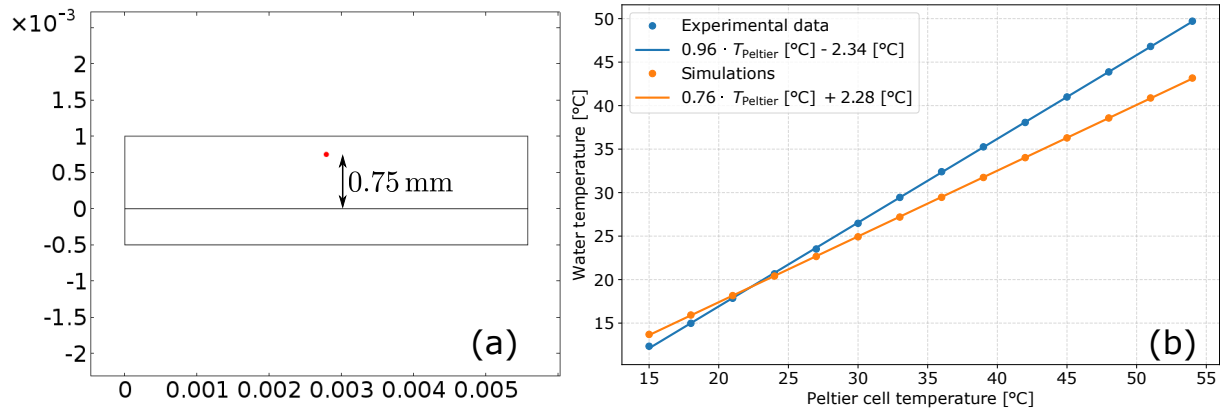


Figure 3.4: **(a)** The red dot on the system, located 0.75mm above the Si layer, is the location where the temperature of water is evaluated. **(b)** Graph showing the experimental results (blue) and the simulation of the temperature of water versus the temperature of the Peltier cell (orange). The parameters are $h_1 = h_2 = 300\text{W}/\text{m}^2 \cdot \text{K}$ and $t_{\text{air}} = 500\text{ nm}$.

The influence of the variation of each parameter individually is emphasized in Figure 3.5(a). It can be noticed that only h_2 significantly modifies the temperature of water at the location where it is estimated. By reducing this parameter by a factor 2 (red line), the slope of the line has increased while the independent term has been decreased, which increases the correspondence with the experimental data. In contrast, the variation of the temperature of water when h_1 and t_{air} are varied is negligible (green and purple lines). Therefore, h_2 can still be decreased in order to get the simulations closer to the reality.

¹Actually, it is not that cold in the room where the experiments were performed. However, this low temperature was required for obtaining results that are able fit the real system.

The physical parameters providing the best fitting of the experimental data are provided in Figure 3.5(b). This linear approximation is the one with the closest slope and independent term compared to the linear fit of the experimental data. The reason why it is complicated to obtain a better fit is that increasing h_2 and t_{air} will significantly decrease the temperature of water at high Peltier cell temperature while it is almost not affected at low Peltier cell temperature where the fit could be enhanced². Therefore, these physical parameters and the external temperature of 10°C are optimal and considered as fixed for the following simulations.

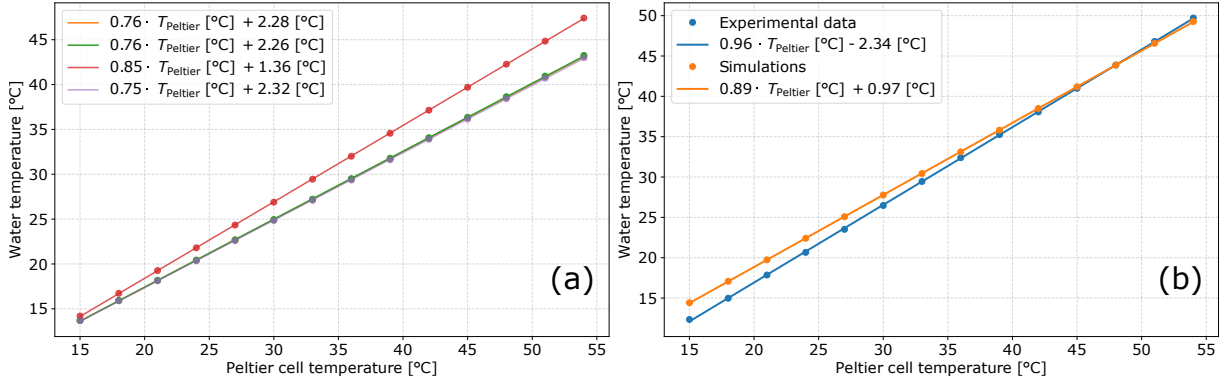


Figure 3.5: **(a)** Graph highlighting the effect of each parameter by varying them individually. The orange line is the reference one. $h_1 = h_2 = 300\text{W/m}^2 \cdot \text{K}$, $t_{\text{air}} = 0.5\mu\text{m}$ (orange) $h_1 = 150\text{W/m}^2 \cdot \text{K}$ (green) $h_2 = 150\text{W/m}^2 \cdot \text{K}$ (red) $t_{\text{air}} = 10\mu\text{m}$ (purple). **(b)** Graph showing the experimental results and the best fit obtained with simulations. The parameters are $h_1 = 10\text{W/m}^2 \cdot \text{K}$, $h_2 = 100\text{W/m}^2 \cdot \text{K}$, and $t_{\text{air}} = 2\mu\text{m}$.

Actually, h_1 mainly affects the temperature profile at the sides of the system but not at all in the center, as depicted in Figure 3.6. There are two reasons to not determine this parameter more precisely. The first is that it is very complicated to measure experimentally the temperature on the edges of the system. The second is that the active area of the sample is in the center of the sample and is very likely to be insensitive to a small variation of h_1 .

3.3 “Pulsing” surface with one circuit

The simulations are now calibrated and can be used for predicting the temperature profile in the sample when the system is heated by the electrodes with the Peltier cell turned off. In a first time, the system is studied with the stationary solution, which is expected to be reached quickly. In a second time, the time dependency of the system will be studied in Section 3.3.4. This section will confirm the relevance of the stationary solution for studying the system and will allow to determine the time constants for the local and global heat transfers in the system. It should be already emphasized that these simulations are not expected to reproduce accurately the real system since it does not include all the complex phenomena of fluid mechanics such as the natural convection

²Since $q = h|T_{\text{air}} - T_{\text{water}}|$, it makes sense that higher temperature differences between air and water are more affected by the increase in h .

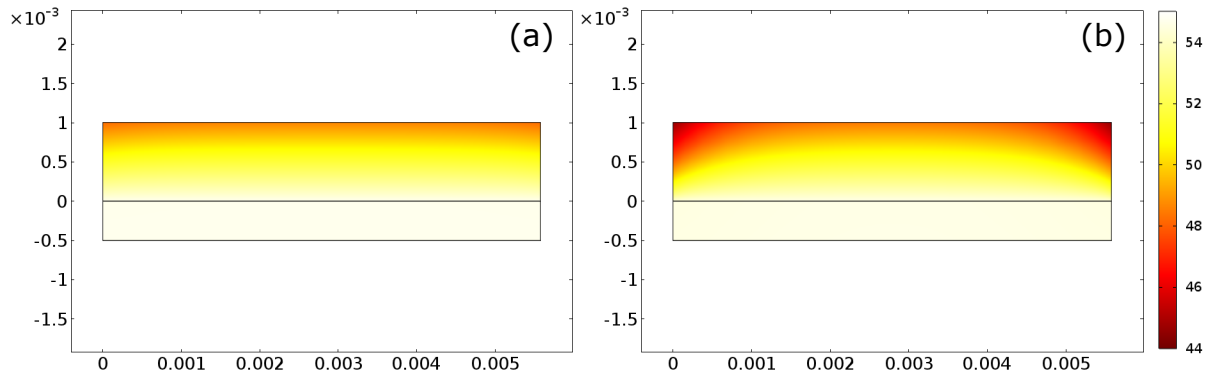


Figure 3.6: Temperature profile in the system with $T_{\text{Peltier}} = 55\text{ }^{\circ}\text{C}$. **(a)** $h_1 = 10\text{ W/m}^2 \cdot \text{K}$ and the temperature of water at the location indicated in Figure 3.4(a) is $50.18\text{ }^{\circ}\text{C}$. **(b)** $h_1 = 100\text{ W/m}^2 \cdot \text{K}$ and the temperature of water is $50.00\text{ }^{\circ}\text{C}$, very close to the value found in (a).

arising from a difference of temperature. However, they are expected to be sufficiently reliable for providing an insight into the design needed for producing a pulsing surface.

Before entering the heart of the matter, it is important to realize that the surface studied here is not really pulsed. Indeed, the samples that will be studied in Chapter 5 do not produce a pulsing surface but rather a surface with oscillating holes above the electrodes. The reason is that the experimental investigation of the polymers with ellipsometry requires a relatively large distance between the electrodes, as it will be discussed in Section 5.5. Therefore, the electrodes cannot be placed sufficiently close to each other in order to create an homogeneously pulsing surface.

Nevertheless, the system with one circuit is still able to create some oscillating holes at the location of the electrodes and can lead to interesting interactions with particles at the surface. Indeed, the polymer brush should remain swollen between the electrodes ($T < \text{LCST}$, not heated) and alternate between collapsed and swollen states above the electrodes. In that case, one could imagine that the particles located between the electrodes will diffuse towards the electrodes because of their favorable interaction with the polymer chains in their collapsed state ($T > \text{LCST}$, heated). If these particles do indeed reach the electrodes, they will be desorbed from the surface when the electrodes will be turned off. This scheme was illustrated in Figure 2.19. In order to have this transition, the difference of temperature has to be equal to $10\text{ }^{\circ}\text{C}$, which is the span of temperature over which the transition from a swollen to a collapsed state occurs for $\text{P}(\text{MEO}_2\text{MA-co-OEGMA})$ brushes (this span can even go up to $15\text{ }^{\circ}\text{C}$) [65]. The transition starts around $20\text{ }^{\circ}\text{C}$ if OEGMA monomer is not added during brush growing but can be tuned by adjusting the OEGMA composition (see Section 2.5).

This section thus focuses on the creation of a design allowing this scenario. To do so, some “knobs” must be found in order to tune the thermal profile at the surface of the sample. Two factors that are both tunable and influencing the thermal profile in water are the thicknesses of the two layers of SiO_2 . More precisely, the thickness of these two layers

will be adjusted to control the temperature of water at a distance of up to 100 nm from the sample surface, which is the typical thickness of the polymer brush. Figure 3.7 indicates the two locations where the temperature is estimated. In addition to its influence on the gradient of temperature, the top oxide layer of SiO_2 acts as a dielectric layer and needs to be thick enough to prevent a dielectric breakdown between the electrodes, wired to a voltage source, and water. Hence, $t_{\text{BottomOxide}}$ has to be adjusted in order to minimize the required voltage for reaching the gradient of temperature while t_{TopOxide} has to be thick enough for preventing the dielectric breakdown but remain thin for allowing a good heat transfer from the electrodes to water.

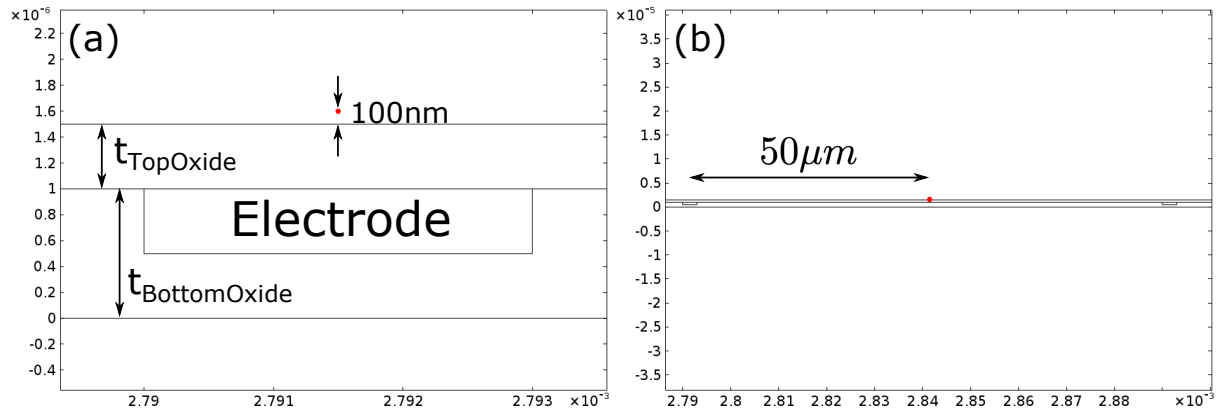


Figure 3.7: The temperature of water is estimated 100 nm (a) above the electrodes (b) between the electrodes.

3.3.1 Influence of the bottom oxide thickness

The resistance of the heat transfer from the electrodes towards the silicon substrate is increased when $t_{\text{BottomOxide}}$ is increased. One can therefore expect an increase of the temperature just above the electrodes during heating, whereas the temperature between the electrodes will be less affected. Hence, the gradient of temperature should increase with an increasing $t_{\text{BottomOxide}}$.

This argument is illustrated in Figure 3.8(a) which shows that increasing the power dissipated by the electrodes increases linearly the gradient of temperature existing at the surface. In fact, it is always possible to reach a temperature difference of 10°C by increasing the dissipated power. For this given geometry of the device, a power equal to 8.48 W is required but this value will be decreased by changing the thicknesses of the SiO_2 layers. In practice, the power dissipated by the electrodes is given by

$$P = RI^2, \quad (3.1)$$

where R is the electrical resistance of the circuit, and I is the current passing through the circuit. Equation 3.1 is associated to the Joule effect and tells that the power dissipated by the electrodes can be increased by increasing the current passing through the circuit. Figure 3.8(b) explains the increase of the temperature gradient by showing that the temperature above the electrodes increases faster than the one between the electrodes,

which is the same logic as in the previous paragraph. However, two problems arise with high voltages. The first is practical; the laboratory has a current source able to apply a maximal voltage of 105 V. The second is physical; applying high voltages increases the probability of a dielectric breakdown to occur.

For instance, the design presented in Figure 3.8 needs a dissipated power of 8.48 W for reaching a difference of temperature of 10 °C. This value is found using the equation of the line fitting the data. Since the typical resistance of a sample is 1.5 kΩ, the voltage to apply for reaching this power is $V = \sqrt{P \cdot R} = 112.82$ V, which is above the maximal voltage of the current source. In addition, the temperature between the electrodes for this dissipated power is equal to 76.69 °C, which is far beyond the LCST. This means that the polymers are always in their collapsed state which is the opposite of what is wanted. This last remark highlights another problem arising when large voltages are applied.

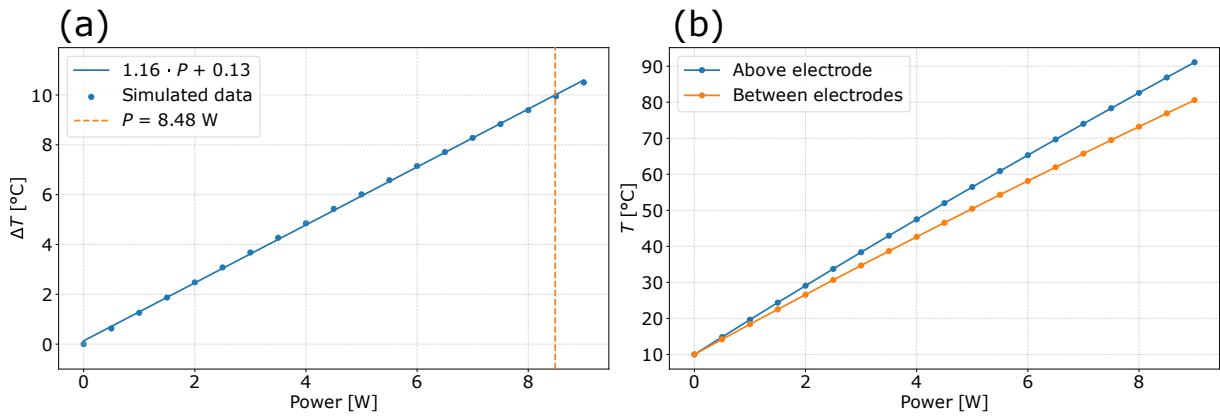


Figure 3.8: Evolution of the temperature for $t_{\text{BottomOxide}} = 1 \mu\text{m}$ and $t_{\text{TopOxide}} = 500 \text{ nm}$. **(a)** Difference of temperature between the two points in Figure 3.7 versus the dissipated power through the circuit. The vertical dotted line represents the power for which $\Delta T = 10^\circ\text{C}$ is reached, equal to 8.48 W. **(b)** Temperature at the two points in Figure 3.7 versus the dissipated power.

Figure 3.8(a) allows to find the required dissipated power for reaching $\Delta T = 10^\circ\text{C}$ with $t_{\text{BottomOxide}} = 1 \mu\text{m}$. By using the same method, it is possible to find the power needed for $t_{\text{BottomOxide}} = 1.5, 2.0, 2.5, 3.0 \mu\text{m}$. Doing so, it is possible to determine the evolution of the required voltage for reaching the temperature gradient as a function of $t_{\text{BottomOxide}}$ (see Figure 3.9(a)). The temperature between the electrodes can also be computed for these thicknesses of bottom oxide (see Figure 3.9(b)). It is observed that both of them decrease exponentially in the same fashion. According to these two fits, the minimal voltage to apply (when $t_{\text{BottomOxide}} \rightarrow \infty$) is 64.22 V and the temperature between electrodes for this voltage should be 33.72 °C. Knowing that the values for $t_{\text{BottomOxide}} = 3 \mu\text{m}$ are 67.29 V and 34.92 °C, it seems reasonable to consider it is not useful to grow a thickness of oxide thicker than 3 μm.

The good news here are that this voltage of 67.29 V is below 105 V and the top oxide should be able to withstand this difference of potential with water, as discussed in next section. However, it will be required to tune the transition temperature (see Section 2.5) for the brush to be swollen at 34.92 °C.

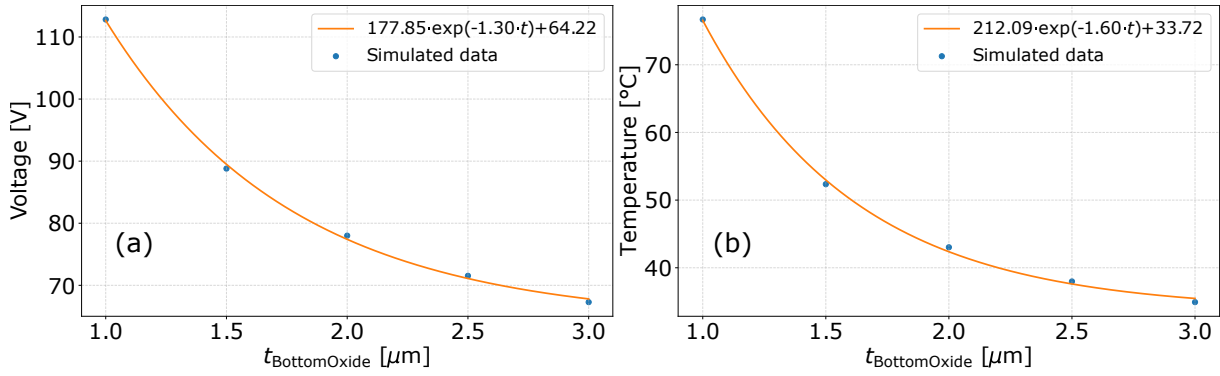


Figure 3.9: **(a)** Graph of the voltage to apply in order to reach $\Delta T = 10^{\circ}\text{C}$ as a function of the thickness of the bottom oxide. **(b)** Graph of the temperature between electrodes (see Figure 3.7(b)) when $\Delta T = 10^{\circ}\text{C}$ as a function of the thickness of the bottom oxide. For both graphs, the orange curve is the exponential that best fits the data.

3.3.2 Influence of the top oxide thickness

The resistance of the heat transfer from the electrodes towards water is increased when t_{TopOxide} is increased. Therefore, the top SiO_2 must be thin in order to have a good thermal transfer but thick enough for preventing a dielectric breakdown to occur.

In a way similar to the study of the bottom oxide, the dissipated power is progressively increased with a fixed thickness of top oxide in order to determine the voltage to apply for reaching $\Delta T = 10^{\circ}\text{C}$. In the same time, the temperature between electrodes is also computed for these voltages to determine what should be the LCST of the polymer brush. It can be observed in Figure 3.10 that both the required voltages and temperatures between electrodes increase linearly with t_{TopOxide} . The extrapolation of the former (see Figure 3.10(a)) until $t_{\text{TopOxide}} = 0 \text{ nm}$ indicates that the smallest voltage for reaching the desired gradient of temperature is 63.41 V . In addition, the dielectric strength of sputtered SiO_2 at a deposition rate of 1.65 nm/min is equal to $100 \text{ V}/\mu\text{m}$ and is plotted in Figure 3.10(a). This value was found for samples produced with the fabrication process detailed in Chapter 4, where the top oxide is deposited using reactive sputtering. In literature, the dielectric strength is larger and equal to $314 \text{ V}/\mu\text{m}$ [66]. The difference can be explained by the fact that this value is affected by many factors such as the temperature of the substrate, the proportion of oxygen in the atmosphere, and the bias applied on the substrate. The intersection of this dielectric strength with the linear fit of the voltage gives the required thickness of top oxide in order to fulfill both the gradient of temperature and the hindrance against dielectric breakdown. The intersection gives a thickness $t_{\text{TopOxide}} \simeq 686 \text{ nm}$ and a voltage of 68.6 V , corresponding to a power of 3.14 W . Table 3.1 summarizes the value of each parameters discussed until here.

According to the linear fit in Figure 3.10(b), the temperature between electrodes is equal to 35.83°C when $t_{\text{TopOxide}} = 686 \text{ nm}$. Again, it will be required to tune the transition temperature (see Section 2.5) for the brush to be swollen at 35.83°C .

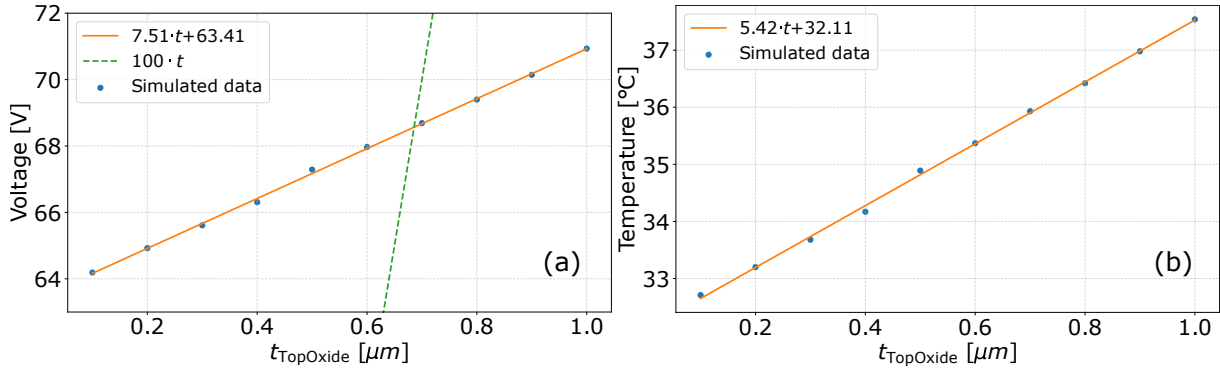


Figure 3.10: **(a)** Graph of the voltage to apply in order to reach $\Delta T = 10^\circ\text{C}$ as a function of the thickness of the top oxide. The green dashed line represents the dielectric strength of sputtered SiO_2 , equal to $100 \text{ V}/\mu\text{m}$. The intersection between these two functions is $(V, t_{\text{TopOxide}}) = (68.6 \text{ V}, 0.686 \mu\text{m})$. **(b)** Graph of the temperature between electrodes (see Figure 3.7(b)) when $\Delta T = 10^\circ\text{C}$ as a function of the thickness of the top oxide. For both graphs, the orange line is the linear fit that best fits the data.

$t_{\text{BottomOxide}}$	t_{TopOxide}	V	P	T between electrodes
$3 \mu\text{m}$	686 nm	68.6 V	3.14 W	35.83°C

Table 3.1: Tabular summarizing the parameters used for reaching the required temperature profile and prevent dielectric breakdown.

3.3.3 Temperature profile along the sample

Until here, the focus has been on the temperature profile above and between specific electrodes without considering the other ones. However, as observed in Figure 3.11, the temperature is progressively increasing when going towards the center of the sample. The difference of temperature between the edge and the center of the active area of the sample is equal to 3.1°C . Therefore, the swelling coefficient of the swollen (between electrodes) and collapsed (above electrodes) polymers in the center will be smaller than the one at the edges of the active area.

This variation of the base temperature could lead to the reduction of the size of active area because the temperature in the center or at the edges could go out of the transition zone in which the swelling coefficient varies. However, the transition zone of P(MEO₂MA-*co*-OEGMA) brushes extends over 15°C allowing to maintain the temperature of the active area in this zone.

3.3.4 Characteristic times of the time-dependent temperature

All the results presented until here came from the stationary solution, considering that the electrodes are always turned on. In practice, the electrodes are alternatively turned on and off (see Figure 3.12(a)) implying that the solution depends on time. There are different characteristic times in the system :

1. The electrodes take a given time, $\tau_{1,\text{heating}}$, to heat the surface just above it (at the location of the red dot in Figure 3.7(a)) when they are turned on. This transferred

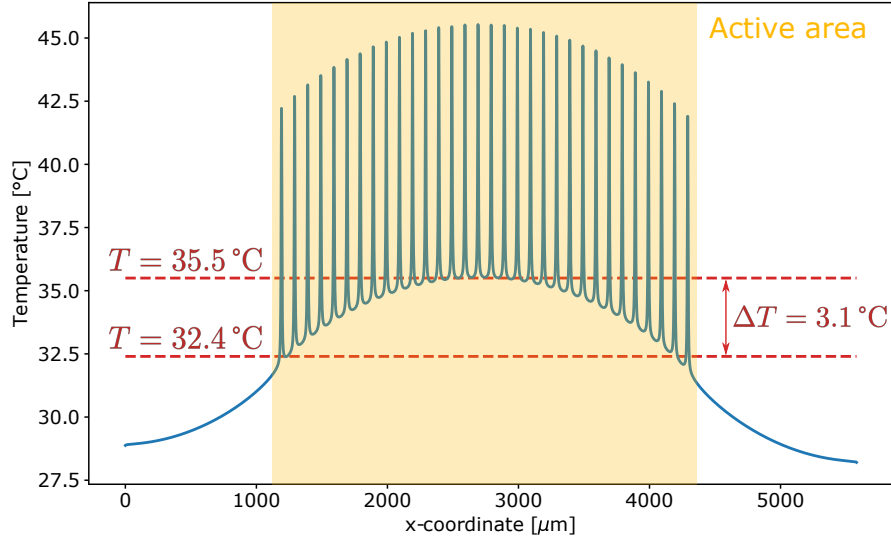


Figure 3.11: Temperature along the sample 100 nm above the surface. The smallest and highest temperatures between electrodes in the active area (highlighted in orange) of the sample are 32.4 °C and 35.5 °C, respectively. The values from Table 3.1 were used.

heat creates a peak in the temperature profile. When the electrodes are turned off, the surface above the electrodes needs to cool during a time $\tau_{1,\text{cooling}}$ to remove this peak.

2. The global temperature above the surface progressively increases when the electrodes are turned on, until reaching the stationary solution after a time $\tau_{2,\text{heating}}$. The temperature just above the surface then takes a time $\tau_{2,\text{cooling}}$ to cool until an homogeneous temperature of 10 °C, the exterior temperature and the temperature of the Peltier cell (which is turned off).

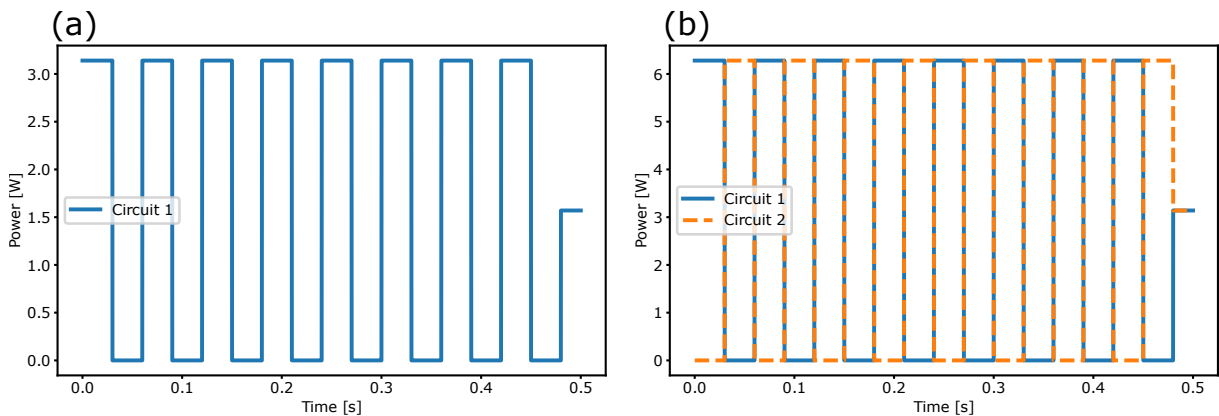


Figure 3.12: Dissipated power in the circuits as a function of time for a device with **(a)** one circuit and a power of 3.14 W **(b)** two circuits and a power of 6.28 W (see Section 3.4). The circuits are alternatively turned on and off with a period of 0.06 s (see Table 3.2).

Temperature just above the electrodes - $\tau_{1,\text{heating}}$ and $\tau_{1,\text{cooling}}$

These characteristic times can be determined using Figure 3.13. The elapsed time between Figure 3.13(a) and (b) is equal to $0.215 - 0.192 = 0.023$ s, which is the time needed for the peak of temperature to reach its maximum. Therefore, $\tau_{1,\text{heating}} = 0.023$ s. The elapsed time between Figure 3.13(c) and (d) is equal to $0.320 - 0.296 = 0.024$ s, which is the time needed for the peak of temperature to be suppressed. Therefore, $\tau_{1,\text{cooling}} = 0.024$ s.

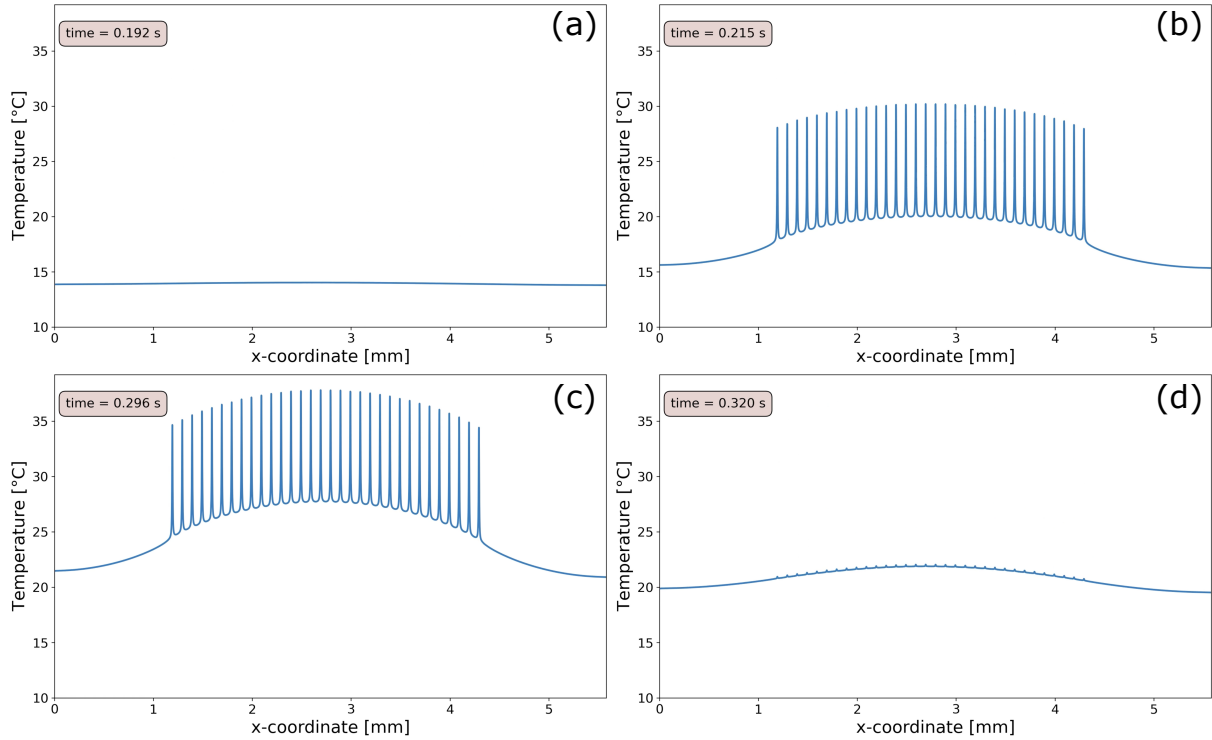


Figure 3.13: Graphs of the temperature profile (a) just before turning on the electrodes (b) when the maximum of the peak is just reached (c) just before the peak starts to decrease (d) when the peak has just been removed.

Global temperature above the surface - $\tau_{2,\text{heating}}$ and $\tau_{2,\text{cooling}}$

$\tau_{2,\text{heating}}$ can be determined by turning on the electrodes and waiting for the time-dependent solution to reach the stationary solution. The dissipated power here is thus constant and is not alternatively turned on and off as it was the case for determining $\tau_{1,\text{heating}}$ and $\tau_{1,\text{cooling}}$. Figure 3.14 presents this time-dependent solution after 1 s and 15 s. It can be noticed in Figure 3.14(a) that the stationary solution is not reached yet. After exactly 15 s (see Figure 3.14(b)), the time-dependent and stationary solutions are merged. The system takes the same time to cool for reaching an homogeneous temperature of 10 °C. Therefore, it can be concluded that $\tau_{2,\text{heating}} = \tau_{2,\text{cooling}} = 15$ s. It should be noted that the electrodes are not kept turned on in the real device but are alternatively turned on and off instead. Therefore, the temperature of the system will be smaller than the one in Figure 3.14.

The four different characteristic times are summarized in Table 3.2. Half the period

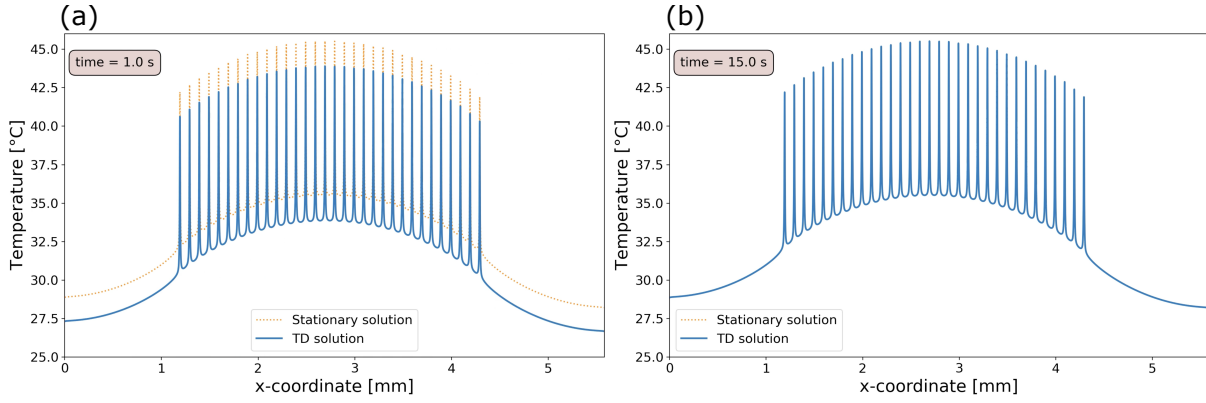


Figure 3.14: The time-dependent (TD) temperature along the sample is plotted after (a) 1 s (b) 15 s. The stationary solution is also plotted with an orange dotted line.

of the square wave function³ describing the dissipated power in the electrodes should be greater or equal to $\tau_{1,\text{heating}}$ and $\tau_{1,\text{cooling}}$ (the peak of temperature must reach its maximum and then disappear) but much smaller than $\tau_{2,\text{cooling}}$ (to not let cool the surface and lose the stationary regime of the base temperature). In addition, one will need to wait at least $\tau_{2,\text{heating}} = 15\text{ s}$ before starting an experiment so that the base temperature of the thermal profile has the time to reach its stationary regime. This value does not take into account the fact that the electrodes are alternatively turned on and off. Nevertheless, since the period of oscillation needs to be much smaller than 15 s, the system should reach equilibrium in a time close to $\tau_{2,\text{heating}}$.

In conclusion, the period of the power dissipated in the circuit can be selected as 0.06 s, as plotted in Figure 3.12(a).

$\tau_{1,\text{heating}}$	$\tau_{1,\text{cooling}}$	$\tau_{2,\text{heating}}$	$\tau_{2,\text{cooling}}$
0.023 s	0.024 s	15 s	15 s

Table 3.2: Tabular summarizing the characteristic times of the system, determined from Figure 3.13 and Figure 3.14.

3.3.5 Time-dependent temperature profile

In contrast with the case considered in Figure 3.14, the electrodes do not heat permanently. Therefore, the temperature profile is varying in time and the temperatures are lower than the ones in Figure 3.11. The temperature profile after 30 s with a period of heating equal to 0.06 s is provided in Figure 3.15.

3.4 Stationary wave with two circuits

Instead of creating some oscillating bumps with one circuit, a stationary wave can be formed at the surface by using *two circuits* that are alternatively turned on and off. The

³Half the period is the time during which with the electrodes are kept turned on or turned off.

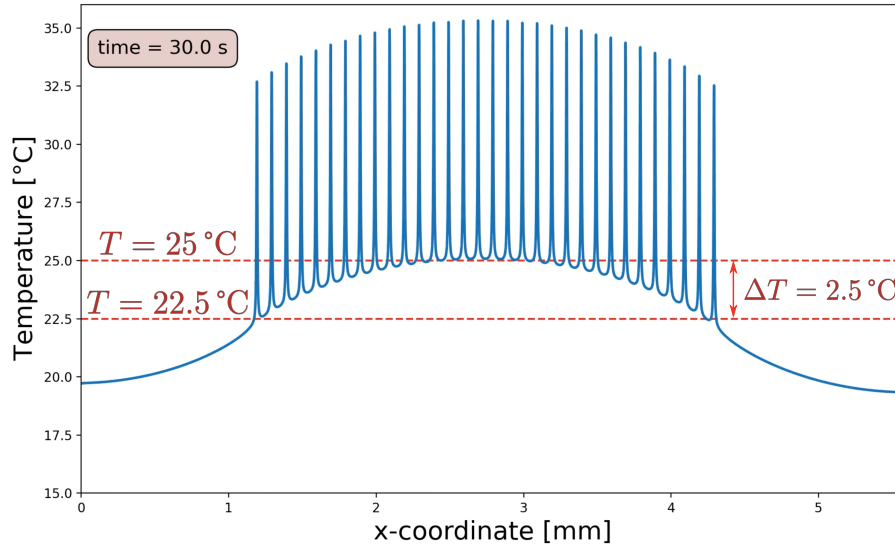


Figure 3.15: Temperature profile along the device with 1 circuit after 30 s, just before turning off the electrodes. The difference between the smallest and the highest base temperatures is equal to 2.5°C .

pattern of the circuit is schematized in Figure 3.16. It can be observed that the pattern of the electrodes is made of two circuits. When looking at the cross-section, as implemented in *Comsol Multiphysics* (see Figure 3.17), the two circuits appear alternatively in space with two adjacent electrodes each time. The thicknesses of SiO_2 that were found in the section with one circuit are kept for the system with two circuits.

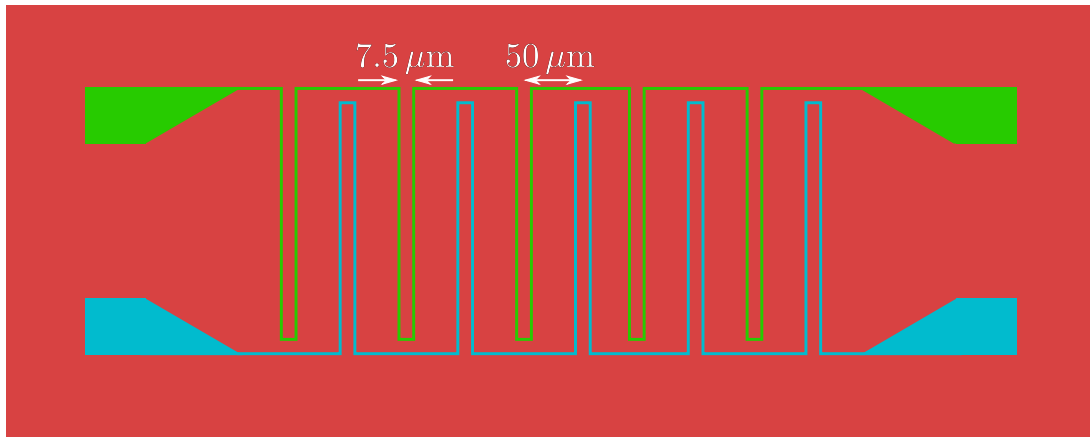


Figure 3.16: Schematic top view of the system with two circuits. The two circuits are represented in different colors for the clarity.

There are many constraints on this design for controlling the underwater motion of colloidal particles and bacteria while being able to measure it experimentally:

1. Constraint on the distance between two adjacent electrodes, forming a duo of electrodes :
 - (a) The two adjacent electrodes must be close enough in order to create only one node of the stationary wave. This constraint can be studied with simulations.

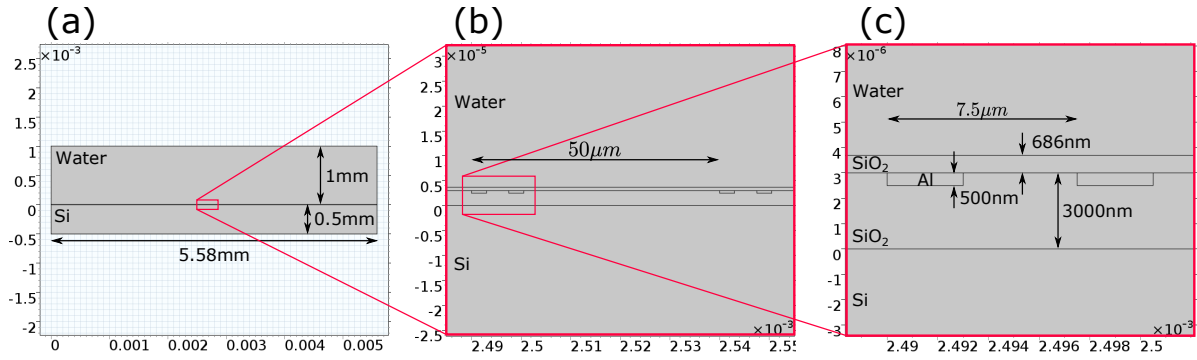


Figure 3.17: Geometry of the simulated system in *Comsol Multiphysics*. **(a)** Overview of the sample with the dimensions of the water-filled cell and Si. **(b)** Magnified view of (a) where the SiO₂ layers and the Al electrodes start to be visible. The distance between two adjacent duo of electrodes is equal to 50 μm. **(c)** Magnified view of (b) where the SiO₂ layers and a duo of electrode is clearly visible with the dimensions. The distance between two adjacent electrodes is 7.5 μm and is explained in Section 3.4.1. The units of both axes are in meters.

2. Constraints on the distance between the adjacent duos of electrodes :

(a) For observing the underwater motion, two adjacent duos of electrodes from the two different circuits must be farther apart than 24 μm. Below this distance, the edge diffraction of light on the metallic electrodes hinders the observation of underwater motion with ellipsometry. A diffraction pattern can be observed in Figure 5.10 and its consequences on the characterization of the surface will be addressed in Chapter 5.

(b) The wavelength of this stationary wave must not be much longer than 30 μm, the typical size of the colloidal particles.

⇒ The distance between two adjacent duo of electrodes from the same circuit is fixed to 100 μm in order to respect these two constraints. The simulations cannot really study these constraints since they depend on the underwater motion, which is not included in the simulated system. Therefore, experimental measurements are needed to determine whether or not this distance is a good choice.

3. Constraints on the frequency of oscillation of the stationary wave :

(a) If the frequency is too high, the heat will not have the time to diffuse in the system while the temperature above the electrodes is wanted to decrease below the LCST when the electrode is turned off. This has already been studied in Section 3.3.4 for the device with one circuit. In addition, a high frequency would not allow the diffusion of the colloidal particles along the surface. While the diffusion of heat can be studied with simulations, the motion of the colloidal particles must be studied experimentally.

(b) If the frequency is too low, the colloidal particles will not feel a stationary

wave but a surface slowly varying. Once again, the study of the motion of the colloidal particles can only be performed experimentally.

→ **Remark:** These two constraints are also applying to the device with one circuit.

Therefore, the points 1.(a) and 3.(a) are studied in this section.

3.4.1 Distance between adjacent electrodes - 1.(a)

In order to create a single node of the stationary wave with two adjacent electrodes, the thermal profile just above the electrodes is studied to see whether the polymers all have the same swelling coefficient or not. For instance, two adjacent peaks in the thermal profile, created by a duo of electrodes, could go above the LCST while maintaining a temperature below the LCST in between them. In this case, the electrodes must be brought closer together. However, the distance between the electrodes cannot be decreased below $1\text{ }\mu\text{m}$ [67, 68] because the microfabrication process is limited by the diffraction limit during the exposure step of the photolithography (see Section 4.2.3).

For having an idea of the desired distance between two adjacent electrodes, the width of the thermal profile above a *single* electrode is fitted in Figure 3.18(a). This width is determined with the geometry and the power of 3.14 W needed for reaching the desired gradient of temperature, as determined in Section 3.3. The full width at half maximum (FWHM) of the lorentzian fit is equal to $6.42\text{ }\mu\text{m}$. Using this result, the system is then simulated with two electrodes separated by $6.42\text{ }\mu\text{m}$ and a dissipated power of $2 \cdot 3.14 = 6.18\text{ W}$ (see Figure 3.12(b)), since there are two times more electrodes. The obtained thermal profile is plotted in Figure 3.18(b) (continuous line). It is observed that the thermal profile above and in between the duo of electrodes remains beyond the threshold value of $\Delta T = 10^\circ\text{C}$, meaning that all the polymers are in their collapsed state as it was intended. The fact that a power two times higher must be used is confirmed with the plotted dotted lines, coming from the fit in Figure 3.18(a). These lines show that the thermal profile with two electrodes is the sum of the thermal profiles with one electrode, each with a dissipated power of 3.14 W .

In conclusion, the two adjacent electrodes from the same circuit must be separated by a distance smaller than $6.42\text{ }\mu\text{m}$ and the total dissipated power must be equal to 6.28 W .

3.4.2 Thermal diffusivity above the electrodes - 3.(a)

The power dissipated by the electrodes follows a square function. This means that the electrode is either turned on with maximal power, or turned off, as depicted in Figure 3.12(b). Using the period of 0.06 s found in Section 3.3.4, the temperature profile in Figure 3.19 is obtained.

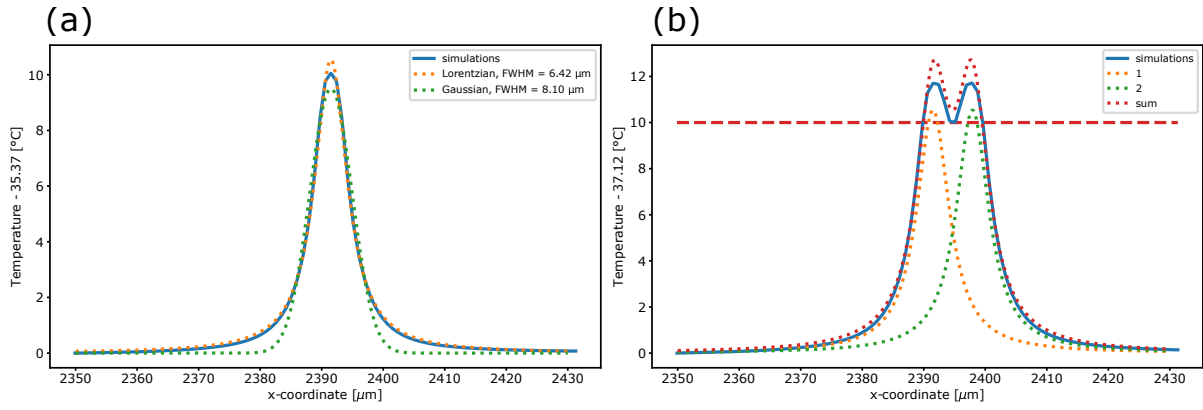


Figure 3.18: **(a)** Simulation of the temperature along the surface (vertically shifted) for a given electrode and a power of 3.14 W (as determined in Section 3.3.2). The profile is fitted with lorentzian and gaussian curves in order to find the FWHM. The lorentzian curve (MSE = 0.010) fits better the profile than the gaussian curve (MSE = 0.136) and has a FWHM = $6.42 \mu\text{m}$. **(b)** Simulation of the temperature along the surface (vertically shifted) for a given duo of electrodes and a power of 6.28 W, two times the value used in (a) for the case with one circuit. The second electrode is placed at a distance of $6.42 \mu\text{m}$ from the first one, which is the FWHM of the lorentzian fit from (a). The orange and green dotted lines are the thermal profile produced by single electrodes and determined from the fit from (a). The red dotted line is the sum of these two thermal profiles. The red dashed line is the threshold above which $\Delta T = 10^\circ\text{C}$ meaning that the polymers are in the collapsed state ($T > \text{LCST}$).

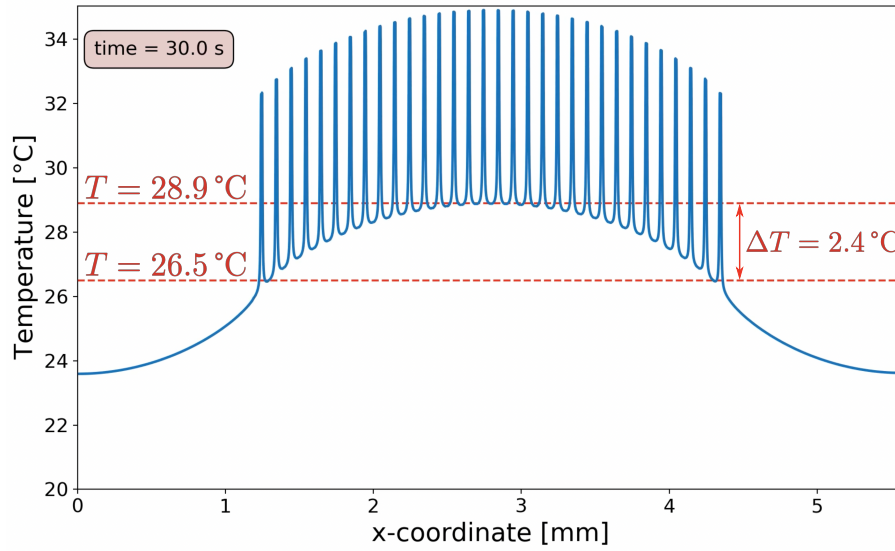


Figure 3.19: Temperature profile along the device with 2 circuits after 30 s. At this moment, the peaks arise from only one of the two circuits, the other being turned off. The difference between the smallest and the highest base temperatures is equal to 2.4°C .

3.5 Discussion

As already mentioned, the reality is more complex than what has been considered with the simulations. It cannot be evaluated in advance whether the phenomena that have been

neglected are influencing significantly the heat transfers in the system or not. However, two phenomena are expected to play a role in the dynamical behavior of the colloidal particles and bacteria : the convection flux and the Marangoni effect. The latter can manifest in the system studied in this work because the surface energy varies depending on the swelling coefficient of the polymer brush, which in turn depends on temperature.

Chapter 4

Fabrication process

The simulations give an idea of the geometry required for the device. This chapter will now explain how this device is fabricated in practice.

Since the electrodes have a width in the micrometer range, microfabrication techniques must be used. Fortunately, the *Winfab* platform, located in Louvain-la-Neuve, makes it possible to manufacture such small devices. Figure 4.1 presents the device that will be fabricated by following the steps detailed in this chapter.

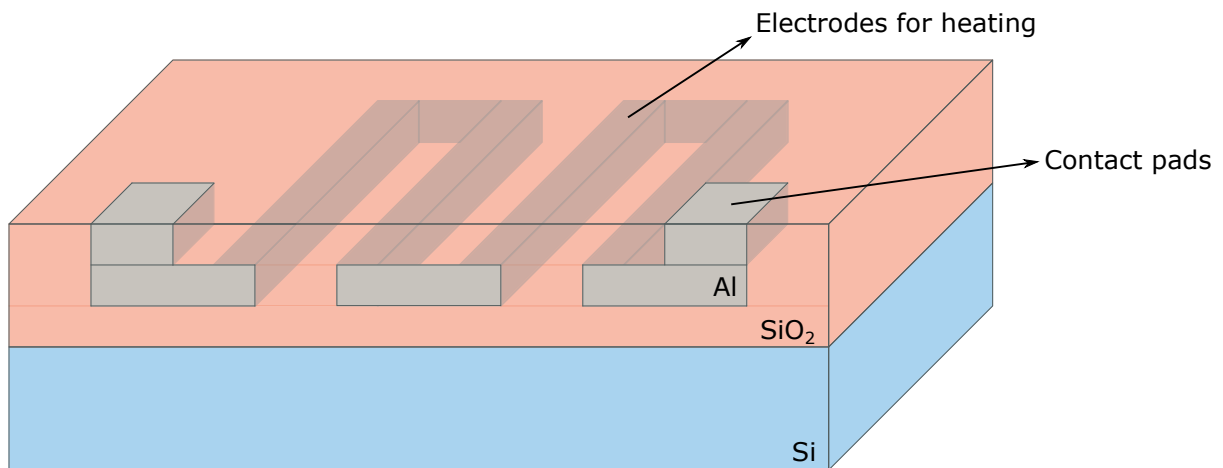


Figure 4.1: 3D schematic of the device to fabricate with the cross-section made visible. The polymer brushes are not represented but should be at the top of the device.

4.1 Overview of the fabrication process

All the steps of the fabrication process are summarized in Figure 4.2. The process starts in (a) with a silicon wafer covered by a thick oxide. The steps from (b) to (d) constitute the first photolithography, during which the pattern of the circuit is created into a photoresist. This lithography is followed in (e) by the etching of trenches inside SiO₂, which are subsequently filled with aluminum in (f). The undesired aluminum on top of the photoresist is removed in (g) by stripping this photoresist. In (h), an additional layer of SiO₂ is deposited on top of the surface and will serve as a dielectric and as a substrate for growing polymer brushes. A second photolithography followed by an SiO₂ etching are

performed in order to open electrical contact pads. Finally, the polymer brushes are grown in the last step (i).

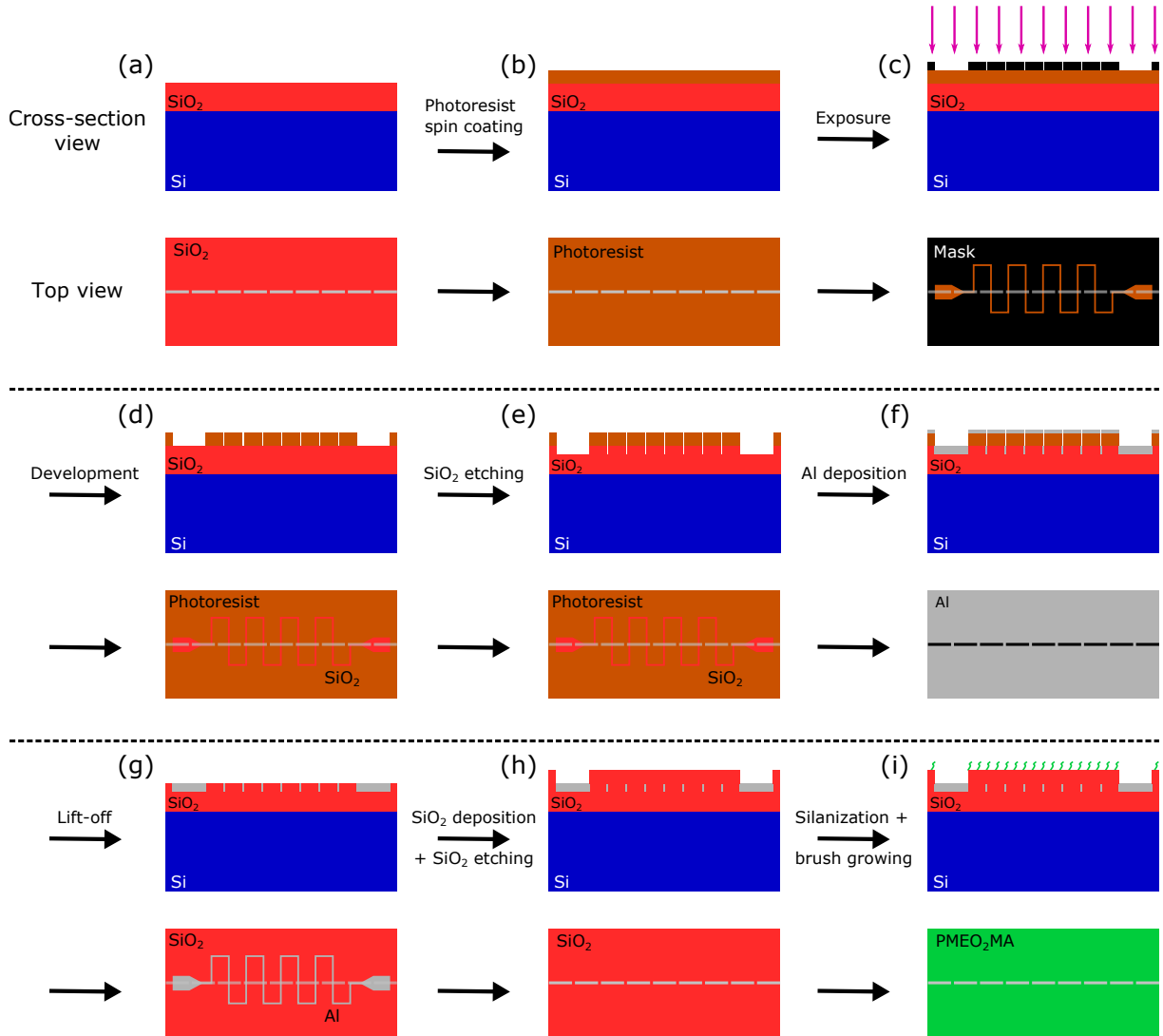


Figure 4.2: Schematics of the fabrication process with cross-section (top schematic) and top (bottom schematic) views. The dashed horizontal line on each schematic of the top view indicates the location where the cross-section is represented.

4.2 Detailed fabrication process

Three wafers, containing three identical samples (see Figure 4.3) on each of them, have been processed in this work. Figure 4.3(a) gives the labels identifying the three different samples that will be fabricated on a single wafer. Figure 4.3(b) anticipates the current section and shows a wafer once the fabrication process has been performed on it. In this section, the steps required for achieving this result are presented in detail.

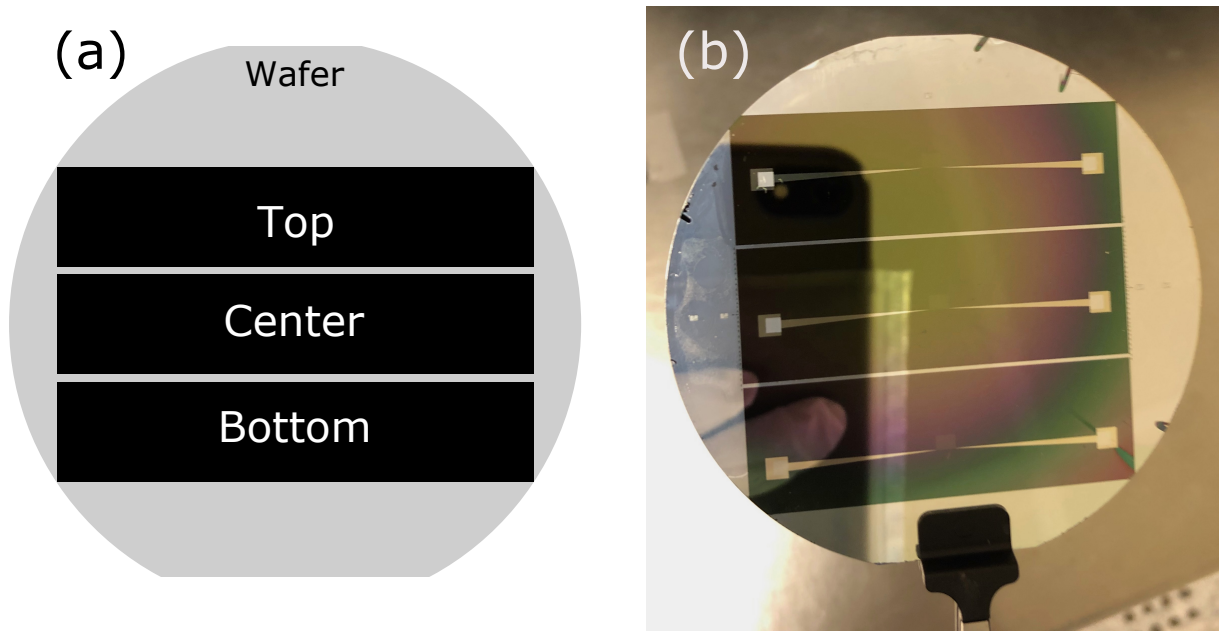


Figure 4.3: Final pattern on the wafer. **(a)** Schematic labeling the top, center, and bottom samples on the wafer. These labels will be used for identifying the three samples on each wafer. **(b)** Finalized wafer, after having followed the steps in Figure 4.2.

4.2.1 Piranha cleaning

Even if not visible to the naked eye, the surface of wafers are always covered by organic residues. This contamination increases the surface roughness and can reduce the adhesion of the films that will be deposited subsequently. Therefore, the wafers are always cleaned prior to the fabrication process [68]. The so-called piranha cleaning, which is able to efficiently remove these organic residues, follow these steps :

1. 10 minutes in a piranha sulfuric peroxide mixture $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ (4:1).
2. 10 minutes in deionized (DI) water with a continuous flow of N_2 bubbles. The bath must be emptied and filled 5 times during these 10 minutes.
3. Repeat step 1.
4. Repeat step 2.
5. 30 s in a dilute HF bath $\text{HF}:\text{H}_2\text{O}$ (1:100).
6. Repeat step 2.
7. 10 minutes in the water fountain.
8. The samples are rinsed in a rinser dryer.

The wafers used for the process of this work are directly bought with a grown thermal oxide with a thickness of $3\text{ }\mu\text{m}$. Therefore, the steps 5 and 6 are skipped because the HF bath etches any oxide at the surface of the wafer.

4.2.2 Wet oxidation of silicon

The first layer of oxide (see Figure 4.2(a)), which acts as a thermal barrier for the heat produced by the electrodes, is grown using thermal oxidation. Although dry oxidation results in a denser film, the thickness of $3\mu\text{m}$ forces to opt for wet oxidation which has a much higher oxidation rate. However, even using a wet oxidation process at 1000°C , the Deal-Grove model predicts that the thermal oxidation takes more than 32 h [69]. There are two reasons for which this step is not feasible in *Winfab*. Firstly, it requests to book an oven used by many users for a very long time. Secondly, it is unusual to grow such a thick oxide. Hence, the staff from *Winfab* does not have the expertise to perform such a long oxidation which requires the calibration of some parameters and to regularly check if the oxidation is running correctly. Therefore, wafers with an already grown $3\mu\text{m}$ thick oxide were bought to *Siebert Wafer*. These wafers have a $\langle 100 \rangle$ orientation.

Metrology : Ellipsometry

The thickness of the thermal oxide can be easily measured with ellipsometry. This characterization technique plays a central role in both the fabrication process for measuring the thickness of thin films, and for in situ measurements performed in Chapter 5. A detailed description of ellipsometry is provided in Section 5.1 and is useful for the uninitiated reader (though a thorough understanding is not yet necessary for simply measuring the thickness of a thin film). Figure 4.4 shows the measured data as well as their fit for wafer #1. The graphs for the two other wafers are identical. This fit is based on a model including a Si substrate, a SiO_2 thin film, and air as the ambient medium. According to this fit, the thickness of SiO_2 is equal to 3087.6 nm for the wafer #1. The mean squared error (MSE) between the experimental measurements and the values of the model is equal to 9.65. Table 4.1 gives the thickness of SiO_2 of each wafer, without distinguishing between the three samples on a single wafer since thermal oxidation is homogeneous at the scale of a wafer.

	Thickness [nm]	MSE
Wafer #1	3087.6	9.65
Wafer #2	3083.9	9.49
Wafer #3	3072.3	8.93

Table 4.1: Table providing the thickness of SiO_2 and the corresponding MSE for each wafer. The angle of incidence was 70° .

4.2.3 First photolithography

A first lithography is performed in order to create the pattern, containing the active area and the contact pads, onto a layer of photoresist (PR). This patterned photoresist will protect the SiO_2 layer underneath during the subsequent SiO_2 etching that will form trenches. The result of this first photolithography is schematized in Figure 4.2(d).

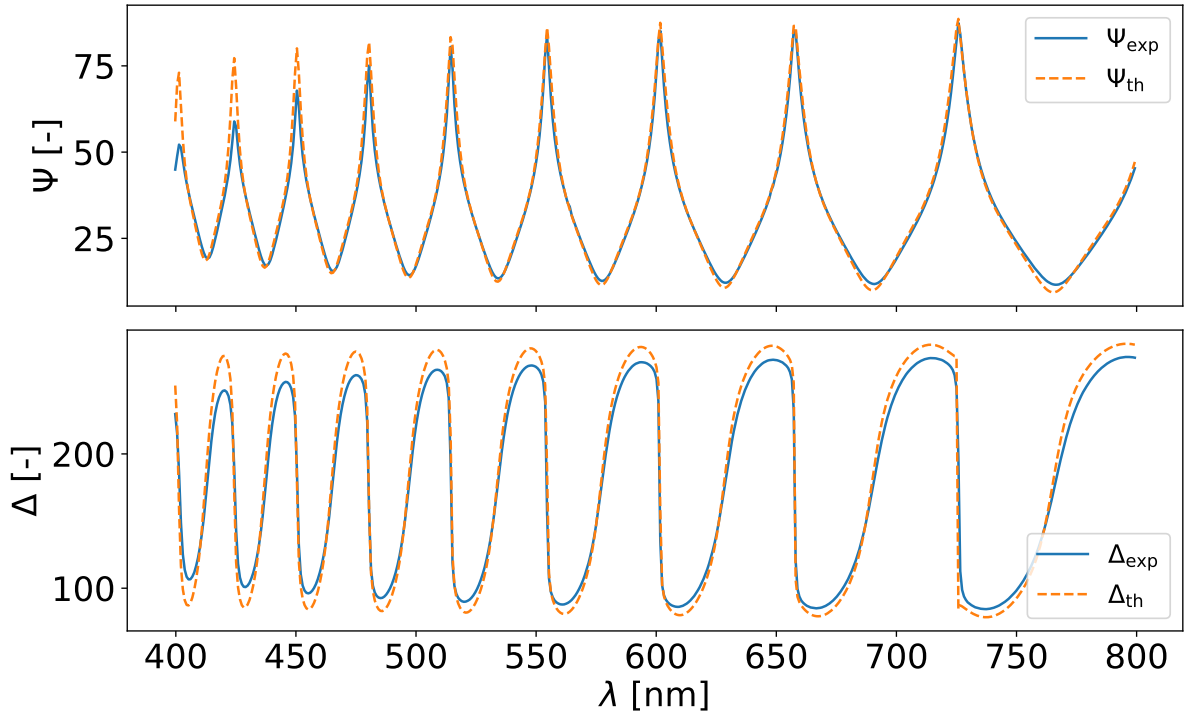


Figure 4.4: Ellipsometry measurements of the angles Ψ (top) and Δ (bottom) for the wafer #1, for finding the initial thickness of SiO_2 . The experimental values are represented with a blue continuous line while the fit of the model is represented with an orange dashed line. The range of wavelengths starts at 400 nm and ends at 800 nm. The angle of incidence was 70° .

Deposition of an adherence promotor

Prior to the deposition of photoresist, hexamethyl disilazane (HMDS) is applied to ensure good wetting of the wafer by the photoresist [68]. To do so, the *LPIII oven* is used at a temperature of 120°C . The whole process (cycles of deposition, pumping, and venting) lasts for 23 min.

Photoresist deposition

2 mL of the positive photoresist *AZ[®] MiRTM 701* is spin-coated during 60 s at 4000 rpm with an acceleration of 1000 rpm/s using the *SEM coater*. Usually, the *Suss Gamma 80* is used to perform this step but is currently out of service. Figure 4.2(b) shows the wafer with the spin-coated photoresist.

Soft bake

Before the exposition to UV, the solvent remaining in the photoresist must be removed. Therefore, the wafer is baked during a step called a soft bake, or a pre-exposure bake. The wafer is baked at 90°C for 90 s on a hotplate. Again, this step is usually performed automatically in *Suss Gamma 80* directly after the photoresist deposition, which provides a good reproducibility of the process. Currently, all the steps are performed “by hand”

which could lead to some discrepancies, though they should not be significant.

Exposure

The photoresist is then exposed to UV light (see Figure 4.2(c)) with a wavelength of 365 nm and an exposure energy of 150 mJ/cm², which necessitates only a few seconds of exposure. The wafer is pressed into an intimate contact, called a vacuum contact, with the photomask. This proximity allows to neglect the diffraction of light by the patterns on the photomask. However, this contact can leave some debris of photoresist on the mask. Therefore, the mask was cleaned after each use. Cleaning simply consists of rubbing the mask with a wipe filled with acetone, rinsing the mask with methanol, and finally dry it with a stream of nitrogen.

Upon exposure, a photoactive compound (diazonaphthoquinine, DNQ) acting as an inhibitor reacts and makes soluble the photoresist [68]. Therefore, the exposed photoresist will be removed and the same pattern as the one on the photomask is reproduced, hence the name of positive photoresist.

Post-exposure bake

A post-exposure bake is performed and leads to the diffusion of photogenerated molecules which smoothes out optical interference effects [68]. The wafers are baked at 110 °C for 60 s on a hotplate.

Development

The exposed photoresist is etched away during development (see Figure 4.2(d)). The wafer is immersed in the developer, *AZ 726MIF*, for 60 s and then rinsed with a stream of DI water during an additional 60 s.

Metrology : Ellipsometry

The thickness of the spin-coated photoresist can be measured with ellipsometry. Figure 4.5 shows the measured data as well as their fit for the wafer #1. The graphs for the two other wafers look very similar. This fit is based on a model including a Si substrate, a SiO₂ thin film with a thickness given by Table 4.1 for each wafer, a photoresist thin film, and air as the ambient medium. Obviously, the measurement must be performed at a location where the photoresist was not removed during the previous development. Table 4.2 gives the thickness of photoresist for each wafer.

Since the complexity of the model has increased compared to the one in Figure 4.4, the model is slightly less well fitting the experimental data. Still, the fit remains good and provides reliable results, as confirmed just after with profilometry.

Metrology : Profilometry

As suggested by its name, profilometry allows to measure the profile at the surface of the sample. Therefore, it can be used to measure the roughness of a surface or the

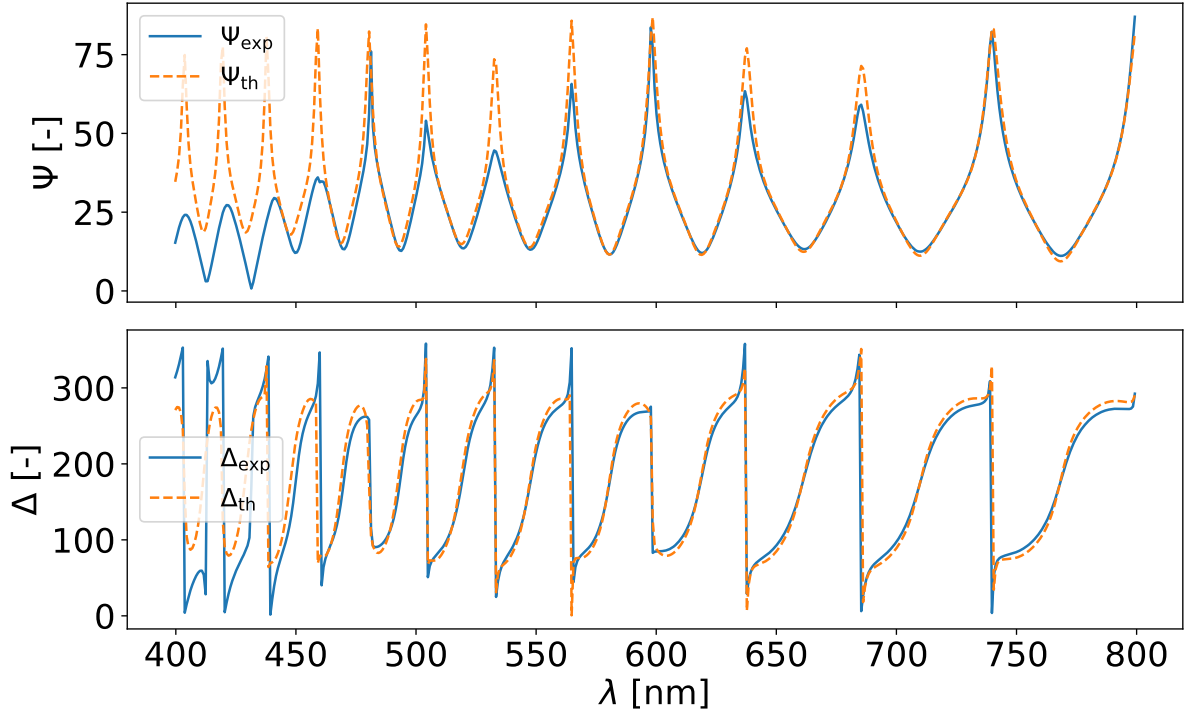


Figure 4.5: Ellipsometry measurements on the wafer #1 for finding the thickness of photoresist. The experimental values are represented with a blue continuous line while the fit of the model is represented with an orange dashed line. The range of wavelengths starts at 400 nm and ends at 800 nm. The angle of incidence was 70° .

	Thickness [nm]	MSE
Wafer #1	881.2	24.46
Wafer #2	889.3	24.27
Wafer #3	871.3	23.55

Table 4.2: Tabular providing the thickness of photoresist, as measured with ellipsometry, and the corresponding MSE for each wafer. The angle of incidence was 70° .

thickness of a deposited thin film. Indeed, this technique is able to measure the height of hills and valleys between the thin films of SiO_2 and photoresist. Since ellipsometry is based on mathematical models for fitting, it is interesting to confirm the previously measured thicknesses with profilometry. The measurements are provided in Table 4.3 and are very close to the results obtained with ellipsometry.

	Thickness [nm]
Wafer #1	902.1
Wafer #2	920.1
Wafer #3	892.6

Table 4.3: Table providing the thickness of photoresist, as measured with profilometry.

Metrology : Optical microscopy

Finally, optical microscopy can be used to check if the pattern of the photomask has been reproduced correctly on the wafer. The alignment marks, which are marks that will be subsequently used to align the pattern of the second photolithography, represent a good indicator of the pattern transfer. The optical microscope images of these alignment marks are shown in Figure 4.6 and confirm that the pattern has been well transferred for the wafer #1. In Figure 4.6(a), a number '2' is shown, but there are alignment marks with other numbers such as '3' which can be used for alignment.

The alignment marks are patterned on the left and on right sides of the wafer. Indeed, during the step of alignment coming later in the process, the photomask aligner allows to align two marks at the same time, one on the left side of the wafer and the other on the right one. This additional constraint allows to not only align laterally the mask with the wafer (in the x and y directions) but also to adjust their relative angle (in the θ direction in the plane of the wafer, since the wafer could be slightly tilted compared to the photomask). It is important to check all the alignment marks. If they are not present or damaged, the second photolithography cannot be aligned with the first one and the subsequent steps becomes difficult, if not impossible. Therefore, the process would need to be started again from scratch. Table 4.4 gives the state of the alignment marks. The mark with the number '2' has not been transferred *at all* on the wafer #2 (which is quite mysterious), but the alignment remains possible using the mark with a number '3'.

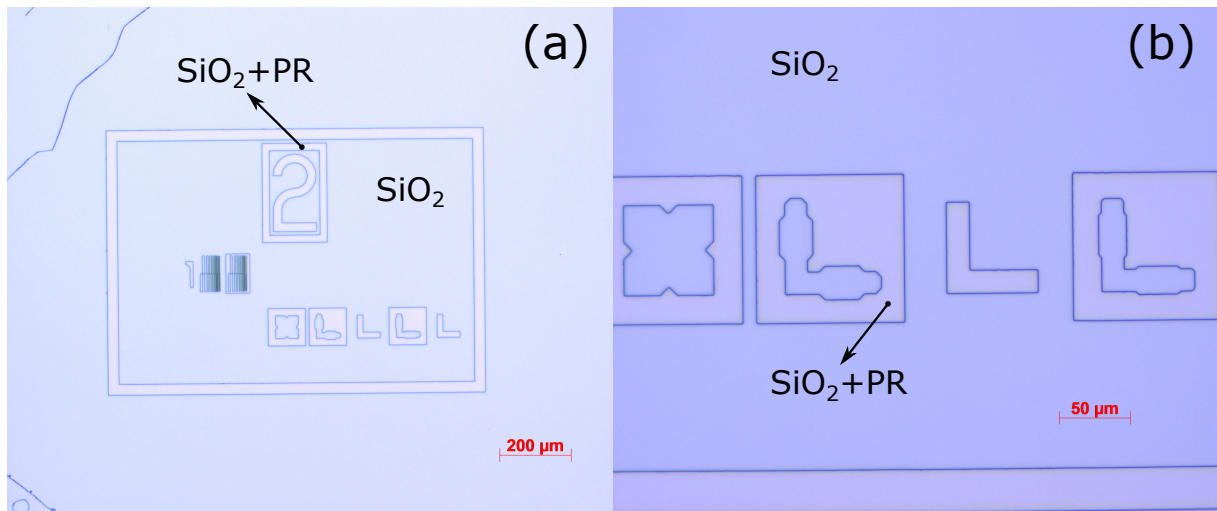


Figure 4.6: Optical microscope images of the alignment marks on the left of the wafer #1 with a magnification (a) $\times 5$ (b) $\times 20$. As indicated on the images, the lightest areas are covered with photoresist while the darkest are not.

It is also essential to check the pattern of the system active area. An impurity on the photomask at the location of the circuit during exposure would lead to an open-circuit and make impossible the study of the sample. Therefore, this investigation is worthwhile if one does not want to waste time and money on a damaged sample. Fortunately, the circuits of the 9 samples were all correctly reproduced, without any damage¹.

¹As previously mentioned, the photomask has been cleaned before each exposition. It would have been quite unfortunate to find a damaged circuit.

	Left side	Right side
Wafer #1	OK	OK
Wafer #2	OK	'2' KO but '3' OK
Wafer #3	OK	OK

Table 4.4: Table telling whether or not the alignment marks have been well transferred onto the sample. 'OK' means that all the alignment marks have been correctly transferred, without any damage, on the left or right side of the wafer. 'KO' means that the pattern has not been transferred.

Optical images of the top circuit on wafer #1 are presented in Figure 4.7. Figure 4.7(a) shows that the distance between two electrodes is approximately equal to the desired $50\text{ }\mu\text{m}$, while Figure 4.7(b) shows that the width of an electrode is equal to $2.66\text{ }\mu\text{m}$, slightly below the $3\text{ }\mu\text{m}$ that were targeted.

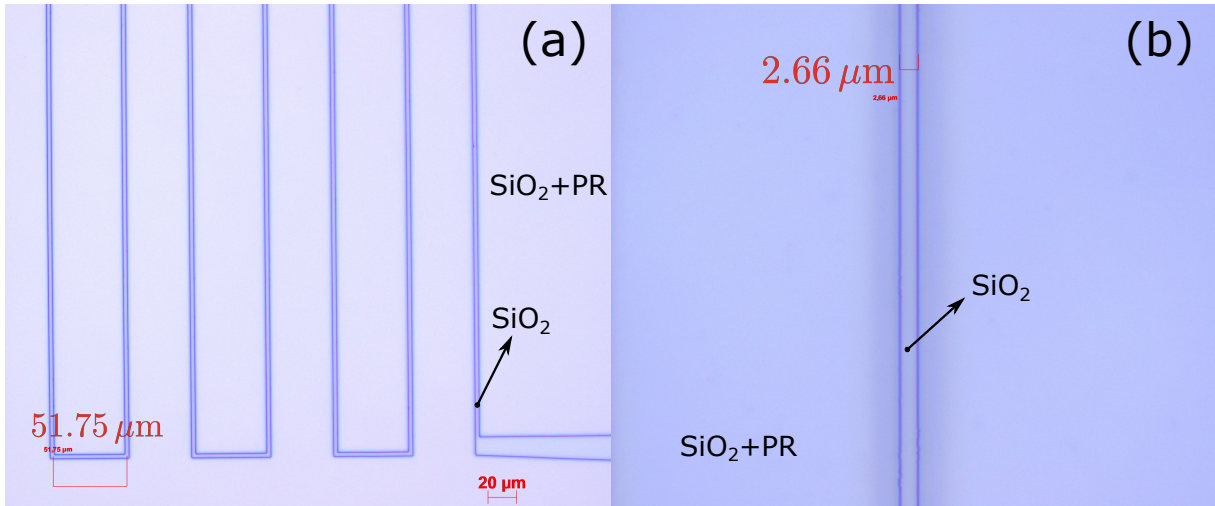


Figure 4.7: Optical microscope images of the top circuit on the wafer #1 with a magnification (a) $\times 20$ (b) $\times 100$. Measured with the optical microscope, the distance between electrodes is equal to $51.75\text{ }\mu\text{m}$ and the width of an electrode is equal to $2.66\text{ }\mu\text{m}$.

4.2.4 Etching of silica for trenches

The next step is to etch trenches in SiO_2 (see Figure 4.2(e)) in order to deposit a metal inside them and create the circuit. To do so, anisotropic dry etching is selected to produce vertical sidewalls and subsequently, electrodes with a well defined profile. As emphasized in Chapter 3, the thermal profile yielding a pulsing surface requires the adjustment of a few geometrical parameters and an uncertainty on the profile of the electrodes would additionally increase the complexity of the system. This is why isotropic etching has been rejected, though being an easier process.

Reactive-ion etching

During plasma etching, also known as reactive ion etching (RIE), SiO_2 chemically reacts with a plasma containing carbon and fluorine compounds. In order to create this plasma, a gas composed of CHF_3 and O_2 is placed in a chamber containing the sample to etch. As illustrated in Figure 4.8(a), the plasma is then generated by passing an RF current in coils, separated from the chamber with a dielectric wall, that are generating a magnetic field setting in motion the electrons of the gas. Indeed, following Faraday's law, the RF current induces an opposing RF current in the plasma. The heavier nuclei cannot follow the rapid movement of the electrons, leading to the creation of ions. Due to this decoupling between the motion of nuclei and electrons, an inductively coupled plasma (ICP) is generated and will etch silica (see Figure 4.8(b)). In the meantime, an RF bias applied on the substrate induces the vertical motion of the ions contained in the plasma. This vertical motion physically impacts the surface of the sample, thereby breaking the strong Si–O bonds and inducing directionality. The sample is thus etched both chemically and physically [70].

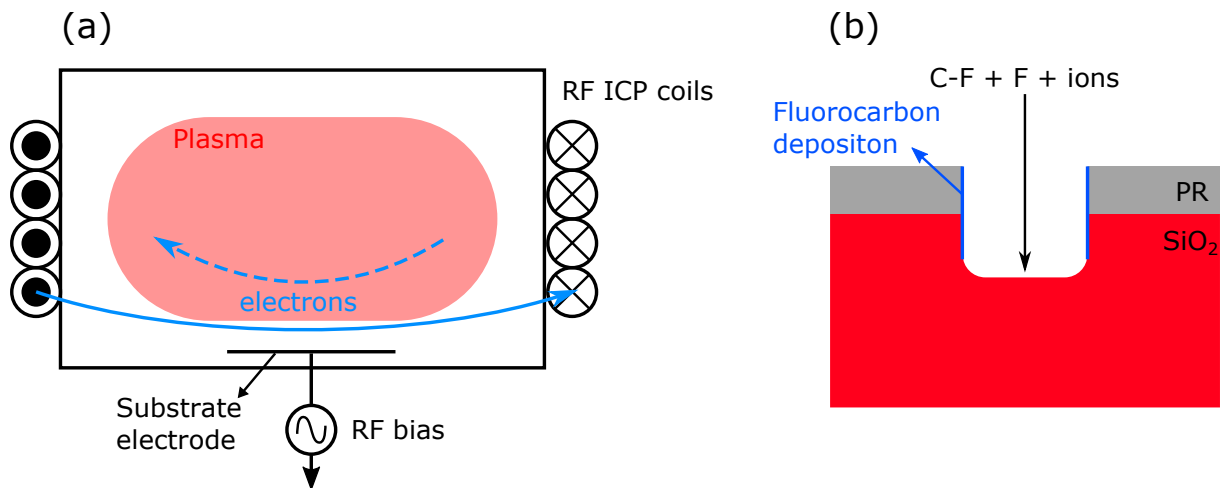


Figure 4.8: Schematics illustrating RIE. **(a)** Schematic of the equipment. A current is flowing through the ICP coils (continuous blue arrow), inducing an opposite current in the gas (dotted blue arrow) thereby creating the plasma. Another RF bias is applied on the substrate electrode for the physical etching. **(b)** Etching of a trench in the sample. Carbon and fluorine (coming from CHF_3) react chemically with silica while the ions impinge the surface vertically. A fluorocarbon is deposited on the sidewalls (in blue) and protect the PR, thereby increasing the directionality.

During the process, 50 sccm of CHF_3 and 3 sccm of O_2 are introduced in the chamber, resulting in a total pressure of 5 mTorr. The power of the ICP coils is equal to 800 W and the one of the RF bias is equal to 50 W. The temperature of the substrate lies around 20°C , though the wafer can heat up during etching. This eventual increase of temperature can lead to the failure of the photoresist which must be investigated after etching. Using these parameters, it is aimed to etch 500 nm of silica after etching for 75 s. A calibration needed to be performed in order to determine the parameters and the time of etching.

Metrology : Ellipsometry

Ellipsometry can be used to measure the remaining thickness of SiO_2 after etching. Knowing this value and the initial thickness of SiO_2 (see Table 4.1), it is easy to compute the etched thickness of SiO_2 . As given by Table 4.5, ~ 560 nm were etched, which is slightly higher than the targeted 500 nm. The ellipsometric graphs are similar to the ones in Figure 4.4 and are not shown here.

	Thickness of SiO_2 [nm]	MSE	Thickness etched [nm]
Wafer #1	2526.4	10.31	561.2
Wafer #2	2522.0	9.01	562.0
Wafer #3	2524.7	9.52	547.6

Table 4.5: Table giving the remaining thickness of SiO_2 , its associated MSE, and the thickness of SiO_2 that has been etched, determined from Table 4.1. The measurements are provided by ellipsometry with an angle of incidence at 70° .

The remaining thickness of photoresist covering SiO_2 must be measured to determine if the oxide was well protected. Table 4.6 shows that more than 520 nm are remaining. It is thus considered that the oxide has been protected from etching.

	Thickness of PR [nm]	MSE
Wafer #1	524.7	14.41
Wafer #2	523.9	15.79
Wafer #3	529.3	14.33

Table 4.6: Table giving the remaining thickness of photoresist and its associated MSE, as determined with ellipsometry. The angle of incidence was 70° .

4.2.5 Aluminum deposition

The aluminum can now be deposited inside the trenches that have just been etched in SiO_2 (see Figure 4.2(f)). The technique chosen for deposition is electron beam evaporation (EBE).

Electron beam evaporation

In EBE, the material to evaporate is locally heated using an electron beam (e-beam) as shown in Figure 4.9. The electrons are produced by thermionic emission and their motion is controlled using a magnetic field. The alignment of the e-beam is very important for preventing the deposition of the material of which the crucible is made, even though the latter is made of a refractory material. Indeed, the main interest in this mode of heating,

for replacing resistive heating, is that the crucible is not heated². and therefore will not be evaporated, which would lead to the contamination of the wafer.

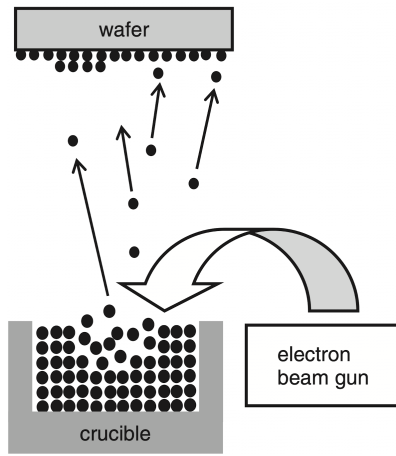


Figure 4.9: Schematic illustrating EBE. A beam of electrons is directed towards the material to deposit. This material, stored in a crucible, heats up and vaporizes. The evaporated atoms are deposited on the wafer. Taken from Franssila (2010) [68].

The pressure of deposition is very low, below 4×10^{-7} Torr which is classified as a high vacuum. The mean free path is thus greater than the size of the chamber, meaning that the evaporated molecules going towards the wafer will not enter in collision during their trip. The combination of the high vacuum with the heating via an e-beam leads to the deposition of a film with a very high purity.

The rate of deposition during evaporation of aluminum was equal to $5 \text{ \AA/s}$ which is very slow. Since it is aimed to deposit $\sim 500 \text{ nm}$ of metal, the deposition time remains reasonable and lasted for 17 min. The thickness of Al is measured during evaporation using a quartz crystal on which aluminum is deposited at the same time. This deposition changes the resonant frequency of the crystal, and this variation be converted into a deposited thickness. The

thickness of aluminum deposited will be measured after the lift-off, in Section 4.2.6.

Electromigration in Aluminum

An open circuit can be formed when a current is passing through a thin metallic wire. This phenomenon is known as electromigration and appears because the metal ions in the wire are dragged by an “electron wind”. The diffusion of the metallic ions can lead to the condensation of vacancies and thus the creation of a void. If sufficiently wide, this void can result in an open circuit.

The median-time-to-failure (MTF) depends on the size of the grains in aluminum as well as on the dimensions of the wire. Since the substrate is not heated during deposition, the grain size is expected to be small and the wire is very thin and narrow. By considering that the wire has respectively a width and a thickness equal to $2.66 \mu\text{m}$ and 700 nm (see Table 4.7), and that the lateral grain size is around $1.2 \mu\text{m}$ at it was the case for similar conditions of deposition [71], then it is expected to be in a regime between low and high polycrystallinity. Black (1969) [71] found that the MTF in hours is given by

$$\text{MTF} = \frac{wt}{2.43 \times 10^{-16} J^2 \exp\left(\frac{-0.48}{kT}\right)} \quad \text{for small grains and} \quad (4.1)$$

$$\text{MTF} = \frac{wt}{5 \times 10^{-13} J^2 \exp\left(\frac{-0.84}{kT}\right)} \quad \text{for large grains,} \quad (4.2)$$

²This heating is at least minimized, but not avoided. The crucible heats up a bit and is therefore cooled

where w and t are the width and the thickness in cm of the wire respectively, J is the density of current in A/cm², $k = 8.62 \times 10^{-5}$ eV/K is the Boltzmann's constant, and $T \simeq 25$ °C is the temperature of the circuit during the experiment. Therefore, if a current of 50 mA is passed through the circuit, the MTF will be somewhere between 1380 h (Equation 4.1) and 816 522 h (Equation 4.2). Electromigration is thus not a problem for this work, but further investigation should be conducted if applications with a long period of use are desired. At this moment, a simple solution would be to increase the temperature of the substrate during deposition for producing a single crystal film with a very high MTF, at least beyond one year [72].

4.2.6 Lift-off

The PR is still on the wafer and had two roles to play. The first was to protect SiO₂ during RIE. The second was to deposit aluminum on SiO₂ only in the trenches, and on PR elsewhere. This aluminum on top of PR can be removed by stripping this PR in a process named lift-off (see Figure 4.2(g)). To do so, the wafers are dipped in a sonicating bath of acetone during 35 min. The wafers are then rinsed with methanol and dried in a N₂ stream.

A negative resist is generally used in lift-off for a deposition over a flat surface, because the profile of the sidewalls are retrograde after development [73]. However, a negative resist is not necessarily the best choice for the deposition in trenches. In fact, the positive resist proved to provide better sidewalls for filling the trenches.

Metrology : Profilometry

The thickness of aluminum cannot be measured with ellipsometry because of its high reflectivity. Indeed, the light used in ellipsometry needs to penetrate a thin layer in order to determine its thickness. However, after lift-off, profilometry can be used to measure the height profile between silica and aluminum. Table 4.7 gives the height of this profile and the deduced aluminum thickness that has been deposited for each sample.

The used recipe for the evaporation aimed to deposit 500 nm and was checked with a crystal. However, it seems that EBE deposited 200 nm beyond the targeted thickness. The created profile might be a problem for studying the interaction of colloidal particles and bacteria with the surface and must be reduced as much as possible. The following sputtering should smooth out the profile. Although it will not be performed in this work³, atomic force microscopy (AFM) would allow to measure, more accurately than a profilometer can, the profile on the final device.

4.2.7 Silica deposition

As shown in Figure 4.2(h), silica is then sputtered all over the surface. This layer of SiO₂ is used for its dielectric and chemical properties. The former is used to prevent an electrical contact between the metallic circuit of the sample and the water in which the

³The cantilever of the AFM was broken when the measurements were to be performed.

Wafer #	Position	Profile height [nm]	Al thickness [nm]
Wafer #1	Top	137.4	698.6
	Center	132.0	693.3
	Bottom	130.3	691.5
Wafer #2	Top	161.2	723.2
	Center	151.2	713.1
	Bottom	136.9	698.9
Wafer #3	Top	158.9	706.6
	Center	85.6	633.2
	Bottom	121.1	668.7

Table 4.7: Table giving the profile height between SiO₂ and Al, as measured with profilometry. The aluminum thickness has been deduced from the profile and the depth of the trenches given in Table 4.5.

circuit will be immersed, while the latter is used to grow the brushes at the end of the process.

Reactive sputtering

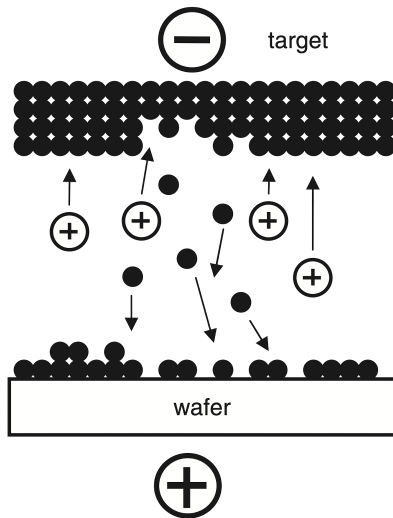


Figure 4.10: Schematic illustrating reactive sputtering. The positively ions are directed towards the target, made of the material to deposit. The atoms of the target are then deposited on the wafer. Taken from Franssila (2010) [68].

The working principle of sputtering is illustrated in Figure 4.10. A plasma is formed by applying an RF electric field to an argon gas introduced in the chamber. The atoms of argon that have been ionized by the RF field, Ar^+ , are then accelerated onto the negatively biased target. For the deposition of silica, this target is made of silicon. This non-conductive target could accumulate a positive charge because of the Ar^+ ions impinging it, but this charging is prevented by the RF electric field which creates the plasma [73]. An oxygen gas, O_2 , is also introduced in the chamber and will react with the sputtered silicon to deposit SiO₂, hence the name of reactive sputtering.

Due to the sputtering of the target with the argon ions, the atoms hitting the substrate have a substantial energy, which improves the adhesion and increase the density of the film because the loosely bound atoms are knocked out [68]. In addition, the substrate is heated with a lamp until a temperature of 80 °C for increasing the quality of the silica film, thereby increasing its dielectric strength. The power of the RF electric field was set

to 250 W. The flow of oxygen and the pressure during the process were equal to 4 sccm and 5 mTorr, respectively. For these deposition parameters, the deposition rate should be around 100 nm/h. It has been found in Section 3.3.2 that 686 nm of oxide should be sputtered, implying that deposition will last around 7 h.

Metrology : Ellipsometry

Ellipsometry can be used to measure the total thickness of SiO_2 at a location where aluminum has not been deposited. Although thermal and sputtered SiO_2 have slightly different optical properties, it is assumed that this difference is negligible. Typical ellipsometry measurements obtained for the sample in the center of the wafer #1 are shown in Figure 4.11.

The total and sputtered thicknesses of silica are given in Table 4.8. The thickness that has been sputtered is slightly too low, around 650 nm. However, if the dielectric strength of this oxide is sufficiently high, this thickness could be enough. The dielectric strength of the oxide will remain unknown until a voltage will be applied onto the circuit of the final device.

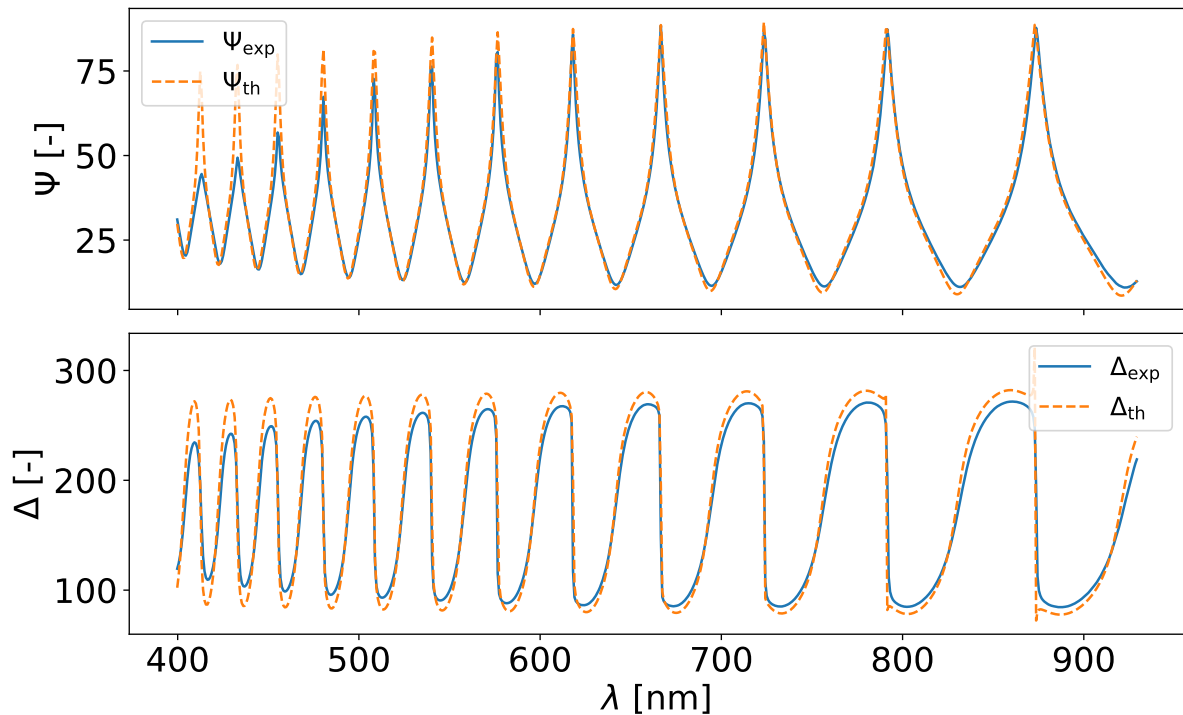


Figure 4.11: Ellipsometry measurements of the angles Ψ (top) and Δ (bottom) for the sample in the center of the wafer #1, for finding the total thickness of SiO_2 (thermal + sputtered). The experimental values are represented with a blue continuous line while the fit of the model is represented with an orange dashed line. The range of wavelengths starts at 400 nm and ends at 930 nm. The total thickness is found to be 3744.4 nm and the thickness of sputtered SiO_2 is deduced to be 656.9 nm. The angle of incidence was 70° .

Wafer #	Position	Total thickness [nm]	MSE	Sputtered thickness [nm]
Wafer #1	Top	3744.4	12.7	656.8
	Center	3744.5	12.4	656.9
	Bottom	3717.6	12.4	630.0
Wafer #2	Top	3732.2	12.6	648.3
	Center	3740.3	13.7	656.3
	Bottom	3728.3	14.0	644.3
Wafer #3	Top	3714.8	13.2	642.4
	Center	3717.4	13.5	645.1
	Bottom	3695.1	/	622.7

Table 4.8: Table giving the total thickness of silica, as measured with ellipsometry. The sputtered thickness has been deduced from the total total and initial (see Table 4.1) thicknesses of SiO₂. The angle of incidence was 70°.

4.2.8 Second photolithography

A second photolithography is performed (after the SiO₂ deposition but before the SiO₂ etching in Figure 4.2(h)) to subsequently etch the SiO₂ on top of the pads. The steps are exactly the same as for the first photolithography, except that the photomask must be aligned with the sample before exposure. To do so, the alignment marks “printed” sooner on the sample are aligned with the complementary alignment marks on the photomask. This alignment is performed using the *Suss Mask aligner MA6*.

Metrology : Ellipsometry

In the same way as for the first photolithography, ellipsometry is used to measure the thickness of PR. The thickness of PR for each sample is given in Table 4.9.

Wafer #	Position	Thickness of PR [nm]	MSE
Wafer #1	Top	916.0	26.2
	Center	926.7	27.0
	Bottom	932.4	28.2
Wafer #2	Top	892.6	25.6
	Center	920.1	25.9
	Bottom	897.8	26.1
Wafer #3	Top	907.2	24.9
	Center	916.5	25.1
	Bottom	916.1	27.6

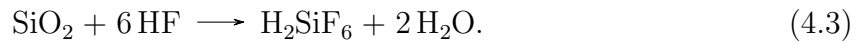
Table 4.9: Table giving the thickness of photoresist and its associated MSE, as measured with ellipsometry. The thickness of SiO₂ below this PR is given in Table 4.8. The angle of incidence was 70°.

4.2.9 Etching of silica for contact pads

The SiO_2 on top of the contact pads is etched in order to form a good electrical contact between the aluminum circuit of the device and the current source. Previously, ICP-RIE etching of SiO_2 was used because of the necessity to etch vertical sidewalls. There is no such constraint for the contact pads. Therefore, isotropic wet etching can be used. This method has the advantages to be faster and cheaper than ICP-RIE.

Isotropic wet etching

A buffered bath of hydrofluoric acid (BHF), containing a solution of NH_4F 40 %:HF 49 % (7:1), is used to etch SiO_2 . Ammonium fluoride NH_4F is used to neutralize the solution and make the etching less aggressive, allowing the utilization of photoresist as a mask. The overall reaction of etching is



The theoretical etching rate of SiO_2 in such bath is equal to 100 nm/min. However, the oxide above the pads has been sputtered and is thus less dense than a thermal oxide. Due to this difference, an etching of 1 min is sufficient to etch the ~ 650 nm of oxide above the pads. The etch rate of an evaporated aluminum film, in a similar BHF bath (5:1 instead of 7:1 here), is equal to 11 nm/min [74], almost $60\times$ slower than SiO_2 .

The fact that the SiO_2 layer was etched so easily by the BHF solution highlights the need to increase the density of this film. Indeed, this low density which is put forward by this etching is the reason why the dielectric strength of the top oxide is so low, as it was already mentioned in Section 3.3.2.

Metrology : Optical microscopy

The first way to determine if the photolithography and the etching went well is to check the alignment marks presented in Figure 4.12. Firstly, it is observed that the second photolithography is well aligned with the first one. Indeed, the pattern printed with the PR in Figure 4.6 is well adjusted with the one of the second photolithography as shown in Figure 4.12(b). Secondly, the SiO_2 that needed to be etched has been correctly removed and the SiO_2 covered by the photoresist has been protected. This last fact and an hypothesis on the dark appearance of aluminum, supported by optical images and additional experiments, are discussed in Appendix B.

The circuit of the samples are then investigated. A part of the circuit is shown in Figure 4.13(a) and reveals some defects. Figure 4.13(b) emphasizes the presence of a hole. The measurement of the resistance (see Table 4.10) of this sample shows indeed that the circuit is open. Samples that have a finite electrical resistance do not display such holes. These defects were not observed on the pattern shown by the optical images after the first photolithography. The removal of aluminum may have occurred during the sputtering of silica. Indeed, the sputtered atoms arrive on the substrate with a sufficient energy to

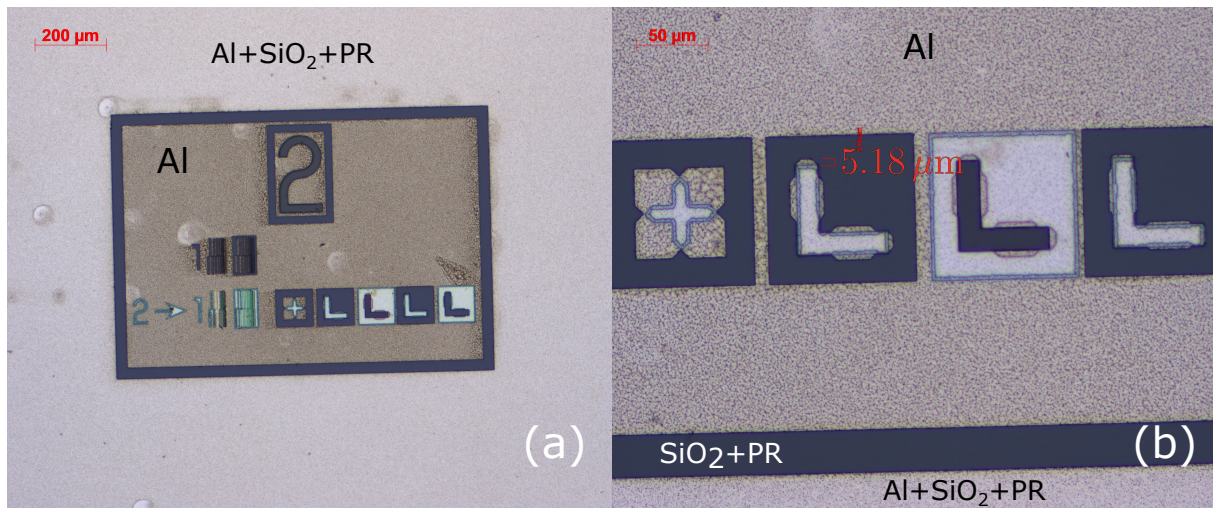


Figure 4.12: Optical microscope images of the alignment marks of the wafer #2 with a magnification (a) $\times 5$ (b) $\times 20$. The darkest material is SiO_2 covered with photoresist. The brightest material is aluminum covered with SiO_2 and photoresist. The “granular” material is aluminum.

remove the loosely bound atoms, as they can be found in an evaporated film of aluminum. Optical images should be acquired at each stage to confirm this hypothesis.

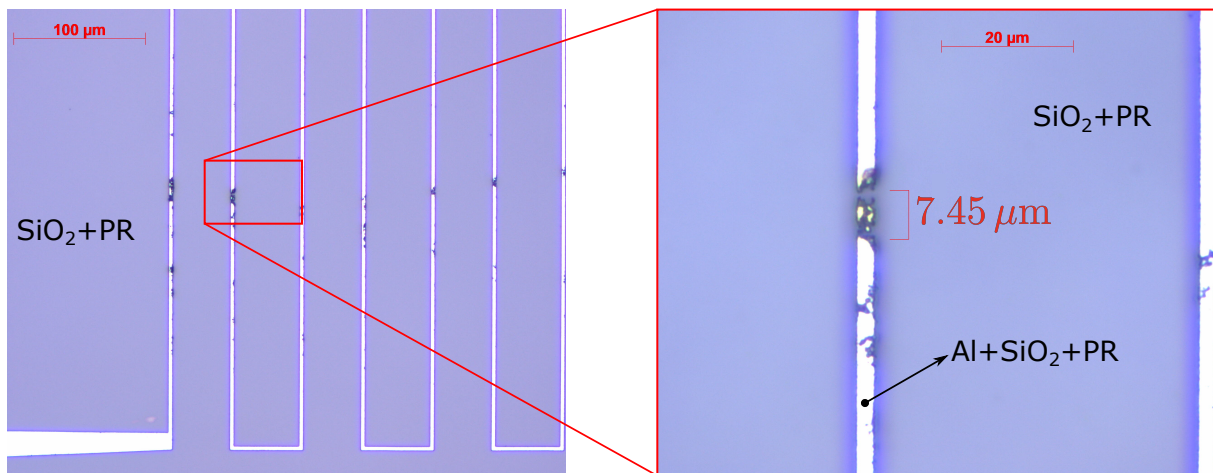


Figure 4.13: Optical microscope images of the circuit of the top sample on the wafer #2, with a magnification (a) $\times 20$ (b) $\times 100$. The hole in the lead is $7.45 \mu\text{m}$ long.

4.2.10 Characterization of the samples

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to characterize the dimensions of the produced samples. Figure 4.14(a) allows to determine that the electrodes are $48.8 \mu\text{m}$ apart. Figure 4.14(b) highlights the fact that the aluminum path connecting the electrodes can have different widths which could be the reason of the slightly different electrical resistances. Finally, the depth and width of the electrodes are respectively 678 nm and $2.68 \mu\text{m}$, as

indicated in Figure 4.14(c). These values are in good agreement with previous results obtained with optical microscopy (width of $2.66\ \mu\text{m}$, see Figure 4.7(b)) and profilometry (thickness of $707\ \text{nm}$, see Table 4.7).

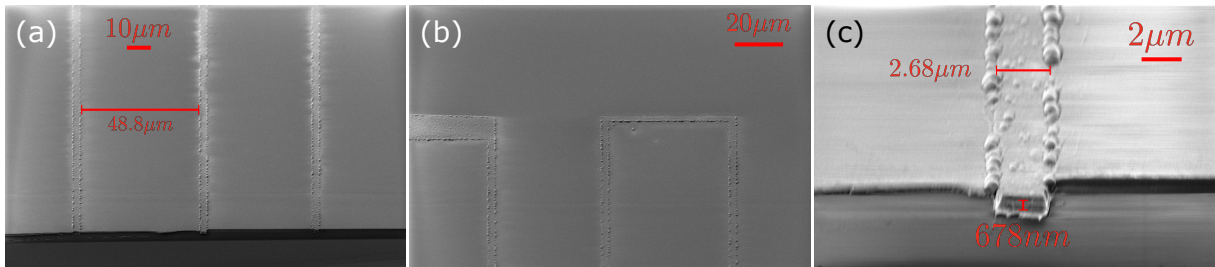


Figure 4.14: SEM images of the circuit on the top sample of the wafer #3 with a magnification (a) $\times 686$ (b) $\times 686$ (c) $\times 5720$. The sample was cut to observe the profile of the electrodes. The 45° tilt angle of the sample was taken into account for computing the thickness of the electrode.

Resistance measurements

Measuring the resistance of the samples is the most direct way to determine whether they have been well processed or not. The theoretical resistance of the circuit can be easily computed by knowing that the length of the circuit L is equal to $49.15\ \text{mm}$, the height h and width w of the electrodes are $\sim 700\ \text{nm}$ and $\sim 2.66\ \mu\text{m}$ (see Figure 4.7(b)) respectively, and the resistivity ρ is equal to $28.2\ \text{n}\Omega \cdot \text{m}$ [75]. Using $R = \rho L / (hw)$, the theoretical resistance is found to be equal to $744\ \Omega$.

The measured resistances of the samples are tabulated in Table 4.10. The resistances are more than two times higher than the theoretical one. Since the resistances of all samples are very close to each other, it is very likely that this factor comes from an error on the resistivity. Indeed, the resistivity of an evaporated thin film on a cold substrate is expected to be higher than the bulk one, because of aluminum high polycrystallinity in such films. It has been shown that the *resistivity* of an aluminum thin film decreases when its thickness increases⁴ [76, 77].

	Top	Center	Bottom
Wafer #1	OC	OC	1.869 k Ω
Wafer #2	OC	1.857 k Ω	1.835 k Ω
Wafer #3	OC	1.847 k Ω	1.883 k Ω

Table 4.10: Tabular summarizing the electrical resistance of each sample. An open circuit is shortened as OC.

⁴It is suggested by Mayadas *et al.* (1969) [76] that this correlation arises from the fact that the grain size increases when the thickness increases, thus reducing the grain-boundary scattering of electrons.

4.3 Preparation of polymer brushes

At this stage, the wafers are not anymore in cleanroom and have been brought in the Boltzmann's laboratory to grow the polymer brushes, as shown in Figure 4.2(i). This section describes the brush synthesis of poly(MEO₂MA-co-EOGMA) on three different wafers, bottom of wafer #1, center of wafer #2, and center of wafer #3.

4.3.1 Additional baking

This step does not serve the aim to grow polymer brushes but is used in order to increase the dielectric strength of the sputtered SiO₂ above the circuit.

The wafer #2 is baked on a hot plate at a temperature of 300 °C for 6 h. During all this time, the wafer lying on the hot plate was covered with an aluminum foil (no contact between the wafer and the foil). Afterwards, the film of silica should have become more dense, thereby increasing its dielectric strength. To verify this variation of density, the ellipsometer *Accurion nanofilm EP4* is used to measure the total thickness of SiO₂ (thermal + sputtered) after this baking, which is found to be equal to 3689.4 nm. By comparing this value to the ones found in Table 4.8 for the wafer #2, it is deduced that the film is indeed denser and should present a higher dielectric strength.

Obviously, the dielectric strength must have increased more than the thickness has been reduced, so that the oxide can withstand a greater voltage. In future, a larger thickness of SiO₂ can be deposited for anticipating this reduction of thickness.

4.3.2 Grafting of the initiator monolayer

Prior to growing the polymer brushes, an initiator must be grafted at the surface of the wafer, as explained in Section 2.3. In the present case, an ester silane initiator is used, namely 2-bromo-2-methyl propionic acid 3-trichlorosilanyl-propyl ester.

Pre-cleaning

The samples are cleaned during 10 min in an air plasma cleaner, *Emitech K1050X*, with a power equal to 100 W. The wafers are then placed in a first piranha bath H₂SO₄:H₂O₂ (3:1) during 10 min, rinsed in Milli-Q grade water for 10 min with changing 3 times water, and placed during another 10 min in a fresh piranha bath with the same proportions as the first one.

Grafting

This step must be performed inside a glove box. The individual samples are placed in a beaker, in which 20 mL of dry toluene 99.85 % and 20 μ L of (3-trimethoxysilyl)propyl 2-bromo-2-methylpropionate. The pressure and the fraction of water inside the glove box must be below 10 mbar and 10 ppm (because the C₁₀H₂₁BrO₅Si just added in the solution slowly reacts with water), respectively. The beaker is then left in the glove box overnight, covered with an aluminum foil to prevent contamination. This method of synthesis is

similar to the one in the supplementary information from Jonas *et al.* (2007) [43] and was adapted from Husseman *et al.* (1999) [78] and Brown *et al.* (2005) [79].

Post-cleaning

Before taking the samples out of the glove box, they are rinsed 3 times with dry toluene. Only after, the samples can be removed from the glove box, inside the last dry toluene bath covered with an aluminum foil. Finally, the samples are rinsed 3 times in acetone and dried with an N_2 stream.

4.3.3 Growing of polymer brushes

Now that the surface has been treated and is covered with initiator molecules, the SI-ATRP process explained in Section 2.3 itself can start. A large Schlenk tube was filled with 60 mL of milli-Q water, 30 mL of C_2H_5OH , and 36.4 g of di(ethylene glycol) methyl ether methacrylate 95 % (the monomer). In order to tune the LCST, poly(ethylene glycol) methyl ether methacrylate can be added, what has not been done here. To this mixture are added 1570 mg of 2,2'-dipyridyl 99 +%, and 43.8 mg of $Cu^{II}Cl_2$. The mixture was degassed by bubbling N_2 for 15 min. Then the Schlenk tube was opened, and 316 mg of $Cu^I Cl_2$ were added to the mixture. The tube was rapidly closed and degassed for an additional 45 min. Meanwhile three smaller Schlenk tubes, each containing a sample, were degassed by pumping on the Schlenk tube during 15 min and then filling them with N_2 . This cycle must be repeated 3 times (ideally 4). The mixture contained in the large Schlenk tube was then syringed and transferred to the smaller Schlenk tubes containing the samples.

The reaction proceeded under N_2 , and the samples were collected after 5 h. The samples with grown polymer brushes were rinsed in flowing milli-Q water, then methanol, and finally dried with an N_2 stream.

4.3.4 Metrology : Ellipsometry

The thickness of the grown polymer brushes can be measured using, for the last time in this chapter, ellipsometry. The obtained thicknesses are provided in Table 4.11.

	Without brush [nm]	Thickness of brush [nm]
Wafer #1 bottom	3706.0 ± 1.3	89.3 ± 0.5
Wafer #2 center	3706.9 ± 1.3	109.5 ± 0.5
Wafer #3 center	3689.3 ± 0.6	68.8 ± 0.5

Table 4.11: Tabular giving the thickness of SiO_2 before the growing of polymer brushes, and the thickness of P(MEO₂MA) brushes after SI-ATRP. The angle of incidence was 65°.

Chapter 5

Experimental results

At this stage, the system has been simulated and fabricated. It is now time to return to the main goal of this master thesis; characterizing the surface to subsequently study its interactions with colloidal particles and bacteria.

This chapter begins by reminding some principles of the reflection of polarized light which will allow to explain the working principle of ellipsometry. This characterization technique will be used to determine the thickness and the refractive index of the brush polymer at different temperatures. These measurements are a reliable way to determine the span over which the transition from a swollen to a collapsed brush occurs.

Unfortunately, ellipsometry does not allow to study in real-time the system. Indeed, the surface will be pulsed several times per second and ellipsometry cannot follow these quick variations. However, it will be shown in Section 5.3 that the swelling of the polymer brush can be directly measured with snapshots of the system over a region of interest, allowing to study of the system in real-time.

5.1 Working principle of ellipsometry

Ellipsometry is a non-destructive technique that allows to characterize a surface by measuring and interpreting its effect on the polarization of incident light. To do so, an elliptically polarized beam is sent onto the sample (see Figure 5.1). After reflection, the amplitude and the polarization of this beam have been modified and contain the information required for determining the wanted physical parameters, computed from modeling.

5.1.1 Some definitions

As illustrated in Figure 5.1, the traveling beam used for studying the sample always remains in the same plane, called the *plane of incidence*. The incident and reflected beams make an angle θ with the normal of the sample contained in the plane of incidence. In this work this angle will be fixed to 65° , near the Brewster angle of the substrate made of silicon.

The light is “made” of oscillating electric fields that can be split into two components in

the present case: One is parallel (p) to the plane of incidence, the other is perpendicular (s) to the plane of incidence.

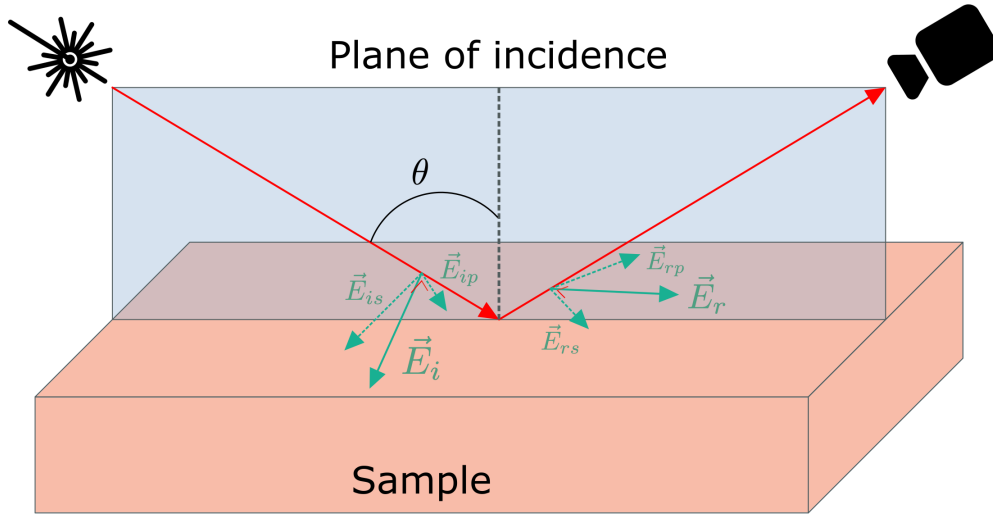


Figure 5.1: Schematic illustrating the plane of incidence which is defined as the plane containing the incident and reflected beams, as well as the normal of the sample. The incident and reflected beams form an angle θ with respect to the normal. The electric fields of the incident and reflected beam (at a given time, these fields are oscillating), as well as their components along s and p , are represented with green arrows.

In this coordinate system, the effect of the sample on the incident beam can be expressed as

$$E_{rp} = r_p E_{ip} \quad \text{and} \quad E_{rs} = r_s E_{is}, \quad (5.1)$$

where $E_{ip/s}$ and $E_{rp/s}$ are the components, along p and s , of the incident and reflected beams respectively (see Figure 5.1), and $r_{p/s}$ are the complex coefficients of reflection along p and s . For instance, $|r_p|$ and $\arg(r_p)$ give respectively the variation of amplitude and phase of the component of the electric field inside the plane of incidence. In ellipsometry, one is not interested in the absolute values of intensity. Actually, the ratio

$$\frac{r_p}{r_s} = \frac{|r_p|}{|r_s|} \exp[i(\arg(r_p) - \arg(r_s))] \triangleq \tan(\Psi) \exp(i\Delta) \triangleq \rho \quad (5.2)$$

is more interesting. Indeed, it contains all the information needed for determining a thickness and a refractive index, and makes the measurements insensitive to the intensity fluctuations of the light source [80]. The ellipsometer is an apparatus capable of determining this ratio ρ , and therefore the ellipsometric angles Ψ and Δ as well.

There are three types of light polarization that must be kept in mind for understanding ellipsometry:

1. *Linearly polarized light* is obtained when the electric field can be decomposed into two components which have the same amplitude and oscillate in phase.

2. *Circularly polarized light* is obtained when the electric field can be decomposed into two components which have the same amplitude but which oscillate with a $\pi/2$ -phase shift.
3. *Elliptically polarized light* is obtained for any other combination.

The light can also be said to be unpolarized when it contains electric fields oscillating in all directions, as it is the case for most light sources.

5.1.2 Instrumentation

The hardware of an ellipsometer allows to perform the three following steps [80, 81]:

1. Incident light is generated, with either a laser or a lamp. This light is unpolarized but it is made linearly polarized by passing through a polarizer (P). The light is then made elliptically polarized by passing through a compensator (C)¹. P and C are both able to rotate, making possible the generation of any elliptical polarization.
2. The incident beam interacts with the sample and reflects a beam with a new polarization (see Equation 5.1).
3. The polarization state of the outgoing beam is partially or fully characterized using an analyzer (A), which is nothing else than another polarizer.

Two additional steps are required to convert the obtained raw data into physical parameters:

4. The parameters that characterize the optical interaction, such as Ψ and Δ , between the beam and the sample are computed.
5. Ψ and Δ are converted into physical parameters such as the thickness or the refractive index.

However, it is not an easy task to determine Ψ and Δ (step 4) using this hardware. A way to fulfill this task, among others, is nulling ellipsometry.

¹This compensator is in fact a quarter-wave plate. This optical device is made of a birefringent material possessing a “fast” (low n) and a “slow” (high n) axis, along which light will travel two different optical path lengths. This difference of path creates exactly a delay of 90° in phase (i.e. a quarter wavelength, hence the name) between the two components of light along the two axes of the quarter-wave plate. If the incident polarized light (two components along optical axes oscillate in phase) makes an angle of 45° with the optical axes, the outgoing electric field will have two components oscillating with a delay of 90° and with the same amplitudes, called circularly polarized light. For any different angle other 45° , the outgoing light will be elliptically polarized.

5.1.3 Nulling ellipsometry

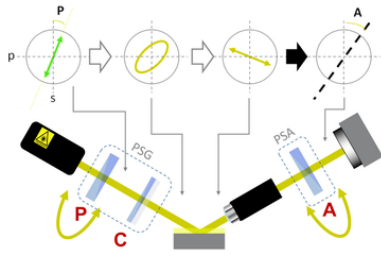


Figure 5.2: Schematic illustrating the principle of nulling ellipsometry. Taken from Ref. [82].

The principle of nulling ellipsometry is to determine ρ by extinguishing the intensity measured at the photodetector.

The steps that are detailed in this paragraph are illustrated in Figure 5.2. As mentioned previously, any elliptical polarization can be generated by rotating P and C. One of them becomes linearly polarized after reflection on the sample. A linearly polarized electric field is readily extinguished by another polarizer, A, by placing the axis of the linear polarization perpendicularly to A. The process for extinguishing the beam is called “nulling”.

There are several iterative routines allowing to determine the angle settings P, C, and A which extinguish the signal. The method used here keeps fixed C but rotates P and A to find the nulling conditions. First, P is rotated to find the minimum signal position. Secondly, P is fixed to that position while A is rotated until finding the nulling conditions [83].

The three angles P, C, and A providing the null conditions can then be used to determine Ψ and Δ . Indeed, these quantities are related by relations as

$$\Psi, \Delta = f(P, C, A), \quad (5.3)$$

which are retrieved by Azzam *et al.* (1978) [83].

5.1.4 Optical modeling

This section describes how to perform the step 5 from Section 5.1.2.

Ellipsometric equations relating ρ to physical parameters are nonlinear and in most cases, transcendental. Therefore, the equations $\rho(\text{refractive index, thickness,...})$ cannot be inverted and the physical parameters cannot be computed from analytical solutions, except for some simple cases.

The most simple case is an incident beam on a substrate without any layer above, schematized in Figure 5.3. If these two media are considered as homogeneous and isotropic, the complex coefficients of reflection at their interface are given by the Fresnel’s equations [84]:

$$r_p = \frac{n_2 \cos \theta_1 - n_1 \cos \theta_2}{n_2 \cos \theta_1 + n_1 \cos \theta_2} \quad \text{and} \quad r_s = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2}, \quad (5.4)$$

where n_1 and n_2 are respectively the complex refractive indices of the ambient medium and substrate, and θ_1 and θ_2 are respectively the angles of incidence and refraction. The

angle of refraction is further related to the angle of incidence by the Snell's law [84]:

$$n_1 \sin \theta_1 = n_2 \sin \theta_2. \quad (5.5)$$

By taking the ratio of the two complex coefficients of reflection (5.4), inserting the Snell's law (5.5), and inverting the obtained equation, one obtains [85]:

$$n_2 = n_1 \tan \theta_1 \sqrt{1 - \frac{4\rho \sin^2 \theta_1}{(\rho + 1)^2}}. \quad (5.6)$$

Using Equation 5.6, one can compute the unknown n_2 from the known n_1 (literature), θ_1 (fixed by the user), and ρ (determined with nulling ellipsometry). Although this model helps to understand the physics behind ellipsometry, it is too simple for practical applications. It can also be noticed that a single measurement, providing Ψ and Δ , is sufficient to determine the real and imaginary parts of n_1 .

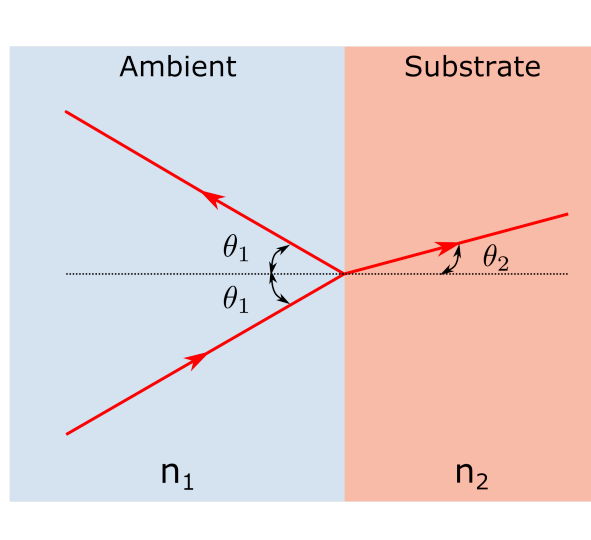


Figure 5.3: Schematic illustrating Snell's law between the ambient environment and a substrate.

Unfortunately, an analytical solution such as the one in Equation 5.6 does not exist for more complex systems with several thin films above the substrate, with unknown thicknesses and indices of refraction. Therefore, optical models have been constructed to replace Equation 5.6. The modeling software of the *Nanofilm EP4* uses the so-called 4×4 -matrix algorithm [84], which is able to calculate the polarizing properties of reflection and transmission of layered thin-film samples [82]. However, the equations obtained with this algorithm are transcendental and non-linear so that it is impossible to find analytical relations providing directly the physical quantities. Therefore, these equations are solved numerically using a non-linear fitting algorithm developed by Levenberg & Marquardt [86].

The system in Figure 5.3 required one measurement to determine the two ellipsometric angles Ψ and Δ , which in turn allowed to determine the real and imaginary parts of n_1 . If one desires to determine the thickness of one or several thin films, as well as their complex

indices of refraction, then multiple measurements are required to obtain more information about the system. This information is obtained by nulling the signal at several wavelengths, providing each time two new ellipsometric angles. This technique is called *spectroscopic ellipsometry* and allows to determine, or overdetermine depending on whether the number of unknowns is equal to or less than the number of ellipsometer angles determined, all the physical parameters [80].

5.1.5 Imaging with the ellipsometer

If an objective and a charge-coupled device (CCD) camera are added to the ellipsometer, it becomes possible to produce images. The objective collects and focuses the light inside the CCD camera. The latter is a photodetector made of an array of capacitors which accumulate charge proportionally to the intensity of light they receive, thereby creating a spatially resolved image.

The combination of this imaging setup with the possibility to nullify the signal with P, C, and A, allows to extinguish a part of the image with given optical properties but not another one with other properties, thus discriminating these two regions. For instance, one region could be silica covered with a polymer brush, and the other one could be aluminum electrodes covered with silica and a polymer brush. The aluminum electrodes are much more reflective than silica and could be readily distinguished without this nullifying, but this setup is still able to provide additional information as will be shown in Section 5.3.

5.1.6 In situ liquid cell

Chapter 2 was focusing on the interaction of polymers in solution, not in air. Therefore, the sample is placed in a liquid cell filled with previously degassed DI water. The windows of this liquid cell must be positioned perpendicularly to the incident and reflected beams to prevent it to be refracted, which would change the polarization states and make the measurement very tedious. The setup with the liquid cell is shown in Figure 5.4

5.2 Spectroscopic ellipsometry

The thickness and the index of refraction of the polymer brush grown on the center sample of the wafer #3 are obtained with spectroscopic ellipsometry for several temperatures between 10 and 40 °C. These measurements allow to verify that there is a transition that takes place around the LCST of P(MEO₂MA). However, spectroscopic ellipsometry will not be used to study the interaction of the surface with colloidal particles or bacteria.

Prior to placing the sample in the liquid cell, the thickness of the polymer brush in air is measured. The so-called dry thickness was determined to be 81.7 nm. Figures 5.5(a) and (b) plot the thickness and the refractive index of the sample, placed in the liquid cell, versus temperature. Firstly, it can be noticed that the polymer brush has been considerably stretched by just placing it in water, with a measured thickness of 185 nm

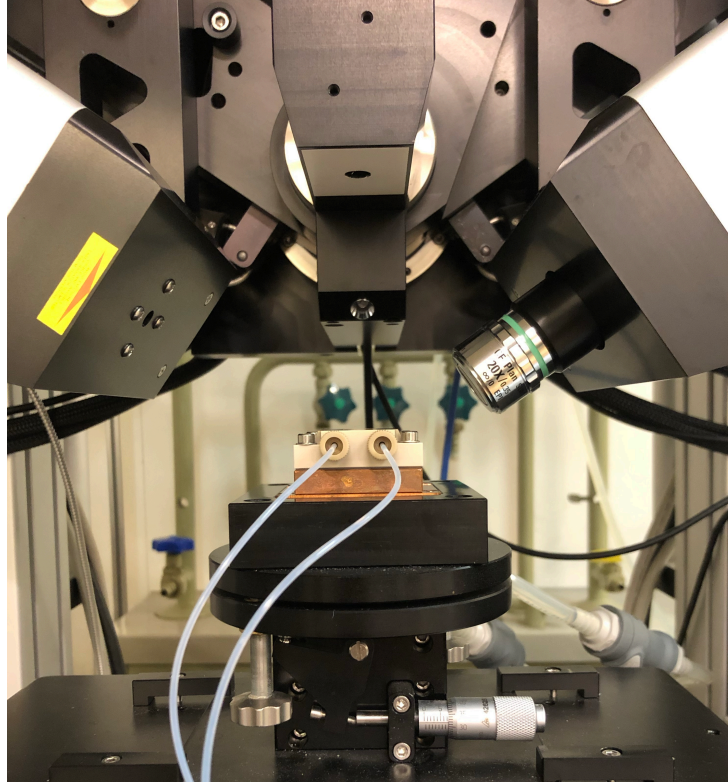


Figure 5.4: Picture of the ellipsometer set up. The sample is placed on the copper plate and is covered by the liquid cell. The copper plate is lying on the Peltier cell.

at 10 °C. Secondly, a clear transition occurs when the temperature is increased from 15 to 30 °C. Indeed, the thickness steadily decreases from 175 to 136 nm while the refractive index steadily increases from 1.39 to 1.42. The refractive index increases because water is progressively expelled from the polymer brush when the temperature is increased above the LCST ($n_{\text{H}_2\text{O}} \simeq 1.34$ in the visible spectrum at 25 °C [87]). The Cauchy dispersion formulas were used to model the real and imaginary parts of the refractive index:

$$N(\lambda) = A_N + \frac{B_N}{\lambda^2} + \frac{C_N}{\lambda^4} \quad \text{and} \quad k(\lambda) = A_k + \frac{B_k}{\lambda^2} + \frac{C_k}{\lambda^4}, \quad (5.7)$$

where N is the real part of the refractive index, k is the absorption coefficient, λ is the wavelength of the incident light, and $A_{N/k}$, $B_{N/k}$, and $C_{N/k}$ are the coefficients giving the variation of N and k with the wavelength. However, the brush is too thin to measure any absorption, so that one can take the approximation $A_k = B_k = C_k = 0$. In addition, the refractive index was not found to significantly vary in the studied range of wavelengths, leading to $B_N = C_N = 0$. Therefore, the complex refractive index n is simply equal to A_N , and is plotted in Figure 5.5.

These two graphs can be compared to the graphs in Figure 5.5(c) measured by Zhuang *et al.* (2016) [65]. Although the absolute values slightly differ, the trends of both curves are the same. Therefore, it can be concluded that the polymer brush was properly grown on this sample and further study can be performed.

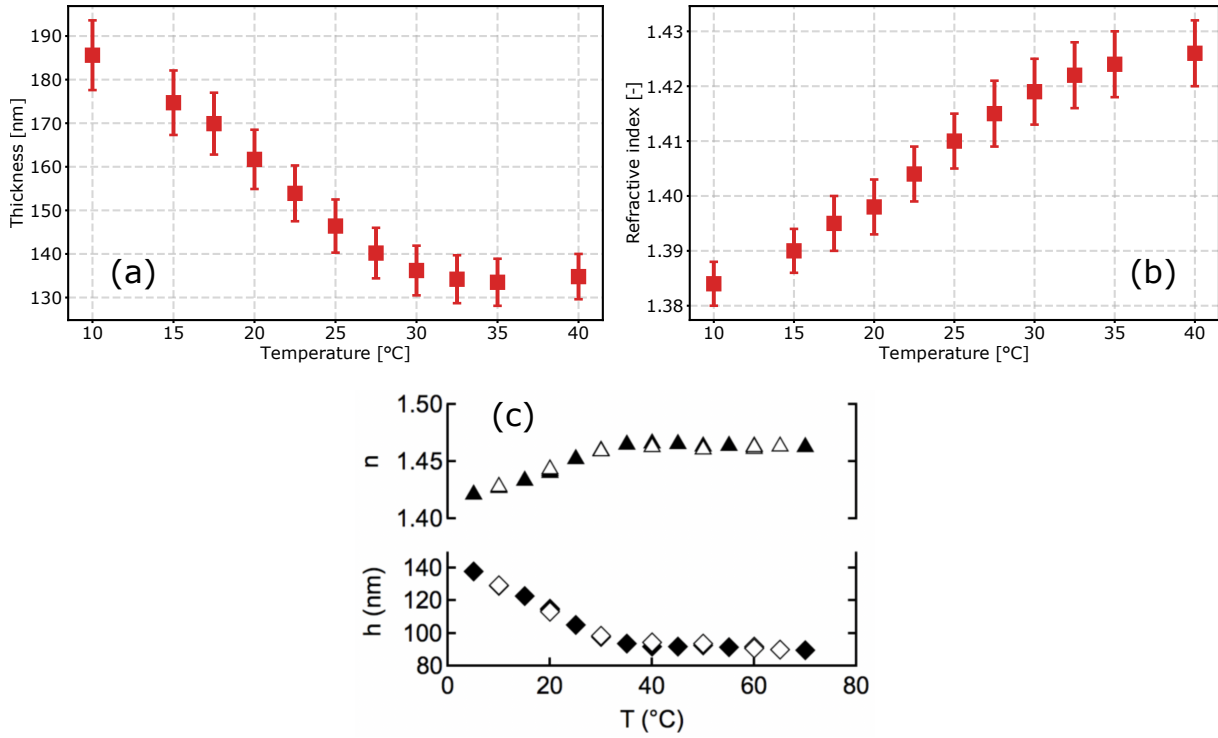


Figure 5.5: **(a)** Thickness and **(b)** refractive index of the polymer brush, with a dry thickness of 81.7 nm, as a function of the temperature, determined with ellipsometry. The angle of incidence was 65° and nulling ellipsometry was performed at 21 wavelengths evenly spaced between 400 and 800 nm. **(c)** Comparison with the results obtained by Zhuang *et al.* (2016) [65] for a PMEO₂MA brush with a dry thickness of 78 nm. Closed symbols are for the measurements during heating while the open ones are during cooling, highlighting the reversibility of the transition.

5.3 Imaging with the ellipsometer

Imaging was performed with the ellipsometer on the same sample, immediately after spectroscopic ellipsometry. This method is used to take snapshots of the sample at different temperatures. The present section aims at determining whether it is possible or not to identify the transition of the brush with this method, without measuring Ψ and Δ but only a change of reflected intensity. No current will flow through the electrodes. The temperature will be changed by the Peltier cell and should be homogeneous over the sample. If it is found that the intensity of the signal significantly varies between the swollen and collapsed states of the brush, then this imaging method will allow to study in real-time the “pulsing” surface when current will pass in the circuit (with Peltier cell turned off).

The way to proceed is the following. The temperature is set to 5°C with the Peltier cell. The signal of the lamp at 658 nm is nulled and the angles of P, C, and A nullifying the signal are kept until the end of the experiment. This nulling allows to reduce the noise and increases the sensitivity to any variation of the system. The first snapshot can then be captured. In order to further reduce the noise, 10 snapshots are taken one after the other to subsequently make a “mean” image. The temperature is then increased in steps

of 2.5 or 5 °C. It is required to wait at least 2 minutes before taking the snapshots to give the system time to reach thermal equilibrium.

Remark: Although a laser can deliver more power at a single wavelength than a lamp, it is excluded to use it. The reason is that a laser produces highly monochromatic light which has consequently a high coherence time. The edge diffraction arising from the interaction of light with the electrodes creates interference patterns which are not desired here. This interference pattern can be observed in the line profile of intensity provided in Figure 5.10. The coherence time is greatly reduced by using the lamp, and thus the interference as well.

5.3.1 Intensity versus temperature: Bare wafer

The first step of this experiment is to find how the intensity varies for a substrate of Si covered with 3576 nm of SiO₂ (determined with spectroscopic ellipsometry). This will allow to grant an eventual transition to the polymer brush and not to the substrate. As explained in the procedure, the angles of P, C, and A for nulling the signal are recorded and are equal to 46.896°, 45.000°, and 10.674°, respectively. Afterwards, 10 snapshots are taken for each temperature. By adding the intensity of these 10 snapshots pixel by pixel and then dividing the intensity of all pixels by 10, a mean image is obtained. An average intensity per pixel can be further computed over this mean image to obtain a single value of intensity for each temperature. The evolution of this mean intensity with temperature is plotted in Figure 5.6. This intensity is fairly constant up to 30 °C. Above this temperature, the intensity suddenly and moderately increases. This increase is probably due to the variation of the refractive indices of SiO₂ and water. This variation leads to a change in the polarization of the reflected light, thereby removing the nulling conditions previously set at 5 °C.

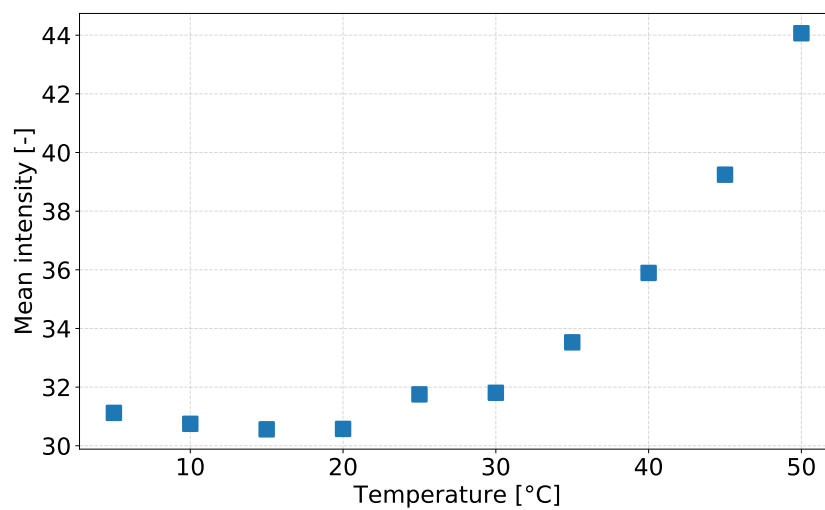


Figure 5.6: Mean intensity per pixel of a bare wafer as a function of temperature.

5.3.2 Intensity versus temperature: Wafer #3 center

Imaging with the ellipsometer can now be performed on a sample with electrodes and a grown polymer brush. The recorded angles of P, C, and A are equal to -35.823° , 45.000° , and -25.113° . The mean intensity per pixel versus temperature is plotted in Figure 5.7. This graph is obtained by following the same scheme as the one for obtaining Figure 5.6. The mean intensity significantly increases in the same temperature range as the thickness and refractive index in Figure 5.5. Since this variation cannot come from the bare wafer, the transition is attributed to the polymer brush. Due to the similar trends followed by the refractive index and the intensity, the variation of intensity is specifically attributed to the variation of the polymer brush refractive index. It is therefore concluded from this graph that this imaging mode succeeds in measuring the transition of a polymer brush and should allow to study in real-time the local swelling of this brush.

This same graph can even be used to roughly determine the temperature over the surface by measuring the intensity. Figure 5.7 would then be a calibration curve. However, this conversion is made by making the hypothesis that the index of refraction of water does not significantly vary over the studied temperature range. Indeed, this calibration curve is obtained by heating with a Peltier cell, leading to an homogeneous temperature in the liquid cell. The temperature of water thus spans from 5 to 50 °C. In contrast, the local swelling of brush will be varied by heating with electrodes with the Peltier cell turned off, which will not heat the entire liquid cell. This means that water in this experiment will always be equal to 20 °C, excepted just above the surface.

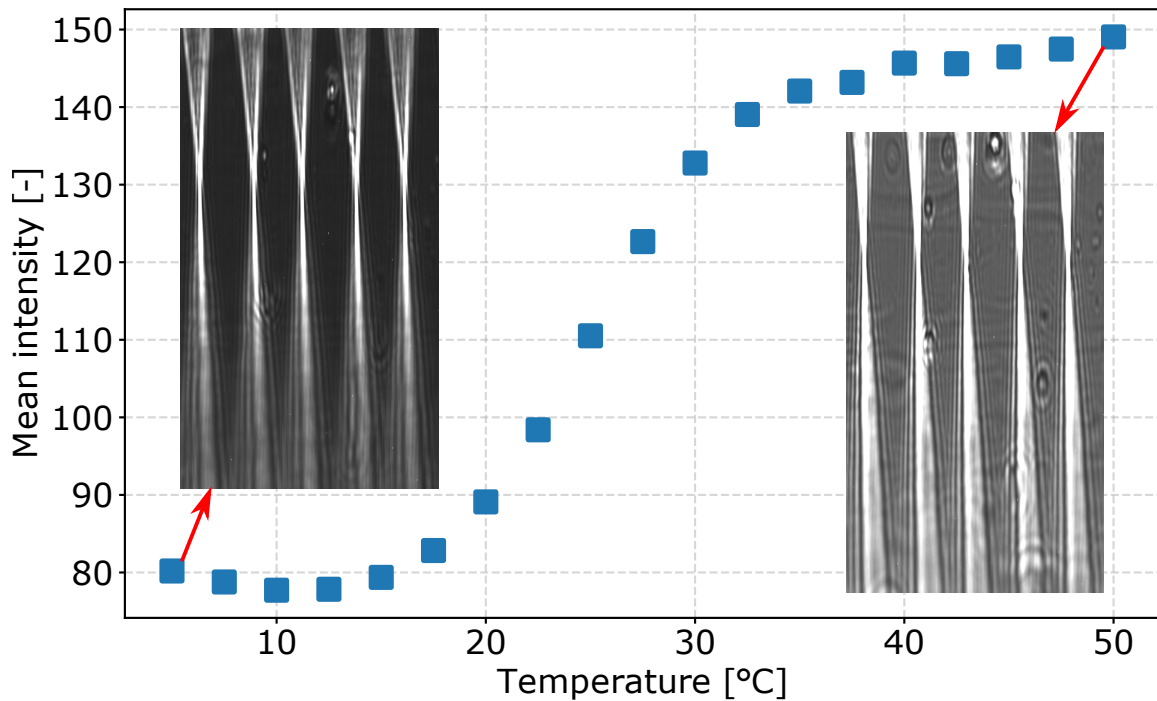


Figure 5.7: Mean intensity per pixel of the sample in the center of the wafer #3 as a function of temperature. Left inset: Mean image at 5 °C. Right inset: Mean image at 50 °C.

If one only considers the reflection at the water/brush interface, then it is possible to

determine whether neglecting the variation in the refractive index of water is reasonable or not. For such interface, one can calculate the reflected intensity for different temperatures of water. The temperature of the polymer brush is fixed in order to isolate the variation of reflected light coming from water. The reflectivity at this interface, which contributes to the intensity measured by the camera, can be computed from the Fresnel's equations (5.4) and the Snell's law (5.5). There are two different experiments to compare. The first is the one during calibration: For instance, the water and the polymer brush can be both at 50 °C. The second is the one during local heating: For instance, the water is at 5 °C and the polymer brush at 50 °C because it is heated by an electrode. These two extreme cases will allow to find a high boundary for the error made if the variation in the refractive index of water is neglected. The reflected intensity at any temperature is computed as

$$I_r(T) = ||\vec{E}_r(T)||^2 = E_{rp}^2(T) + E_{rs}^2(T) = r_p^2(T)E_{ip}^2 + r_s^2(T)E_{is}^2, \quad (5.8)$$

where $\vec{E}_r$ is the reflected field at the interface, and the components of the incident electric field are considered to be independent from temperature because the absorbance of water is negligible. From there, the relative difference of intensity (RDI) between the two systems just mentioned is readily found:

$$\frac{|I_r(50^\circ\text{C}) - I_r(5^\circ\text{C})|}{I_r(5^\circ\text{C})} = \frac{|E_{ip}^2[r_p^2(50^\circ\text{C}) - r_p^2(5^\circ\text{C})] + E_{is}^2[r_s^2(50^\circ\text{C}) - r_s^2(5^\circ\text{C})]|}{E_{ip}^2 r_p^2(5^\circ\text{C}) + E_{is}^2 r_s^2(5^\circ\text{C})}, \quad (5.9)$$

where the temperatures are those of water, since the polymer brush is always at 50 °C. The angle of incidence θ_1 is fixed at 65° and the refractive indices are provided in Table 5.1 (at temperatures slightly different than 5 and 50 °C, but still sufficiently close to consider that the refractive indices would not significantly differ). The RDI is equal to 0.080 for an electric field totally polarized along s (i.e. $E_{ip} = 0$), and equal to 0.064 for an electric field totally polarized along p (i.e. $E_{is} = 0$). Any value of the RDI is comprised between these two extreme values. The highest RDI equal to 0.08 creates an uncertainty when one wants to convert intensity into temperature. This high boundary will be used to estimate the uncertainty on the measured temperature arising from the fact that the variation of the water refractive index was neglected.

The case of a polymer brush which is not locally heated is not considered because this brush would be at the same temperature as water. The system would therefore be exactly the same as the one during calibration and no uncertainty would be induced.

$n(T[^\circ\text{C}], \lambda[\text{nm}])$	$n_{\text{H}_2\text{O}}(10, 589)$	$n_{\text{H}_2\text{O}}(50, 589)$	$n_{\text{brush}}(40, 400 - 800)$
Value	1.33341	1.32892	1.426

Table 5.1: Values of the refractive indices of water [88] and polymer brush (see Figure 5.5).

The insets in Figure 5.7 at 5 and 50 °C contain also much information and two remarks are worth noting:

1. The image is properly focused over a single line of the image because of the angle between the incident beam and the normal to the surface. This so-called “focus line”

is shifted upwards when the temperature is increased. This shift must be taken into account during the analysis of the images. The physical origin of the focus line drift as well as a method to find the position of the focus line at each temperature are presented in Section 5.3.3.

2. There are two distinct regions: One region with the aluminum electrodes, which are very reflective, and one region between the electrodes, acting as a background. These two regions need to be treated separately for the calibration that will allow to determine the temperature from the intensity. Indeed, their behaviors are very different and the intensity averaged over the whole image in Figure 5.7 cannot be used to determine locally the temperature. On one hand, the background is constant and has a low intensity. The mean intensity, which also contains the bright electrodes, would therefore underestimate the temperature of this background. On the other hand, the region with the electrodes has a high intensity and displays a diffraction pattern, making even impossible the estimation of a single intensity that would allow to determine the temperature. Therefore, two distinct methods must be used for the calibration of these two regions and are detailed in Section 5.3.4.

5.3.3 Shift of the focus line

Since the incident and reflected beams are not perpendicular to the sample, only a few lines of the image are correctly focused. It is possible to scan the region of interest by progressively moving the position of the objective, and thus obtain a fully focused image. However, the process takes several seconds, making impossible the observation of the surface in real-time.

This focus line is of tremendous importance in this work because it will allow to properly determine the calibration curve relating the intensity to the temperature. It can be noticed in the insets of Figure 5.7 that this focus line contains many bright points. Therefore, it is assumed that the focus line is the line with the largest number of pixels with an intensity higher than 90 %² of the brightest pixel contained in the image. The position of the focus line for each temperature is provided in Figure 5.8. This position is progressively drifting when the temperature is increased, which must be taken into account for calibration.

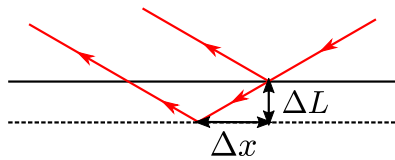


Figure 5.9: Schematic illustrating the lateral shift.

This drift comes from the thermal expansion of the copper plate on which the sample lies. The coefficient of linear thermal expansion of copper at 20 °C is equal to $16.54 \times 10^{-6} \text{ K}^{-1}$ [89] and the copper plate has a height around 10 mm. Between 5 and 50 °C, the sample is thus raised by a height ΔL (see Figure 5.9) equal to $7.44 \mu\text{m}$. Considering an incident beam arriving with an angle of 65° with respect to the normal of the substrate, the lateral shift along the surface Δx is equal to $\Delta L / \tan(25^\circ) = 16 \mu\text{m}$. By remembering that the width of the electrodes is equal to $2.66 \mu\text{m}$ (see Figure 4.7) and noticing that

²The choice of 90 % is kind of arbitrary and was tuned for providing reliable results at all temperatures. It is to be hoped that this value is “universal”, but this must be verified with other samples.

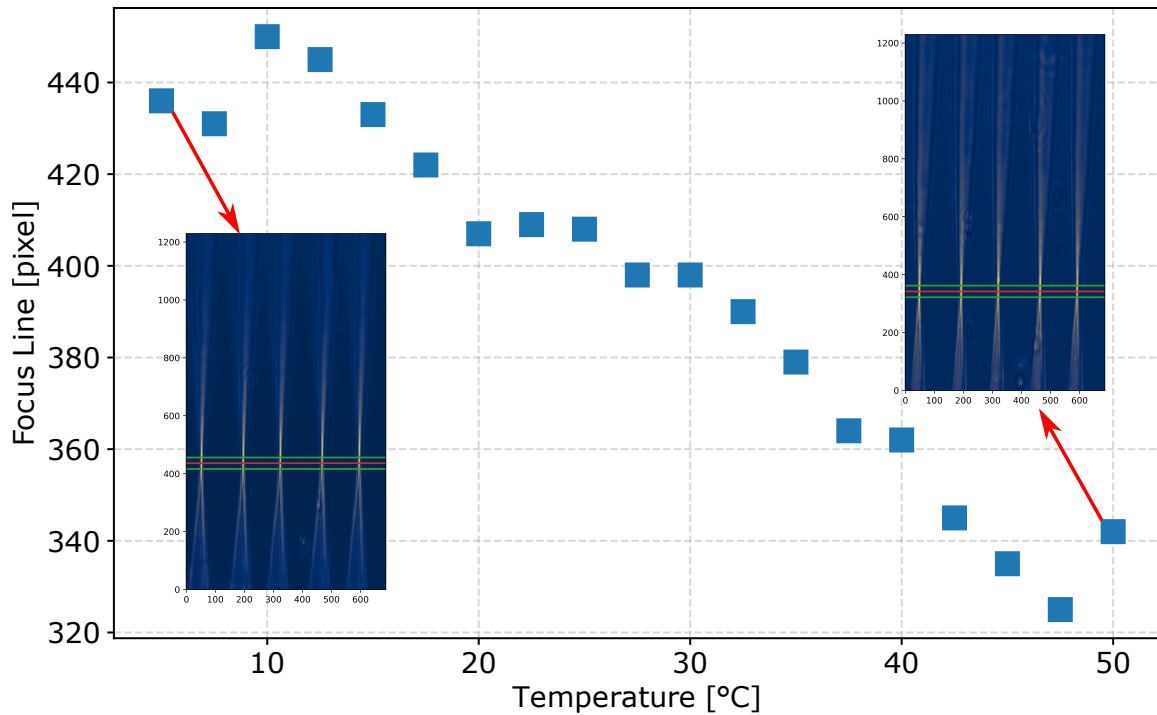


Figure 5.8: Graph giving the position of the focus line as a function of temperature. Insets: Mean images at 5 and 50 °C. The red horizontal line is the focus line. The green horizontal lines, located 20 pixels above and below the focal line, delineate the area studied for calibration.

the width of an electrode is ~ 15 pixels in the images, it is possible to determine that the lateral shift of the focus line is equal to $\sim 18 \mu\text{m}$ (considering a shift of 100 pixels, determined from Figure 5.8). It is thus concluded that the drift of the focus line is due to the thermal expansion of the copper plate. Such drift should not be observed when water will be locally heated with the electrodes because the copper plate will remain at the same temperature, around 20 °C.

5.3.4 Calibration over and between electrodes

Heating homogeneously the sample with a Peltier cell does not directly serve the aim of creating a pulsing surface, but rather to characterize it. It allows not only to determine the transition zone of the polymer brush with spectroscopic ellipsometry, but also to relate the local intensity to a local temperature with the images produced by the ellipsometer. Such calibration is very useful because it allows to determine locally and in real-time the temperature of a locally heated surface. However, two different calibrations need to be performed because of the presence of aluminum electrodes at the surface, creating both very bright pixels and a diffraction pattern.

The quantities used to calibrate these two regions are still to be determined. In order to find them, it is interesting to have a look at the intensity along the focus line at different temperatures, provided in Figure 5.10. The intensity between the electrodes is significantly increasing when the temperature is raised from 5 to 50 °C. The mean intensity of the background will thus be used for the calibration between electrodes. The width and height

of the 5 largest peaks are both increasing, making the integral of these peaks a good candidate for the calibration above electrodes.

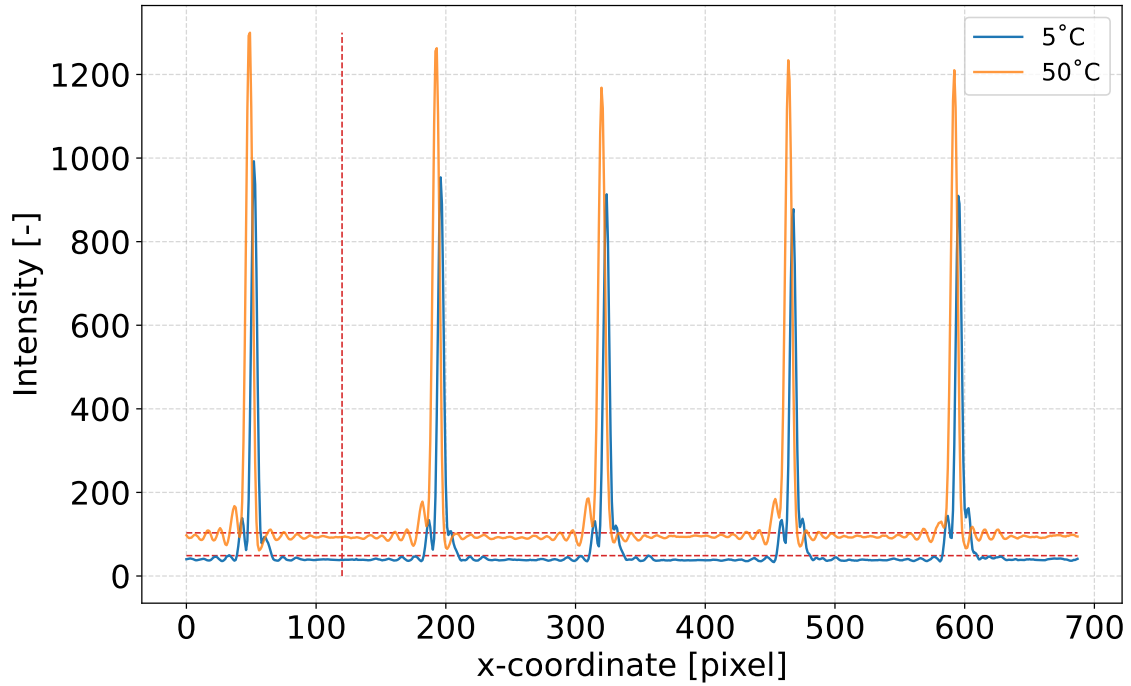


Figure 5.10: Intensities of the signal along the focus line, including 20 pixels above and below this line to reduce noise, at 5 and 50 °C. The vertical dashed red line is the location at which the line profile is estimated for determining the threshold value of intensity below which the intensity is considered as belonging to the background. The two horizontal dashed red lines indicate the threshold values at 5 and 50 °C, respectively.

Calibration between electrodes

An average intensity per pixel, which excludes the pixels belonging to the electrodes and to the diffraction pattern, must be computed for calibrating the region between the electrodes. To do so, one takes a threshold value of intensity above which the pixels are excluded during the calculation of the average. Since the background intensity increases with temperature, the threshold value must be raised accordingly. Therefore, one can take the intensity of a pixel between electrodes (see vertical dashed line in Figure 5.10) added to a constant. This constant is fixed to 10 and is selected so that the electrodes and the diffraction pattern are excluded while keeping the background. The threshold values at 5 and 50 °C are indicated in Figure 5.10.

The mean intensities per pixel between and above³ electrodes are plotted in Figure 5.11. These values are divided by the intensity at 5 °C because it provides a better idea of the intensity sensitivity when temperature varies. It is observed that the mean intensity per pixel between electrodes can be used for calibration. Indeed, the intensity monotonously

³The mean intensity per pixel above the electrodes only keep the pixels with an intensity higher than the threshold value just discussed.

increases with temperature. This curve has the highest sensitivity in the transition zone which is convenient since the temperatures with local heating will lie around this zone. Although the temperature below 15 °C and above 35 °C cannot be determined (the intensity is constant), it is not a problem because it is sufficient to know whether the polymer brush is collapsed or not.

A polynomial fit of the temperature as a function of the intensity $T(I)$ (see the caption of Figure 5.11) provides the calibration for each intensity in this range. In contrast, the mean intensity per pixel above electrodes cannot be used for calibration because it is not a monotonous curve.

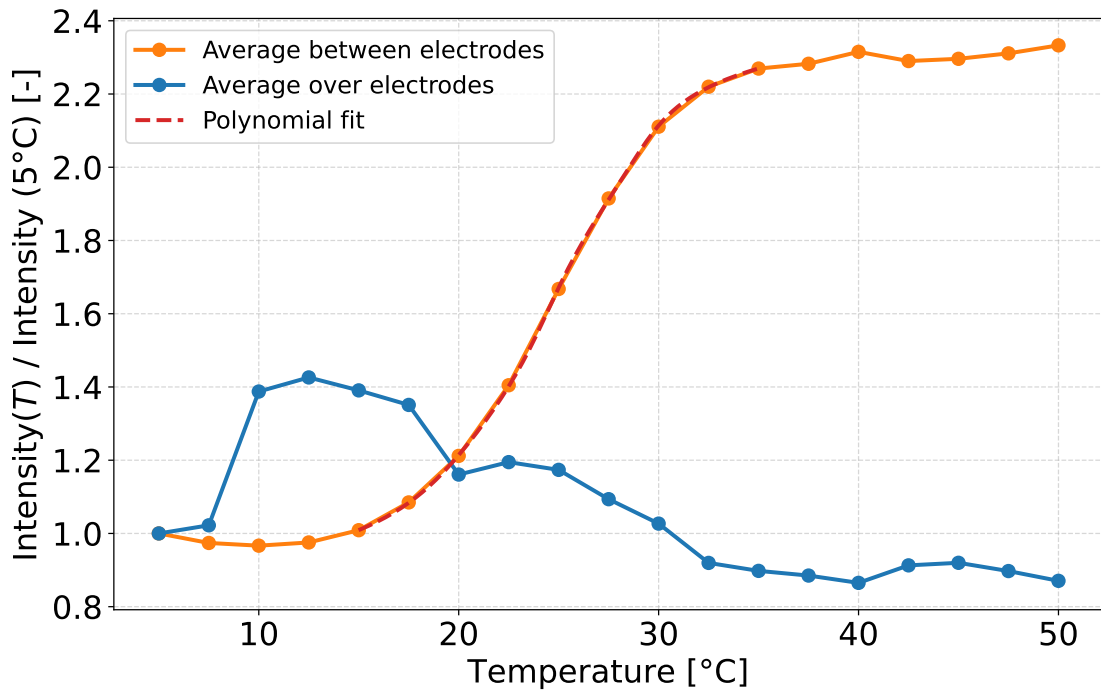


Figure 5.11: Mean intensity per pixel over the focus line for the regions over and between electrodes versus temperature. The intensities are divided by the intensity at 5 °C for emphasizing the sensitivity. The polynomial used for fitting is: $T(I) = 223.6 \cdot I^7 - 2511.7 \cdot I^6 + 11\,979.4 \cdot I^5 - 31\,449.7 \cdot I^4 + 49\,097.4 \cdot I^3 - 45\,609.0 \cdot I^2 + 23\,379.9 \cdot I - 5095.4$ with $MSE = 1.10 \times 10^{-2}$.

Calibration above electrodes

The diffraction pattern prevents the use of an average intensity per pixel above the electrodes. Instead, the temperature over the whole electrode is determined at once by calculating the integral of its associated main peak in the intensity profile. For calibrating the temperature above the electrodes, the five main peaks, which arise from the presence of 5 electrodes on the image, are extracted (see insets in Figure 5.12) from the line profile. Their individual integrals are summed at a given temperature and this scheme is performed for each temperature. The graph in Figure 5.12 is obtained by plotting this sum (divided by the sum at 5 °C) versus temperature. As desired, this curve increases monotonously and displays the highest sensitivity between 15 and 35 °C.

By using the polynomial fit given in the caption of Figure 5.12, one can determine the temperature over the electrodes from the computed integrals.

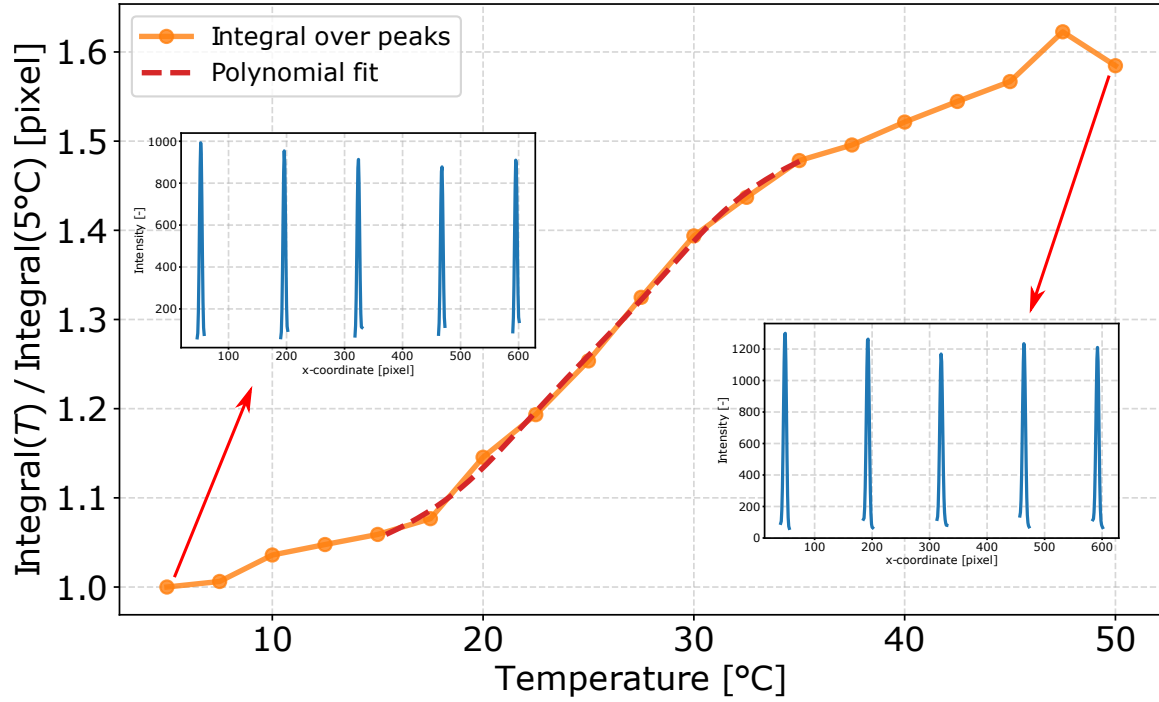


Figure 5.12: Integral over the 5 main peaks as a function of temperature. Left inset: 5 main peaks at 5 °C. Right inset: 5 main peaks at 50 °C. The polynomial used for fitting is: $T(I) = 8290.6 \cdot I^5 - 52\,580.4 \cdot I^4 + 133\,169.4 \cdot I^3 - 168\,360.1 \cdot I^2 + 106\,290.7 \cdot I - 26\,803.1$ with $MSE = 1.06$

5.3.5 Uncertainty on the temperature measurement

The error considered here is the one coming from the fact that the variation of the water refractive index is neglected, as previously discussed. The propagation of uncertainty is used to determine the uncertainty on temperature from the one on intensity. Using a Taylor's expansion of first order on $T(I + \Delta I)$ yields

$$\Delta T = \left| \frac{dT}{d(I/I(5^\circ\text{C}))} \right| \Delta \left(\frac{I}{I(5^\circ\text{C})} \right), \quad (5.10)$$

where $\Delta(I/I(5^\circ\text{C}))$ is the uncertainty on the relative intensity computed with Equation 5.9, and $\Delta T = T(I + \Delta I) - T(I)$ is the uncertainty on the calibrated temperature.

Uncertainty between electrodes

By taking the water/brush interface, it was found that a high boundary for RDI ($=\Delta(I/I(5^\circ\text{C}))$) is equal to 0.08. The derivative in Equation 5.10 can be computed from the polynomial fit found in Figure 5.11 and depends on temperature. By multiplying the derivative at each temperature by 0.08, one obtains a high boundary of the uncertainty on temperature, plotted in Figure 5.13.

For instance, during the experiment where the electrodes heat locally, if one measures a pixel with a relative intensity $I/I(5^\circ\text{C})$ equal to 1.6, the temperature will be estimated to be equal to 25°C using Figure 5.11. For this temperature, it is determined with Figure 5.13 that the uncertainty is equal to 0.71°C .

As it has been emphasized, the value of 0.08 for the RDI is a high boundary. In reality, if the temperature of the brush is measured to be 20°C during local heating, then the uncertainty is much lower than the one computed with Figure 5.13. Indeed, the water is at room temperature, also around 20°C , meaning that the conditions are identical to the ones during calibration, where the water and brush were at the same temperature. Therefore, there is *no uncertainty* induced around 20°C . More generally, there is no uncertainty induced around the temperature of water during local heating.

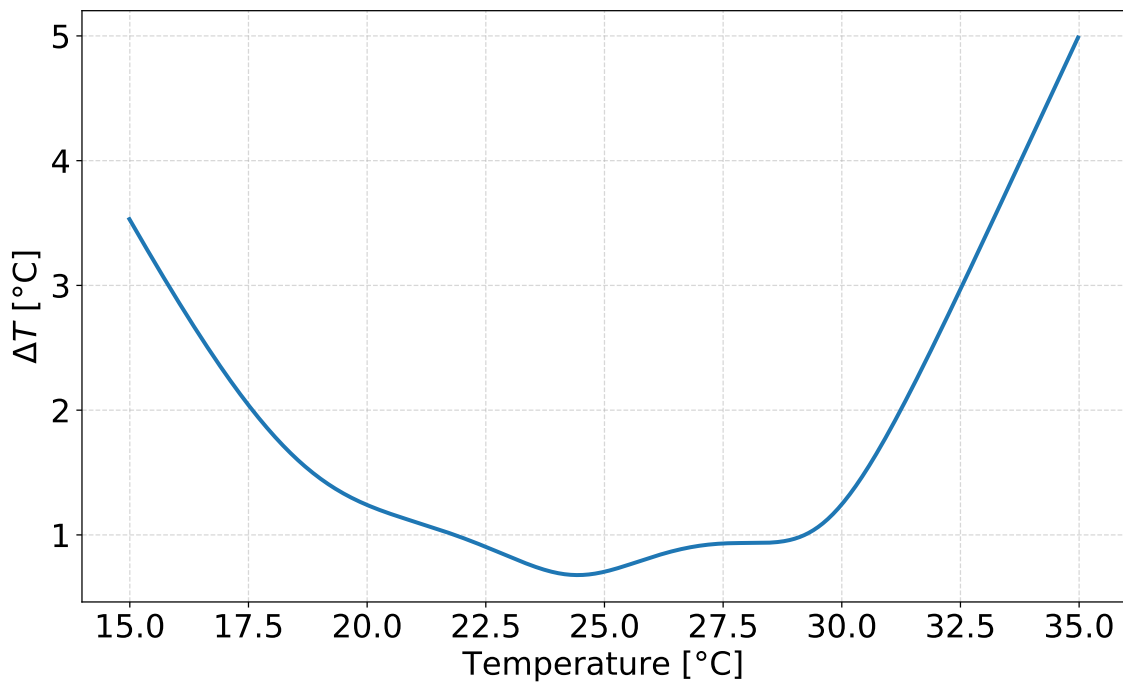


Figure 5.13: Uncertainty on the temperature measured with the calibration versus temperature. These values are high bounds and the uncertainty can be much lower than the one computed with this graph, especially around the water temperature during local heating.

Uncertainty above electrodes

The water/aluminum interface needs to be considered above electrodes. Since the electrodes are very reflective, it is very unlikely that the reflection will be affected by the variation of the refractive index of water. Therefore, it can be approximated that $\Delta I \simeq 0$. However, the reflection is affected by the variation of the refractive index of the polymer brush, as evidenced by the sensitivity in Figure 5.12. If the reflectivity was not affected by the variation of the refractive index of the brush, it would not be possible to calibrate the temperature above electrodes.

5.4 Local heating with electrodes

Using the calibration curves in Figures 5.11 and 5.12, one is able to measure the local temperature when the surface is heated locally with the electrodes and with the Peltier cell turned off. Several values of current can be passed through the electrodes to find the voltage to apply on the circuit for reaching the required gradient of temperature at the surface of the device. This gradient of temperature must create a pulsing surface by collapsing the polymer brush above the electrodes while maintaining the polymer brush in its swollen state between electrodes.

There are two solutions if the gradient of temperature cannot be reached:

- Decrease the base temperature with the Peltier cell. Doing so, the current in the electrodes can be increased while keeping the temperatures at the surface in the transition range of the polymer brush. However, the dielectric strength of the SiO_2 thin film above the electrodes must be high enough to withstand these higher values of voltage applied on the circuit.
- Increase the LCST of the polymer brush, as discussed in Section 2.5. This solution shifts the transition range of the polymer brush towards higher temperatures. However, it is still required to have a sufficiently high dielectric strength for increasing the current in the electrodes.

By using the determined voltage to apply, one can start to study the interaction of colloidal particles and bacteria with the pulsing surface. Square wave voltages with different periods can be applied on the circuit in order to find, if they exist, frequencies where colloidal particles and bacteria react particularly well with the surface. Unfortunately, these experiments would have required a few more weeks and could not be performed in this work. Still, this master thesis provides the necessary tools to carry out the upcoming steps.

5.5 Discussion on the distance between electrodes

One point that has not been raised in this chapter is the selected distance between the electrodes, equal to $51.75\ \mu\text{m}$ (see Figure 4.7). Although the interaction with colloidal particles and bacteria would be enhanced with a smaller distance, it is required to have well separated electrodes to characterize the surface. Indeed, the diffraction pattern around the electrodes extends over $\sim 9\ \mu\text{m}$ (~ 50 pixels), making impossible the study of closely spaced electrodes. However, when the surface will be well understood with optimal parameters, the electrodes will be progressively brought together.

Chapter 6

Conclusion and perspectives

In this master thesis, a dynamic surface based on thermoresponsive polymer brushes was produced and characterized.

Chapter 2 provided an introduction to polymers in solution allowing to understand thermoresponsive polymer brushes. Their synthesis and the importance to reach a high grafting density were presented. Currently existing antifouling surfaces were briefly described.

Chapter 3 performed finite element simulations in two dimensions to find the optimal dimensions for the thin films of silica. The temperature profile was studied 100 nm above the surface, approximately the distance at which the polymer brush extends. It was found that, for creating a pulsing surface, the top and bottom oxides thicknesses need to be equal to 686 nm and $3\text{ }\mu\text{m}$ respectively, and that the dissipated power in the electrodes must be equal to 3.14 W. Two different characteristic times were identified: One just above the electrodes, very short and around 0.02 s, and another one for the whole sample, longer and equal to 15 s. Simulations of a device with two circuits, aiming at producing a stationary wave at the surface, were also performed to determine the optimal distance between the two arrays of electrodes.

The simulations performed in this work offer an insight into the heat transfer in the device. However, only thermal conduction was considered, totally neglecting thermal convection. Another phenomenon, known as the Marangoni effect and arising from the difference of surface tension between the swollen and collapsed states of a polymer brush, was also neglected. These two effects are expected to play a significant role and should be considered if future simulations are required.

The device with two circuits has been simulated but not yet fabricated. This system will be considered in the future, when the interaction of colloidal particles and bacteria with the surface heated by one circuit will have been characterized and understood. Afterwards, a system with three circuits will be studied for creating propagating waves at the surface of the device. While it took many months to fabricate and characterize the device with only one circuit, its understanding should greatly accelerate the study of these two more complex systems.

Chapter 4 was dedicated to the fabrication of the device using the optimal dimensions determined by simulations. To reach this goal, it was necessary to use microfabrication techniques made available by the *Winfab* platform. A first photolithography was performed to pattern the electrodes and the contact pads in a thick layer of $\sim 3\ \mu\text{m}$ of wet oxidized silica. These electrodes had a width of $2.66\ \mu\text{m}$ and were spaced $51.75\ \mu\text{m}$ apart. Reactive-ion etching was used to etch the trenches in this silica layer, and these trenches were subsequently filled with aluminum using electron beam evaporation. The undesired photoresist and aluminum were removed from the surface using a lift-off process, and the whole surface was then covered by silica using reactive sputtering. Afterwards, an aligned photolithography followed by the isotropic wet etching of silica was performed to expose the aluminum on the contact pads. It was determined, using simple resistance measurements, that 5 electrodes out of the 9 fabricated were functional. Finally, the polymer brush of P(MEO₂MA) was grown and characterized. Ellipsometry, profilometry, and scanning electron microscopy have been used throughout the process for characterizing the sample at each step of fabrication.

A step height was created during evaporation of aluminum for filling the trenches, eventually leading to difficulties for studying the interaction of colloidal particles and bacteria with the surface. The created profile should have been smoothed out during sputtering, which can be verified with atomic force microscopy. Unfortunately, the apparatus was out of service when the measurements were to be performed, hindering the determination of the profile. This characterization will nevertheless have to be carried out in the future. The main drawback of this fabrication process is the dielectric strength of the sputtered silica, which can significantly change from one sample to another. The low dielectric strength of this oxide at the top of the device still hinders local heating because it does not allow to pass currents on the order of 50 mA, which are necessary for pulsing the surface. A solution is to further increase the temperature of the substrate during sputtering, tune the ratio of oxygen in the atmosphere and to perform post-annealing on each sample.

The last chapter focused on the characterization of the surface using both spectroscopic ellipsometry and images produced with the ellipsometer. Chapter 5 started by explaining the required background for understanding ellipsometry and the experiments that followed. The surface was first characterized with a conventional but time consuming technique, spectroscopic ellipsometry. However, a technique capable of measuring locally the swelling of the polymer brush in real-time is required for studying the interaction of colloidal particles and bacteria with the dynamic surface. An imaging method performed with the ellipsometer, which takes snapshots of a region of interest on the sample, was thus used in combination with a Peltier cell. By heating homogeneously the system with this Peltier cell, it was shown that the intensity of individual pixels was affected by temperature, making this homogeneous heating a way to calibrate the temperature as a function of the intensity. By splitting the snapshots into two regions, one between and one above the electrodes, it was possible to find two calibration curves allowing to determine locally the temperature from the intensity of individual pixels (or rather over a few pixels in the case of the calibration above the electrodes). Finally, the uncertainty on the temperature determined using the calibration between electrodes was estimated.

The next step of the project is to turn off the Peltier cell and heat locally the surface with the electrodes. The thermal profile over the entire region of interest will be mapped by converting the intensity of pixels into a temperature. Increasing values of electric currents will be passed through the electrodes to study their effect on the temperature field. Ultimately, this study should allow to find the required voltage to apply for creating a pulsing surface. Afterwards, colloidal particles and bacteria will be added in water, and their interaction with the surface will be directly observed with the imaging method developed in this work. By tuning the frequency of the square wave function that describes the passage of the current in the electrodes, resonant frequencies where the bacteria strongly interact with the surface might be found.

In conclusion, there are still a few steps before achieving the goal of this ambitious project. Nevertheless, this master thesis has allowed to better understand and characterize this pulsing surface which could one day, hopefully, save lives.

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Appendices

Appendix A

Simulations

A.1 Coefficients of the materials

The coefficient that have been used for the simulations are the ones embedded in *Comsol Multiphysics*. They are provided in Table A.1. The parameters of silica significantly varies with temperature. Therefore, this dependence is taken into account with the three following functions.

$$c_{p,\text{SiO}_2}(T[\text{K}]) = 61.49405 + 1.926794 \cdot T + 0.004463629 \cdot T^2 \\ - 1.704271 \times 10^{-5} \cdot T^3 + 1.88109 \times 10^{-8} \cdot T^4 - 7.062466 \times 10^{-12} \cdot T^5$$

$$k_{\text{SiO}_2}(T[\text{K}]) = -0.9854696 + 0.01820907 \cdot T - 5.290512 \times 10^{-5} \cdot T^2 \\ + 7.552525 \times 10^{-8} \cdot T^3 - 5.008123 \times 10^{-11} \cdot T^4 + 1.311324 \times 10^{-14} \cdot T^5$$

$$\rho_{\text{SiO}_2}(T[\text{K}]) = 2219.39 + 0.01105999 \cdot T - 4.708012 \times 10^{-5} \cdot T^2 \\ + 6.980692 \times 10^{-8} \cdot T^3 - 4.995273 \times 10^{-11} \cdot T^4 + 1.430874 \times 10^{-14} \cdot T^5$$

Material	c_p [J/(kg · K)]	k [W/(m · K)]	ρ [kg/m ³]
Si	700	130	2329
SiO ₂	$c_{p,\text{SiO}_2}(T)$	$k_{\text{SiO}_2}(T)$	$\rho_{\text{SiO}_2}(T)$
Al	900	238	2700

Table A.1: Table giving the specific heat capacity at constant pressure, thermal conductivity, and density of silicon, silica, and aluminum.

A.2 Physical equations

Stationary heat transfer in solids and liquids:

$$d_z \rho c_p \mathbf{u} \cdot \nabla T = \nabla \cdot (d_z k \nabla T) + d_z Q + Q_{OOP} \quad (\text{A.1})$$

where d_z [m] is the depth of the system, ρ [kg/m³] is the density, c_p [J/(kg · K)] is the specific heat at constant pressure, $\mathbf{u}$ [m/s] is the velocity field in the plane of the device, T [K] is the temperature, Q [W/m³] is the overall heat transfer rate generated by the electrodes, and Q_{OOP} [W/m²] is the heat transfer along the depth of the device. The velocity field must be specified by the user and is fixed as $\mathbf{u} = \mathbf{0}$, meaning that convection is neglected and only conduction is considered.

Time-dependent heat transfer in solids and liquids:

$$\underbrace{d_z \rho c_p \frac{\partial T}{\partial t}}_{\text{additional term}} + d_z \rho c_p \mathbf{u} \cdot \nabla T = \nabla \cdot (d_z k \nabla T) + d_z Q + Q_{OOP} \quad (\text{A.2})$$

where t [s] is the time. Again, the velocity field was fixed as $\mathbf{u} = \mathbf{0}$, thus neglecting convection.

Heat source:

$$Q = \frac{P_{\text{tot}}}{V} \quad (\text{A.3})$$

where P_{tot} [W] = V^2/R is the power dissipated at the electrodes, and V [m³] is the volume of the system. The dissipated power is fixed by the user, and was varied in order to vary the voltage to apply on the circuit.

Heat flux on the sides of the system:

$$q_0 = h(T_{\text{ext}} - T) \quad (\text{A.4})$$

where q_0 [W/m²] is the convective heat flux, h [W/(m² · K)] is the heat transfer coefficient, T_{ext} [K] = 283.15 is the external temperature, and T [K] is the temperature field in the system.

Temperature at the bottom of the system:

$$T = T_0 \quad (\text{A.5})$$

where T_0 [K] is the temperature at which the bottom of the system is fixed with the Peltier cell.

A.3 Mesh size

The mesh must be sufficiently refined to provide reliable results but also relatively coarse for computing the results in a reasonable delay. Figure A.1 shows the convergence of the temperature at key points of the system, in the final conditions presented in Chapter 3. Only the temperature above the electrodes vary, though not significantly. Since it is very

close to the value of the “extremely fine” mesh which can be considered as a reference in precision, the “normal” mesh is selected. This mesh is presented in Figure A.2.

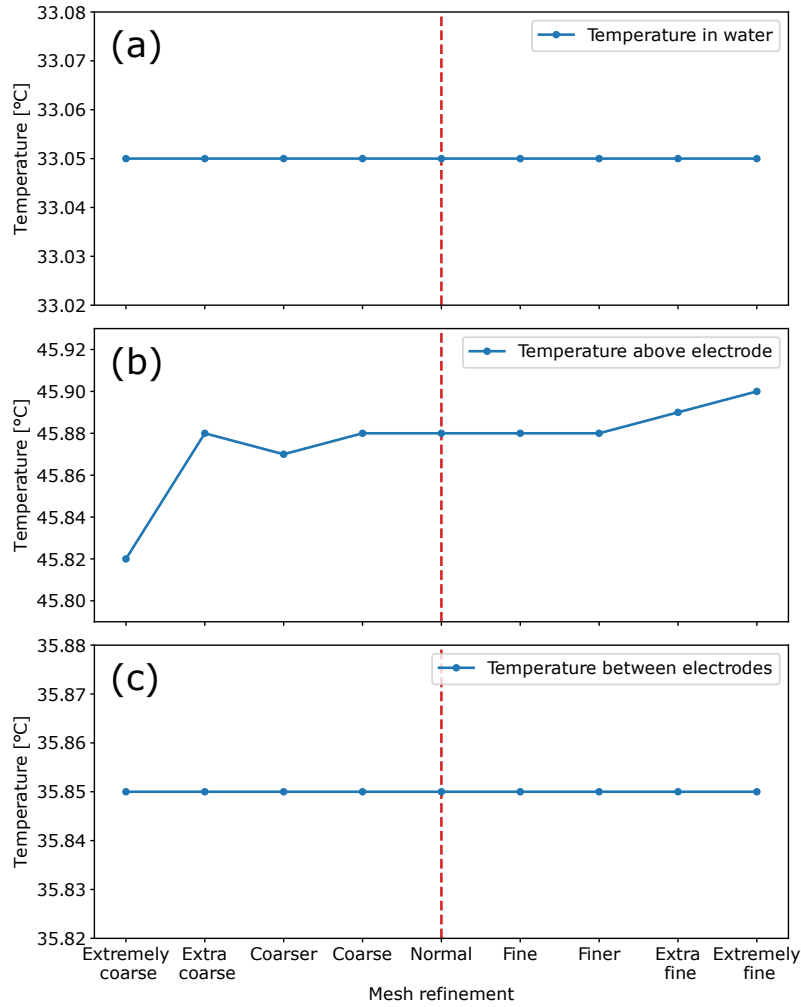


Figure A.1: Temperature at three different locations of the system for several meshes. **(a)** Temperature in water at the location shown in Figure 3.4(a). **(b)** Temperature above the electrode shown in Figure 3.7(a) **(c)** Temperature between the electrodes shown in Figure 3.7(b). The vertical red dashed line is placed for emphasizing that the “normal” mesh was selected for the simulations.

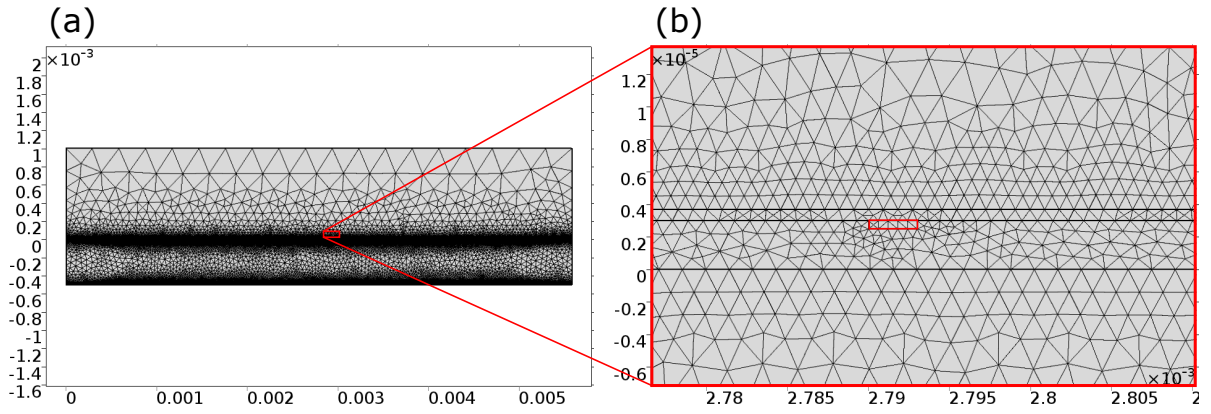


Figure A.2: “Normal” mesh that was selected for performing the simulations. **(a)** Overview of the mesh over the whole system. **(b)** Magnified view containing the mesh of an electrode, highlighted with a red box. The units of both axes are in meters.

Appendix B

Etching of the contact pads

Optical microscopy is used to determine if the pads have been correctly etched in the BHF bath, detailed in Section 4.2.9. Figure B.1(a) shows the pink texture of silica before etching. Figure B.1(b) shows that the pink has been totally removed, suggesting that silica has been well removed. However, the dark and porous aspect of the pad does not look like the shiny aluminum usually observed.

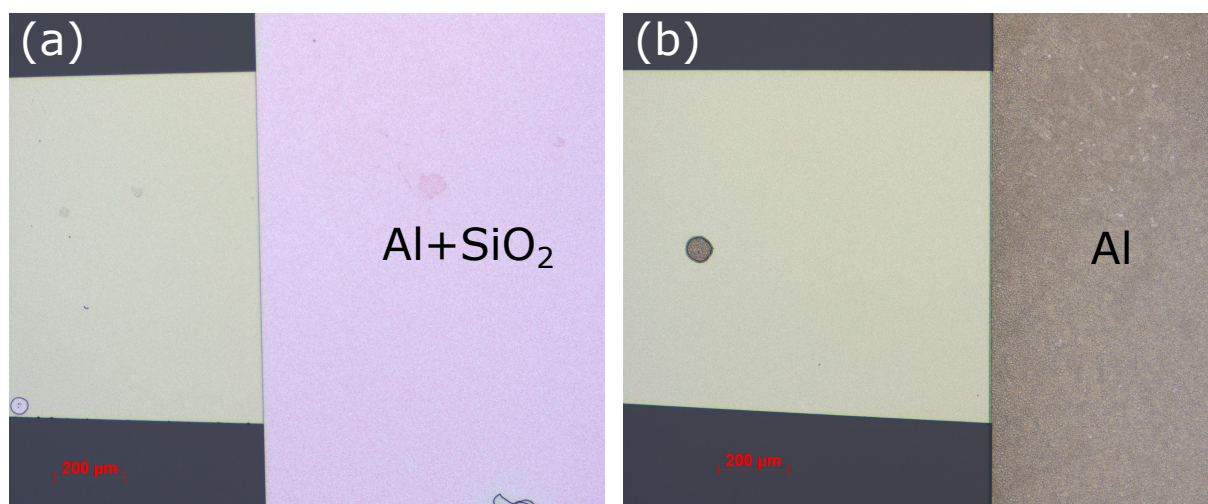


Figure B.1: Optical microscope images of the electrical pads **(a)** before and **(b)** after etching in the BHF bath.

Figure B.2(a) shows that there are bright and dark areas on a contact pad, and that the dark area becomes bright after having been scratched by the probe of a multimeter. Figure B.2(b) is a graph showing that the attack of an etchant (not BHF) on aluminum creates a roughness at its surface. This effect is even more pronounced after BHF etching because of the heavy attack of BHF onto the grain boundaries in aluminum [90]. Therefore, it is likely that the Al film looks dark because of this roughness. Some areas may look bright because of a protection of this Al against etching, maybe residues of PR or a difference of density in the SiO_2 film. Scratched areas may appear bright because they have been smoothed by the multimeter probe.

Prior to this hypothesis of roughening, it was thought that there could be some residues

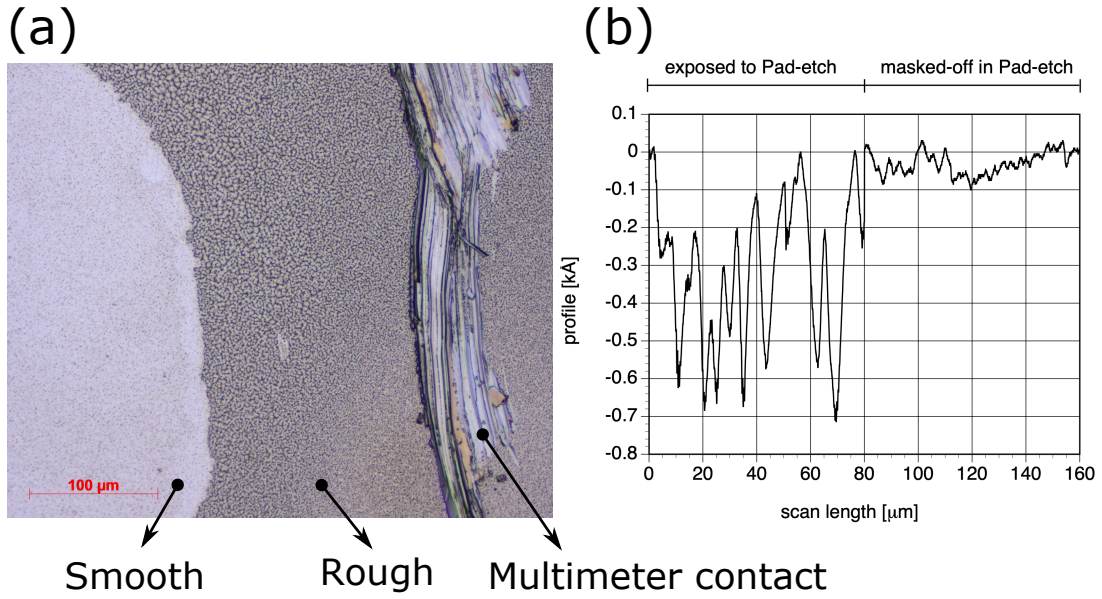


Figure B.2: This figure studies the roughness of aluminum. **(a)** Optical microscope image of a contact pad with smooth, rough, and scratched areas. **(b)** Profile of an aluminum film after exposition (left part of the graph) or not (right part) to an etchant, different from BHF. A similar effect occurs for BHF too [90].

of PR on top of the pads. Therefore, the sample was wiped in acetone to remove this eventual PR. After observation with the optical microscope, no significant difference was noticed. The surface is not smoothed by the wipe which is a soft material, unlike the multimeter probe. The *TePla 300E* has been also used to perform an additional O_2 plasma etching, with a maximal power of 500 W and for a duration of 10 min, but did not change anything either. Since there was no remaining resin but the roughness was still present (checked with ellipsometry), it could be deduced that the dark appearance of the contact pad did not come from residues of PR.

The conclusion of this appendix is that the silica on top of the contact pad has been correctly etched by the BHF bath, using the process explained in Section 4.2.9.

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