FABRICATION OF C-SI MICROSTRUCTURES THROUGH REORGANIZATION AT HIGH TEMPERATURES

Author: Maria Magdalena Solà Garcia
Supervisor: Moisés Garín Escrivà

Escola Superior d’Enginyeria de Telecomunicació
Universitat Politècnica de Catalunya
Barcelona, June 2015
Contents

Abstract xi
Resumen xiii
Resum xv

1 Introduction 1

2 Theory 7
  2.1 Preliminary considerations: Curvature of a surface . . . . . . . . . . . . . . 7
  2.2 Morphological changes in surfaces . . . . . . . . . . . . . . . . . . . . . . . 8
    2.2.1 Evaporation/condensation versus surface diffusion . . . . . . . . . . . 9
    2.2.2 Profile evolution due to surface diffusion . . . . . . . . . . . . . . . 10
  2.3 Simulation program . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 13
    2.3.1 Main structure of the code . . . . . . . . . . . . . . . . . . . . . . 13
    2.3.2 Considerations of the code . . . . . . . . . . . . . . . . . . . . . . 14
    2.3.3 Optimization of pillars for maximum sphericity . . . . . . . . . . . . 15

3 Experimental method 21
  3.1 General overview . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 21
  3.2 Experimental details . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 22
    3.2.1 Preparation of the wafer . . . . . . . . . . . . . . . . . . . . . . . 22
    3.2.2 Photolithography . . . . . . . . . . . . . . . . . . . . . . . . . . . 23
    3.2.3 Chromium deposition . . . . . . . . . . . . . . . . . . . . . . . . . 24
    3.2.4 Lift-off . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 25
    3.2.5 Reactive-ion etching . . . . . . . . . . . . . . . . . . . . . . . . . . 26
    3.2.6 Chromium removal . . . . . . . . . . . . . . . . . . . . . . . . . . . 27
    3.2.7 Annealing with Ar/H₂ . . . . . . . . . . . . . . . . . . . . . . . . . . 28

4 Results 31
  4.1 Characterization . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 31
    4.1.1 Scanning electron microscopy (SEM) . . . . . . . . . . . . . . . . . . 31
| 4.1.2 | Focused ion beam (FIB) | 32 |
| 4.1.3 | Energy-dispersive X-ray spectroscopy (EDS) | 33 |
| 4.2  | Annealing results | 34 |
| 4.2.1 | Morphology of pillars and annealed structures | 35 |
| 4.2.2 | Crystallinity | 36 |
| 4.2.3 | Effect of the aspect ratio | 39 |
| 4.2.4 | Effect of annealing time | 40 |
| 4.2.5 | Annealing temperature, atmosphere and pressure | 41 |
| 4.2.6 | Scaling of the structures | 44 |
| 4.2.7 | Defects on the surface | 45 |
| 4.2.8 | Other problems arising from the annealing treatment | 46 |
| 4.2.9 | Annealing of 2D structures | 47 |
| 4.3  | Adjustment with theory | 48 |
| 4.3.1 | Adjustment of the profiles | 48 |
| 4.3.2 | Approximation of model constants | 49 |

5 Conclusions & future work 53
List of Figures

1.1 SEM images of spherical polydisperse particles. The scale bars .......................... 2
1.2 Scheme of the obtained spherical device (a) and its band diagram (b) .................. 2
1.3 Spectral response of the proposed device as a function of wavelength (a) and the size parameter (b), where \( d \) is the sphere diameter. ............................. 3
1.4 Fabrication of the silicon-on-nothing structure. Si vertical trenches are annealed, producing spherical voids that, after a second annealing, combine to form an empty layer\(^{26}\) .......................................................... 4

2.1 Curve with its corresponding osculating circle (a) and surface with its two principal planes. In red, the curves obtained from their intersection with the surface, from which the mean curvature is reckoned. ......................................................... 8
2.2 Profile evolution due to evaporation/condensation mechanism. ......................... 10
2.3 Profile evolution due to surface diffusion mechanism. ..................................... 10
2.4 Main scheme of the simulation program. ......................................................... 13
2.5 Representation of the value of the curvature with respect to the perimeter of two profiles: a perfect sphere (blue) and an arbitrary profile (orange). In this case, only half of the profiles are taken into account, as there is symmetry. ................. 17
2.6 Three-dimensional representation of the figure of merit with dependences on the simulation time and the initial aspect ratio. ................................. 18
2.7 Figure of merit \( \beta \) with respect to the simulation time for a given initial aspect ratio, \( \sigma_0=2.9(a) \) and evolution of a profile with that value of \( \sigma_0 \). The colours of each profile indicate the time instant at which it has been stopped, which corresponds with data from a. .................................................. 19

3.1 Main scheme of the method. The figure shows the main steps, starting with the plain wafer (I), the photoresist deposition (II), photolithography (III), chromium deposition (IV), lift-off (V), reactive-ion etching (VI), chromium removal (VII) and finally, annealing with Ar/H\(_2\) (VIII). ......................................................... 22
3.2 Main scheme of the photolithography process. ............................................. 23
3.3 Relation between the height of the micropillars after RIE and the time needed for the process. The two plots refer to different wafers. ......................... 27
3.4 Reminders of Cr even after removal. The first image (a) corresponds to a micropillar after 5 min of Cr etching with the commercial product, thus an entire layer (in a brighter colour) can be seen. The second one, b, was taken after 40 min of etching. It is shown that Cr remains at random micropillars, thus making the complete etch very difficult.

4.1 Same image taken with SE (a) and SE in-lens (b) detectors. Whereas SE produces a higher 3D perception, SE in-lens display higher contrast images. Moreover, surface details become more visible with it, specially for higher magnifications.

4.2 SEM images of different samples after etched with FIB. The Pt covering before the etching step allows a higher contrast and avoids material redeposition in the sample itself and its surroundings. Arrows in a indicate the redeposition that has taken place in adjacent structures. Tilt correction has been applied in both images.

4.3 SEM image of micropillars with some remainders of Cr (a) and its corresponding spectra obtained with the EDS technique. The spot in (a) shows the exact point where the analysis is performed.

4.4 SEM images of a sample before (a,b) and after (c,d) annealing at 1150 °C for 1h 30min. Their initial dimensions were 2 μm width and 4.6 μm height and were arranged in an hexagonal array.

4.5 SEM image of a profile etched with FIB with the most visible planes. At the left, there is depicted the chosen coordinate system (top) and a scheme of how angles are considered (down).

4.6 Identified planes with images from a sample seen from above (a) and from a bird’s-eye perspective (b). In the latter view, only some planes are visible, hence only they have been marked.

4.7 Difference between samples annealed with the usual procedure (a) and ended with a N2+O2 atmosphere (b). In the second case, facets from the surface tend to smooth.

4.8 SEM images of different samples annealed at identical conditions during the same time (1h 30min). Initial aspect ratios are σ0 = 1, 2.2, 2.6 and 3.5 respectively.

4.9 SEM images of samples with equal σ0=2.1 that have been annealed during different times (1h, 1h 30min and 2h, correspondingly). The cross-sections have a Pt layer on the top, deposited during the FIB milling.

4.10 SEM images of samples with equal σ0=2.4 that have been annealed during 1h 30min and 2h, correspondingly. The notable different among the previous ones suggests that the critical point is between σ0=2.2 and 2.4.

4.11 SEM images of samples with equal σ0=2.5 that have been annealed at 1150 and 1100 °C, respectively. Sample b was annealed during 3h 30min in total, but still shows a less spherical morphology.

4.12 SEM images of samples annealed at 1000 °C in vacuum for 1h (a) and 2h (b).

4.13 1 μm-width samples annealed during 1h 30min. The initial aspect ratios are 4.2, 3.2 and 2, respectively.

4.14 Images of different samples with remarkably visible surface defects. Whereas on the left (a, the imperfections are more focused at the bottom of each Ω-sphere, sample on the right (a) shows a high number of defects on the substrate and also on some structures.
4.15 SEM image of one of the problematic samples. Figure b shows the EDS spectra focused on one point of the same sample. ................................................................. 47

4.16 SEM images from a bird’s-eye (a) and frontal (b) view of the same sample, with initial aspect ratio of approximately 3.5 and annealing time of 1h 45min. The trenches from b have been covered with a Pt layer before being melted with the FIB. 48

4.17 Cross-section images of samples with equal initial aspect ratio, $\sigma_0=2.1$, annealed for different times. The results from the simulation have been superposed, showing that it only reproduces the evolution successfully at the start of the process. .......... 49

4.18 Fittings of the results from the simulation with the experimental cross-sections. Whereas the single-profile approach (a,b) reproduces more poorly the time evolution, the assumption of having neighbours in all directions exhibits a better performance. ................................................................. 50

5.1 SEM images of $\Omega$-spheres obtained from initial micropillars of aspect ratio $\sigma_0=2.3$ that were annealed in an Ar/H$_2$ atmosphere for 105 min. The images have been taken from a bird’s-eye perspective (a, b and c) and from above (d). ............... 54
## List of Tables

3.1 Different solutions tested to remove completely the Cr layer. ................. 27

4.1 Data with the most visible planes, the measured angle, the possible matching plane and its theoretical angle. All angles are measured with respect to the (100) plane. 38

4.2 Data extracted from the different tested profiles and the corresponding value of B. As it can be seen, the second approach is, once again, closer to the reality. ................................................................. 50
Abstract

Silicon photonics has gained increasing interest in recent years as it promises high performance, cost-effective integrated optical devices. The advent of Si fabrication techniques at the micro and nano-scales, in conjunction with the interesting optical properties of this material, such as its high refractive index, has enabled the development of new methods of light confinement. In particular, Si microspheres behave as excellent resonators with ultra-high quality factors, resulting in an enhancement in light harvesting. This work presents a new fabrication method of monocristalline Si spheres connected to the substrate, which is also c-Si, through a narrow neck.

The fabrication process relies on the surface reorganization in solid phase that occurs when silicon is exposed to high temperatures (above 1100 °C). Therefore, initial sharp structures, such as micropillars with relatively high aspect ratios, evolve into rounded shapes, ideally spheres, while keeping attached to the Si bulk through a narrow neck. In this project we fabricate micropillars of varying dimensions and reorganize them through high-temperature annealing at different conditions. As a result, it is proved that the initial aspect ratio together with both the annealing time and atmosphere are decisive in the final shape of the structures. Moreover, they exhibit a faceted surface, confirming that their monocristalline nature is not altered during the fabrication process.

In addition to that, we develop a comparison between the experimental results and the ones obtained through a theoretical model. This analysis shows a satisfactory agreement between both approaches, indicating that the evolution of a given profile can be accurately predicted and simulated. Furthermore, we also verify that the principal mechanism inducing this atomic migration is surface diffusion, in contrast with evaporation/condensation that becomes almost negligible in our experimental conditions.
El interés en la fotónica basada en silicio ha aumentado en los últimos años debido a que promete dispositivos económicos y de alto rendimiento. La aparición y avances en las técnicas de fabricación a escalas micro y nano, junto con algunas de las propiedades ópticas de este material, como por ejemplo su alto índice de refracción, han permitido el desarrollo de nuevos métodos para el confinamiento de la luz. En particular, las microesferas de Si se comportan como excelentes resonadores con factores de calidad muy altos, lo que resulta en un mayor aprovechamiento de la luz. Este trabajo presenta un nuevo método de fabricación de esferas monocristalinas de silicio conectadas al sustrato, también de c-Si, a través de un cuello estrecho.

El proceso de fabricación se basa en la reorganización de la superficie en estado sólido que ocurre cuando el silicio se somete a altas temperaturas (superiores a 1100 °C). De esta forma, estructuras con bordes inicialmente agudos, como micropilares con relaciones de aspecto relativamente altas, evolucionan en formas redondeadas, idealmente esferas, a la vez que se mantienen unidas al silicio mediante un cuello. En este proyecto fabricamos micropilares de dimensiones variadas y los reorganizamos mediante un tratamiento de recocido a altas temperaturas en diferentes condiciones. Demostramos que tanto la relación de aspecto inicial como el tiempo y la atmósfera del proceso de recocido son determinantes en la forma final de las estructuras. Además, éstas presentan una superficie con los planos cristalinos claramente marcados, hecho que confirma que su naturaleza monocristalina no se ve afectada durante el proceso de fabricación.

Asimismo, también comparamos los resultados obtenidos experimentalmente y mediante el modelo teórico. Este análisis muestra un acuerdo satisfactorio entre ambos enfoques, hecho que indica que la evolución de un determinado perfil se puede predecir y simular correctamente. Adicionalmente, también verificamos que el mecanismo principal que provoca esta migración atómica es la difusión superficial, en contraste con la evaporación/condensación, que es prácticamente negligible en las condiciones experimentales dadas.
Resumen
L’interès en la fotònica basada en silici ha augmentat durant els últims anys donat que promet dispositius econòmics i d’alt rendiment. L’aparició i avanç en les tècniques de fabricació a escales micro i nano, junt amb algunes de les propietats òptiques d’aquest material, com per exemple el seu alt índex de refracció, han permès el desenvolupament de nous mètodes per al confinament de llum. En particular, les microesferes de Si es comporten com a excel·lents ressonadors amb factors de qualitat molt alts, fet que permet un major aprofitament de la llum. En aquest treball es presenta un nou mètode de fabricació d’esferes cristal·lines de silici connectades al substrat, també de c-Si, a través d’un coll estret.

El procés de fabricació es basa en la reorganització de la superfície en estat sòlid que es produceix quan el silici es sotmet a altes temperatures (superiors a 1100 °C). D’aquesta forma, estructures amb vores afilades, com micropilars amb relacions d’aspecte relativament altes, evolucionen en formes arrodonides, idealment esferes, a la vegada que es mantenen unides al silici a través d’un coll. En aquest projecte fabriquem micropilars de diverses dimensions i els reorganitzem mitjançant un tractament de recuita a altes temperatures en diferents condicions. Demostrem que tant la relació d’aspecte com el temps i l’atmosfera del procés de recuita són determinants per a la forma final de les estructures. A més, aquestes presenten una superfície amb els plans cristal·lins clarament marcats, fet que confirma que la seva naturalesa monocristal·lina no es veu afectada durant el procés de fabricació.

Així mateix, també comparem els resultats obtinguts experimentalment i mitjançant el model teòric. Aquest anàlisi mostra un acord satisfactori entre ambdós enfocaments, fet que indica que l’evolució d’un determinat perfil es pot predir i simular correctament. Addicionalment, també verifiquem que el mecanisme principal que provoca aquesta migració atòmica és la difusió superficial, en contrast amb l’evaporació/condensació, que és pràcticament negligible en les condicions experimentals donades.
Nomenclature & abbreviations

Nomenclature

- **H**: Mean curvature of a given surface.
- **Ω-sphere**: Almost-spherical structure with a narrow neck that connects it to the substrate.
- **σ**: Aspect ratio, i.e., relation between the height and width of a given profile, $\sigma = h/w$.
- **σ₀**: Initial aspect ratio of a given micropillar.
- **σᵣ**: Critical aspect ratio, above which the *pinch-off* takes place.
- **τ**: Simulation time of the program.

Abbreviations

- **c-Si**: Crystalline silicon, even though it is usually used to refer specifically to monocrystalline silicon.
- **EDS**: Energy-dispersive X-ray spectroscopy.
- **FIB**: Focused ion beam.
- **RIE**: Reactive-ion etching.
- **SEM**: Scanning electron microscope.
1 | Introduction

Silicon is the prevailing material in the semiconductor industry and, principally, in the fields of electronics and photovoltaics. This predominance over other semiconductors, such as germanium, follows from the conjunction of several physical and technological advantages, including a convenient band gap size, the possibility of easily forming an oxide (SiO$_2$) that can work as a good insulator and, very importantly, its natural abundance. As a result, silicon has become one of the best known materials on earth, and its technology has reached an unprecedented level of development, making possible from the growth of huge ultra-pure monocrystalline ingots to the sculpturing of the tiniest structures in the micro- and nano-scale. The advent of fabrication techniques at these scales, enabling the production of structures with dimensions of the order of the wavelength of light, has also allowed the invention of new methods for light confinement and its manipulation and, consequently, has favoured a rapid development of photonics sciences. In particular, silicon photonics has gained special interest due to the opportunity it offers to exploit some of the optical properties of Si, such as its high refractive index, and combine them with its traditional applications.

A new kind of silicon which has increasingly gained interest during the past decade is silicon colloids. Silicon colloids is a form of particulate Si consisting in particles with sizes in the micro and nano-scale that exhibit a highly spherical shape. Several techniques have been reported on the fabrication of these types of structures. A particular case of these methods is the synthesis of microspheres by chemical vapour deposition (CVD) from disilane gas (Si$_2$H$_6$). When the appropriate conditions are set, i.e., low pressure ($\sim 10^{-6}$ mbar) and a relatively high temperature (400-600 °C), Si$_2$H$_6$ is decomposed and silicon colloids can be synthesized, which become spherical due to surface tension and end up precipitating on the desired substrate. The spherical and smooth shape, together with the high refractive index of silicon, make these particles behave as good resonators with very strong and high-quality resonances matching those predicted by the Mie theory. There are many potential applications for Si microspheres, specially concerning their ultrahigh quality factor resonances, for instance in fiber lasers, photovoltaics, sensors, UV-VIS-IR filters, photonic barcodes, wave-guide couplers, cancer therapy and Raman scattering enhancers.

An application of particular interest for this project is the fabrication of solar cells with silicon microspheres. These type of structures present high quality...
Introduction

(a)

Figure 1.1: SEM images of spherical polydisperse particles. The scale bars factors, thus when a photon is trapped in a Mie resonance it can stay there for very long times, which would be equivalent to travelling hundreds of micrometers in bulk silicon. Therefore, this idea can be profited to achieve higher efficiencies with a less amount of silicon and, hence, lower material costs. M. Garín et al. has recently published in Nature Communications 2 a proof-of-concept of such a device in a single silicon microsphere. In order to do so, they deposited a thin layer of disperse amorphous Si spheres produced by the previously mentioned CVD technique (figure 1.1) on a c-Si sample with a n⁺ layer on the top. A subsequent annealing of these structures, at temperatures above 800 °C in N₂ ambient, allows the recrystallization of the microspheres, an improvement of the sphere-substrate electrical contact and the diffusion of the n-type impurities towards the bottom of the sphere. Finally, a thin ITO layer is deposited on the top of the spheres through sputtering, producing a final arrangement that resembles a p − i − n structure (corresponding to ITO-sphere-substrate, respectively) (see figure 1.2). From this set-up, Garin et al. tested a single spherical device by using a conductive AFM tip and they obtained the photocurrent spectra through a monochromatic source focused on the sphere. This spectral response showed clearly MIE resonances due to the enhanced absorption by spherical particles, as can be seen in figure 1.3. Moreover, they were detected at wavelength values below the typical absorption edge of silicon (1600 nm), which would allow the harvesting of light in a wider spectrum range, up to the near infrared region.

(b)

Figure 1.2: Scheme of the obtained spherical device (a) and its band diagram (b).
In spite of the promising applications and enhancements in light absorption, specially in photovoltaic cells, these devices present some limitations. Firstly, the colloids obtained through the CVD technique can be amorphous or polycrystalline, depending on the synthesis conditions and further treatment, but monocrystalline spheres cannot be obtained with this method. Secondly, the produced particles are polydisperse (not uniform in size). Moreover, the exact location of the spheres cannot be controlled easily, making the devices based on this technique random in nature. Even further, the fabrication and study of ordered arrangements of microspheres or simply the analysis of the interaction of a few spherical particles become impossible.

In order to overcome these constraints, an alternative procedure has been considered, based on the fact that many materials, with silicon among them, can alter their morphology at temperatures below their melting point, i.e., in solid phase. This shape modification can be explained according to the theory of atomic migration on surfaces proposed by Mullins in 1957. The model, which was initially developed to reproduce the evolution of a groove on a heated polycrystal surface, states that the change in time of a given profile is related to its curvature, tending to minimize or homogenize it under the appropriate conditions. Hence, initially sharp structures will become more rounded or even spherical if the proper parameters are chosen.

Even though plenty of research has been developed on the phenomenon of atomic migration, and specially on surface diffusion, the predominant mechanism involved, only a few studies have been focused on its application to the shaping and smoothing of 3D Si structures. The first works were presented by Sato et al. in 1998, where initial rectangular trenches of a few micrometers were annealed with hydrogen, causing the rounding of their inside. Moreover, deep enough trenches were divided into fragments which, at the same time, evolved into spherical
voids, producing a line of empty spheres inside the silicon substrate. Similar events were analysed by Kuribayashi et al. a few years later.\textsuperscript{24}

Succeeding works include the fabrication of a silicon-on-nothing structure (Sato and Mizushima\textsuperscript{25,26} and Depauw et al.\textsuperscript{29,30}), which relies on the combination of several spherical voids, forming an empty layer parallel to the surface (figure 1.4). Furthermore, a similar idea has been also recently developed in our department (Hernández et al.\textsuperscript{28}) as a technology to obtain numerous films of crystalline silicon from a wafer in a single step, thus allowing a reduction in cost and wafer thickness. In addition to these works, the Mullins model has also been studied both numerically\textsuperscript{32,33} and experimentally\textsuperscript{34} in order to achieve other types of 3D structures, such as microbeams and microspheres. In contrast to the previous ones, these structures were made up of silicon, instead of being empty. However, these shapes were only developed from silicon-on-insulator (SOI) substrates, producing silicon microstructures connected to a silicon dioxide ($\text{SiO}_2$) film.

![Figure 1.4: Fabrication of the silicon-on-nothing structure. Si vertical trenches are annealed, producing spherical voids that, after a second annealing, combine to form an empty layer.\textsuperscript{26}]()
raphy and etching techniques. It will be followed by an annealing treatment in a nonoxidizing atmosphere. During this step, the samples are exposed to high temperatures ($\sim 1150 ^\circ C$), but always below the Si melting point ($\sim 1414 ^\circ C$), allowing the activation of the mechanisms that yield the migration of atoms on the surface and, hence, producing morphological changes of it. In addition, a study of the main parameters implied in the experimental procedures and their effects on the final structures will be also developed. Moreover, we will perform the morphological characterization of the resulting samples and we will discuss the obtained results. Finally, they will be compared to the ones obtained from the theory.
2 | Theory

The change in the shape of sharp structures when annealed at high temperatures was modelled by Mullins in 1957. In this chapter, a review of the physical phenomena that occur during the annealing process is developed, with a brief comparison of the main thermally activated mass transport processes. Among them, surface diffusion, which seems to be the most important one, is summarized in some more depth. Moreover, the evolution of a given profile is tested according to the Mullins model through a simulation program, which will become the first approach towards our final goal.

2.1 Preliminary considerations: Curvature of a surface

Before starting with the theoretical development, we should dedicate some words to the concept of curvature, which will be of notable importance when discussing the evolution of a certain structure. When dealing with surface morphologies, a useful idea to take into account is the curvature. Even though it has several definitions, it can be usually thought as a parameter that gives an idea of how different is a surface from a totally flat one. In physical terms, the curvature refers to the speed at which the unit tangent vector of a curve changes. Hence, a small curvature means that the curve or surface tangent hardly changes, thus being almost a straight line or flat surface. In contrast, a sphere or circumference will have a non-zero constant curvature.

In the case of a two-dimensional curve, \( C \), at a given point, \( P \), \( C \) can be approximated by a circumference with radius \( R \), usually known as its osculating circle (2.1(a)). Therefore, the curvature, \( k \), at \( P \) is defined as the inverse of the radius:

\[
k = \frac{1}{R}
\]

(2.1)

Following this idea, it is possible to show that the curvature of a curve expressed in Cartesian coordinates can be calculated as:

\[
k = \frac{x'y'' - y'x''}{(x'^2 + y'^2)^{3/2}}
\]

(2.2)

with the prime refering to the derivative with respect to the arclength of the curve, \( s \). Notice that \( k \) can be either positive or negative, depending on how the tangent
vector rotates: clockwise \((k < 0)\) or counterclockwise \((k > 0)\).

When it comes to a three-dimensional surface, there are several ways of evaluating its curvature. Of special interest are the principal curvatures, usually expressed as \(k_1\) and \(k_2\). Considering a point on a surface, with \(n\) being its unit normal vector, there exist infinite planes containing both \(n\) and a vector tangent to the surface, \(t\). The intersection of these planes with the surface produces different curves, each one with its own curvature \(k\). From all of them, the maximum and minimum \(k\) are the principal curvatures \((2.1(b))\). The average of both yields to the mean curvature, \(H = (k_1 + k_2)/2\), which will be the parameter considered in what follows.

### 2.2 Morphological changes in surfaces

When a material is exposed to high temperatures, atoms from the outer surfaces can acquire enough energy to become mobile, even if the temperature has not reached the melting point of the material, i.e., in solid phase. In the case of silicon, melting occurs at 1414 °C at atmospheric pressure, but changes in the shape of the surface can already be observed at lower temperatures. These alterations are due to different mechanisms that produce the movement of the atoms, which will be next discussed.

We can start the development by considering a solid particle in contact with the atmosphere, i.e., a gas. Our study will be focused on the phenomena that take place on the interface between both phases. The number of atoms lying on a particular point of the surface can vary due to mainly two effects. On the one hand, phase changes might occur, leading to the exchange of atoms with the atmosphere, which can be in the form of evaporation (extraction of atoms from the material) or condensation (addition of atoms). On the other hand, these parti-
2.2 Morphological changes in surfaces

Particles might just move to other sites of the surface, which is known as surface diffusion.

A model to describe the effect of these two mechanisms was proposed by Mullins in 1957\(^2\). In fact, it was developed to study the evolution of a groove from a heated surface, but it can be applied to a general case, as the one in hand. Hence, Mullins obtained two equations, one corresponding to each mechanism, which determine the progress in time of a surface in terms of its normal vector. Equation 2.3 refers to the effect of evaporation/condensation, while equation 2.4 describes the influence of surface diffusion.

\[
v_{n,mig} = -AH
\]

\[
v_{n,diff} = B\nabla^2_{s}H
\]

Notice that in the previous equations, \(v_n\) depicts the velocity of a surface element along its normal axis. Moreover, \(H\) is the mean curvature of the surface (details in section 2.1) and \(\nabla^2_{s}\) is the Laplacian with respect to the arclength, \(s\). Both \(A\) and \(B\) are constants containing different parameters from the specific material and atmosphere, with their precise expressions being

\[
A = \frac{p_0\gamma\Omega^2}{\sqrt{2\pi M(k_BT)^3}}\quad (2.5)
\]

with \(p_0\) as the vapor pressure in equilibrium with a flat surface, \(\gamma\) the free energy of the surface per unit area, \(\Omega\) the volume occupied by an atom or molecule, \(M\) the molecular weight, \(k_B\) the Boltzmann constant and \(T\) the temperature at which the material is heated, and

\[
B = \frac{D_s\gamma\Omega^2\nu}{k_BT}\quad (2.6)
\]

where \(D_s\) is the coefficient of surface diffusion and \(\nu\) refers to the number of atoms per unit area.

Mullins proposed a solution to these equations for the cases where the height of the structure is little compared to the flat surface, i.e., the small slope approximation. Even though this assumption is reasonable for grooves and shapes that exhibit low aspect ratios, arbitrary structures cannot be included in that solution. Consequently, a more suitable way to study the evolution of a general shape is through simulation.

2.2.1 Evaporation/condensation versus surface diffusion

As it has already been stated, morphological changes in the surface can be caused by two main phenomena: atoms changing of phase, i.e., evaporation/condensation, and surface diffusion. Nevertheless, each of them is restrained to a given constant (\(A\) or \(B\), expressions 2.5 and 2.6), depending on the properties of the material and the conditions considered. Therefore, the magnitude of their effect can be strongly different. The reckoning of their exact value can be complex, as they...
depend on specific parameters that rely heavily on the experimental conditions. Nevertheless, from the literature it can be shown that in a micrometer scale and the desired conditions (temperature around 1100°C and atmospheric pressure) surface diffusion is prevailing over any other migration mechanism\textsuperscript{32,41,42}. 

In addition to the references, an additional test has been developed computationally. Both mechanisms have been tested separately in the simulation program. The same initial profile, with a chosen aspect ratio, is evolved considering only one of the effects each time. Figures 2.2 and 2.3 show the progress of the profiles in both cases for an initial structure of aspect ratio 3. When only evaporation/condensation is taken into account, the final shape is always a flat surface, regardless of the starting aspect ratio. This outcome is in accordance with equation 2.3, as the evolution of the profile is directly proportional to the curvature. Thus, areas with positive curvature, as the bottom of the cylinder, will broaden, while regions with negative curvature, i.e., the top of the profile, tends to narrow. On the contrary, the evolution of a structure when only surface diffusion is considered depends on the initial aspect ratio. When the former is relatively small (generally speaking, \( \leq 2.5 \)), a plain surface is also obtained. Nevertheless, for higher ratios, the profile tends to form a neck at the bottom, leading to the formation of a rounded structure connected to the substrate through a neck. The diameter of the latter depends on time: it tends to thin and ends up disappearing, causing the separation of the profile in two. Notice that gravity effects are not considered in the program.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.pdf}
\caption{Profile evolution due to evaporation/condensation mechanism.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.pdf}
\caption{Profile evolution due to surface diffusion mechanism.}
\end{figure}

2.2.2 Profile evolution due to surface diffusion

As it has already been stated, the evolution of a given profile will be mainly subject to the effects arising from surface diffusion. Next, we will delve a little into the study of this mechanism in order to get some insight in the physical phenomena behind it. In addition to that, in some conditions the profile will end up separating from the substrate, which is related to the Rayleigh instability, which will also be
2.2 Morphological changes in surfaces

Diffusion is usually defined as the migration of a substance, atoms in this case, in the direction of decreasing concentration, i.e., particles move from high to low concentration areas. Therefore, a gradient is the main force driving this movement. When a given solid particle is considered, two main diffusion mechanisms could be taken into account: bulk diffusion, defined as the movement of atoms over the entire volume, and surface diffusion, which is specific to the external layer of the particle. Henceforth, only the latter will be considered, as we are dealing with changes in the surface, thus effects arising from mass transport in the bulk volume can be neglected.

The relation between the evolution of a surface and its curvature has already been given, according to the model proposed by Mullins. Let us recall the expression,

\[ v_{n,\text{diff}} = B \nabla^2 H \]  

(2.7)

with

\[ B = \frac{D_s \gamma \Omega^2 \nu}{k_B T} \]  

(2.8)

In the following, a brief derivation of this relation will be developed in order to get some insight in the physics behind this phenomenon. Notice that this development is not unique and other demonstrations can be followed in different works\textsuperscript{27,36,37}.

Diffusion responds to a change in a given variable, which is usually concentration. Therefore, particles flow from high to low concentrations. In the case of surface diffusion, the source of this movement is not concentration but surface energy: atoms will tend to minimize their energy and, hence, will move towards a more favourable state. One way of taking into account this parameter is through the chemical potential, \( \mu \), which is usually defined as the released energy when a certain quantity of substance is added or extracted. Therefore, atoms with higher \( \mu \) will tend to move towards lower potential regions. Following this approach, we can consider a given surface with a shape defined by its curvature, \( k \). Taking into account the convention for signed curvature previously mentioned (section 2.1), we can imagine an atom on a surface with \( k < 0 \). The number bonds that it forms with neighbouring particles is lower than that for an atom with \( k > 0 \). Hence, less bonds will have to be broken, which implies a lower \( \mu \). From this point of view, it can be understood that the variation of chemical potential when an atom moves from a point \( A \) with \( k_A \) to \( B, k_B \), will be proportional to the change in curvature, i.e.,

\[ \Delta \mu \propto \Delta k \]

The proportionality constant can be related to several physical parameters through a dimensional approach. Curvature, with \( m^{-1} \) units, can be associated to an energetic parameter through surface energy, \( \gamma \ (J/m^2) \) and it is extended to more than one atom through the atomic volume, \( \Omega \ (m^3/atom) \). Thus, we can obtain an expression of the chemical potential depending on the surface curvature,
\[ \Delta \mu = \gamma \Omega \Delta k \]  

(2.9)

Next, in order to relate this potential with the velocity of atoms that it produces, the Nernst-Einstein equation is considered, which states the following:

\[ D = \rho k_B T \]  

(2.10)

where \( D \) is the diffusion coefficient, \( k_B \) the Boltzmann’s constant, \( T \) the temperature and \( \rho \) the mobility of atoms. This last variable refers to how easily atoms move and, thus, depends on the force that they receive and the velocity they acquire, \( \rho = F \cdot v = F \mu \). The last step has taken into account that atoms move in the same direction as the applied force. In the case at hand, this force is conservative and, thus, can be expressed as the gradient of a given potential, \( \mu \), which is the ultimate source of the atomic migration, i.e., \( F = -\nabla \mu \). Gathering these expressions, the velocity can be stated as

\[ v = -\frac{D}{k_B T} \nabla \mu \]  

(2.11)

and, in terms of a flow through a given region of a surface,

\[ J = -\frac{D \nu}{k_B T} \nabla \mu \]  

(2.12)

where \( \nu \) refers to the number of atoms per unit area.

Now, we want to obtain a final, and general, expression of the increase in the number of atoms in a certain direction. Thus, the negative divergence of eq. 2.12 will indicate the difference between the entering and leaving number of atoms. The negative sign comes from the fact that we expect a positive value with incoming flow, which is opposite to the general convention. Finally, an expression regarding this change of atoms in the normal direction of the surface is obtained by multiplying by the atomic volume, \( \Omega \), and replacing \( \mu \) by its expression from 2.9.

\[ v_n = \frac{D \nu \Omega}{k_B T} \nabla^2 \mu = \frac{D \nu \gamma \Omega^2}{k_B T} \nabla^2 k \]  

(2.13)

This equation is the one that governs atomic migration due to surface diffusion, as stated by Mullins\textsuperscript{27}. As we can see, its solution is not straightforward and it will be studied with the aid of a simulation program. Nevertheless, before that, we should mention an additional phenomenon that occurs as a consequence of this mechanism. Structures with a high aspect ratio, i.e., ratio between its height and width, will become more rounded while forming a neck at the bottom, as we have already seen in figure 2.3. This neck will generally tend to diminish until, at some point, it will separate from the substrate. This splitting is caused by the Rayleigh instability and is usually referred to as universal pinch off\textsuperscript{36,38}. This type of instability is similar to what happens to a column of liquid that breaks into droplets. This effect is a consequence of the minimization of surface tension, that is achieved for spherical shapes. In a similar fashion, in our structures, the neck
formed due to surface diffusion is narrowed to such an extent that this minimization of energy becomes more relevant, resulting in its breaking. Therefore, we end up obtaining two separated profiles (the pseudo-sphere and the substrate).

2.3 Simulation program

The theoretical study of the model has been performed using a simulation program developed *ab initio* in the department. The goal is to compute and visualize the evolution in time of a given profile. The basic methodology, considerations and limitations are explained below, together with a proposal of a certain figure of merit that evaluates our $\Omega$-spheres.

2.3.1 Main structure of the code

The main objective of the code is to evolve an initial profile subject to one (or both) of the migration mechanisms, i.e., evaporation/condensation or surface diffusion. Figure 2.4 summarizes the main stages of the program. The simulation starts with a given profile, which is discretized with a finite number of control points, meaning that it is defined through two vectors, representing points in $x$ and $y$ directions (2D). At each time step, the profile, i.e., these vectors, are modified according to the corresponding equation. Four main quantities are reckoned and updated every time: the perimeter of the whole profile, the first and second derivatives, the curvature and the laplacian. These computations are developed through a finite differences method. From them, we can evolve the profile according to expressions 2.3 or 2.4. Notice that they describe the evolution of a certain region in the direction normal to the surface, thus we have to obtain the corresponding coordinates ($x$ and $y$) through a geometrical projection. Moreover, we should remark the shape of the profile changes at every step. Consequently, all its properties have to be recalculated each time.

![Figure 2.4: Main scheme of the simulation program.](image)

Recalling the idea of a pillar evolving into a rounded structure, ideally a sphere, the initial configuration given to the program is, in 2D, a rectangle of dimensions $w$
x \ h. We will see that cylindrical symmetry is considered, thus this profile represents a section of the cylinder with diameter \( d = w \) and height \( h \). Of special interest will be the aspect ratio, defined as

\[
\sigma = \frac{h}{w}
\]  

(2.14)

which becomes decisive in the final shape. In concrete, we will refer to the initial aspect ratio as \( \sigma_0 \).

2.3.2 Considerations of the code

Some simplifications are implemented in the program in order to avoid complex calculations and slow routines. In the following, we discuss briefly the most essential ones. It is important to keep them in mind, as they could be the source of some of the inconsistencies that arise when comparing with the experimental results.

1. Symmetries:

   (a) **Cylindrical symmetry**, with the axis of ordinates as the axis of rotation. This assumption is important as it allows to work with a 2D model, as the present one, in order to reproduce a 3D shape (solid of revolution). In the case in hand, the initial profile will be modelled as a cylinder with radius \( R \) and height \( h \). From this point on, the simulation profile will be considered only in two dimensions.

   (b) **Mirror symmetry** with respect to the axis of ordinates.

2. Periodicity

Periodicity conditions are needed in the algorithm in order to reckon all the mentioned quantities. Nevertheless, in the program we only study the evolution of a section of the actual profile and we then consider that there is cylindrical symmetry. Therefore, when we impose the boundary conditions, for instance when we stablish that at the end of each profile comes another identical one, we assume that they will be accomplished in all directions. When dealing with a 2D structure, as a long (almost-infinite) trench, the proper conditions can be applied without any problem. We shall mention that the program can admit a 2D profile, and reckon all its quantities properly (2D curvature, laplacian, etc.), in this case without considering cylindrical symmetry. Nevertheless, for our 3D micropillar, imposing a certain boundary condition would imply that it is accomplished in any direction. Therefore, we cannot consider that each pillar is surrounded by other ones, for instance four (front, rear, left and right), as the program will in fact be assuming that there are neighbours in all directions, like a sort of ring. In order to avoid this inaccuracy, in all the simulations the periodicity pitch will be considered long enough so as if the profile was alone. Therefore, effects arising from the presence of neighbouring structures will be neglected. In the experimental results, however, profiles are not alone but arranged in a matrix of
pitch around 4 \mu m (depending on the photomask used during the lithography).

3. Normalization of the parameters
The evolution of a profile depends on a constant, A or B depending on the active mechanism. These constants are arduous to calculate, as some of the parameters involved have strong dependences on the exact conditions. These problems can be avoided in the simulation by normalizing all the units. In other words, the dependence on A or B is introduced into the simulation time:

\[ \tau_A = At = \frac{p_0 \gamma \Omega^2}{\sqrt{2\pi M(k_BT)^3}} \]  

\[ \tau_B = Bt = \frac{D_s \gamma \Omega^2 \nu}{k_BT} \]  

This normalization does not affect the evolution of the profile, as it is scale independent, i.e., the final effects in the morphology do not depend on the dimensions of the profile. Nonetheless, this assumption will be important if some numerical value has to be extracted. For instance, a direct relation between the simulation time and the annealing duration cannot be obtained, as the constants A or B should be considered. Furthermore, the two mechanisms, evaporation/condensation and surface diffusion, cannot be active at the same time, as they depend on different constants and, thus, the time needed to achieve a certain change will in each case.

4. Crystal planes
The Mullins model, and consequently, the simulation program, only considers the evolution of isotropic surfaces. In fact, our samples are crystalline, meaning that the movement of atoms will be anisotropic. If this property was desired to be implemented in the program, other models regarding the differences in chemical potential depending on the crystallographic planes should be considered. In spite of that, this issue will not be a significant problem because the general evolution (rounding of the corners and formation of a neck) is still the same.

2.3.3 Optimization of pillars for maximum sphericity
As it has already been seen, we can obtain the evolution of a given initial profile through simulation. The main goal of the project is to obtain almost-spherical c-Si microstructures (\Omega-spheres) with a narrow neck, allowing its direct connection to the substrate. According to the theory, the obtained morphologies depend deeply on both the initial aspect ratio (\sigma_0) and the annealing time, i.e., the time at which samples are exposed to a high temperature. The relation between the real time needed in the laboratory and the simulation time cannot be directly obtained, as they are related through a constant (eq. 2.16) that is difficult to calculate. In contrast, the aspect ratio can be more easily controlled both in the experiments and
the simulation. In order to have an idea of which $\sigma_0$ would be the most appropriate, a method to evaluate the rightness of the obtained structures has been reckoned. Two main criteria have to be taken into account:

1. Even though a perfect sphere might be practically impossible to achieve with the proposed method, $\Omega$-spheres should be as spherical as possible. Hence, the main parameter to consider is how far are the obtained structures from a perfect sphere.

2. In addition to the sphericity criterion, it is important that the neck connecting the bulk Si with the $\Omega$-sphere is sufficiently narrow.

Figure of merit

Taking into account the above, we have reckoned a figure of merit to evaluate how ideal is a given shape. It has been developed considering a 2D profile, which should yield the same results as in the 3D case because cylindrical symmetry is assumed. Thence, in the following justification a perfect sphere will be treated as a circumference.

A perfect circumference will have a constant curvature equal to $k = 1/R$, where $R$ is its radius. In the case of an arbitrary profile, we can take its perimeter and build a circumference with the same length, $P = 2\pi R_*$, where $P$ is the perimeter and $R_*$ is the radius of the circumference. This will correspond to the ideal case, when the profile is perfectly circular. Therefore, the representation of its curvature with respect to the perimeter will simply be a horizontal line, $k_* = 1/R_*$. In addition, we can also represent the curvature of the actual profile along the contour, $k(p)$. A simplified scheme is shown in figure 2.5. Finally, we can take the absolute difference ($|A_* - A(p)|$) of the area between the ideal case and the real one, which is reckoned through numerical integration. The result will be an indicative of how far is the obtained profile to the perfect one. In fact, the final figure of merit ($\beta$) is a normalization of this: the final difference in areas is divided by the total area, $2\pi$, and subtracted from 1. Hence, the closer the result is to 1, the more ideal it is.

$$\beta = 1 - \frac{|A_* - A(p)|}{2\pi}$$  

(2.17)

We shall point out that when we are talking about a profile we are actually interested only in the part that will form the sphere, i.e., from the neck to above. Taking into account that the simulation provides the whole profile, a criterion to cut it has been chosen. We can consider half of the profile (as in figure 2.5), given that there is symmetry. The spherical (circular in 2D) part we are interested in will have negative curvature, which will change towards positive when approaching to the neck. Thus, this change in the sign of $k$ is taken into account. Moreover, in order to avoid errors for large aspect ratios (where the sign of the curvature along the desired profile may also change), the maximum of the curvature is searched, which corresponds to the neck. From this point backwards, the first change in sign
of $k$ will be the one we are looking for.

Finally, we should notice that this method takes into consideration the two criteria mentioned before. On the one hand, if we have an almost circular contour but with a thick neck, the ideal radius computed from the perimeter will be small, causing a big curvature and, thus, the difference in areas will still be significant. On the other hand, an ellipsoid with a narrow neck will have a perimeter larger than the one from the ideal sphere, thus a low curvature and, once again, the area will be different.
Ideal conditions

In the following, we will evaluate the ideal conditions, i.e., aspect ratio ($\sigma_0$) and simulation time ($\tau$) of our $\Omega$-spheres based on the simulation results. With this purpose, we have computed $\beta$ for a large number of $\sigma_0$ and in several time steps. The results are shown in figure 2.6, which presents $\beta$ as a function of these two parameters and offers a general overview of their suitability. We can observe that there exists an interval of $\sigma_0$ for which our $\Omega$-spheres should be more similar to a sphere. When it comes to the simulation time, which is proportional to the real duration of the annealing treatment, the outcome is not surprising: more spherical changes are produced right before the pinch-off. In the figure, missing dots correspond to profiles that have already been divided.

![Figure 2.6](image.png)

**Figure 2.6**: Three-dimensional representation of the figure of merit with dependences on the simulation time and the initial aspect ratio.

The exact parameters that produce a maximum $\beta$ are $\sigma_0=2.9$ and $\tau=0.12$. Figure 2.7 shows the dependence on time of the figure of merit for $\sigma_0 = 2.9$. In purple (subfigure b), the profile corresponding to the ideal parameters ($\sigma_0=2.9$ and $\tau=0.12$). The time cannot be easily controlled, as we do not know the proportional constant that relates $\tau$ with the actual value of time. Therefore, we will have to make some tests to achieve the adequate annealing duration. Instead, the information regarding the aspect ratio is more useful, as it gives us an indicator of how the initial samples should be.

Even though the obtained aspect ratio, 2.9, produces more spherical $\Omega$-spheres, it might be difficult to control the exact time instant at which the annealing treatment has to be stopped as it is an unstable point (right before the pinch-off). Therefore, a more convenient aspect ratio would be one a little lower, 2.7 or 2.8 for instance, which also exhibits good performances but does not have that instability
2.3 Simulation program

Figure 2.7: Figure of merit $\beta$ with respect to the simulation time for a given initial aspect ratio, $\sigma_0=2.9(a)$ and evolution of a profile with that value of $\sigma_0$. The colours of each profile indicate the time instant at which it has been stopped, which corresponds with data from a.

and, thus, the annealing time is less critical.
2  Theory
3 | Experimental method

The rounding of initial sharp structures has been proved to work theoretically. Hence, the next step consists in its application in the laboratory. This chapter is aimed to describe the experimental development of the project, which has been entirely developed in a clean room. Let us recall that the main goal is to obtain rounded Si structures, which we have called Ω-spheres, as spherical as possible and connected to the substrate. Moreover, they have to evolve from the substrate itself, a c-Si wafer, meaning that the microstructures will still be crystalline and directly connected to bulk silicon.

3.1 General overview

The application of the theory in order to obtain the desired microstructures is not straightforward and the experimental method has to be developed in several steps. We have designed a procedure that relies on the fabrication of Si micropillars which are later annealed at high temperatures, allowing the surface reorganization. The main scheme of the procedure is shown in figure 3.1 and the steps are next summarized.

1. The initial substrate is a 4-inch, <100> oriented, n-type crystalline Si wafer, with at least one polished side (which is the one that will be processed) (I).

2. A geometrical pattern is transferred to the wafer through photolithography. For this purpose, a thin film of a photosensitive material (a photoresist) is deposited on the wafer (II) and is exposed to UV light, which passes through a photomask. Therefore, the template from the photomask is transferred to the photoresist. The solubility of the photoresist from the exposed parts changes and they are removed, resulting in the engraving of the pattern from the photomask to the wafer (III).

3. Subsequently, we deposit a metal, concretely chromium, on the resulting patterned wafer via sputtering (IV).

4. We remove the remaining photoresist, and the Cr on it, through a lift-off process (V). As a result, we obtain the inverse pattern from the one of the photomask.

5. The remaining Cr acts as a mask during the dry etching step, which is performed via reactive-ion etching (RIE) (VI). The material that is not covered
with the metal is removed, thus we obtain 3D structures. The anisotropic behaviour of this technique allows the formation of vertical pillars with a height controlled by the RIE parameters.

6. The chromium mask is chemically removed (VII).

7. Finally, we introduce the micropillars in a furnace at a high temperature. If the proper atmosphere is chosen, surface diffusion activates and results in morphological changes of the initial structures (VII).

![Diagram](image)

**Figure 3.1**: Main scheme of the method. The figure shows the main steps, starting with the plain wafer (I), the photoresist deposition (II), photolithography (III), chromium deposition (IV), lift-off (V), reactive-ion etching (VI), chromium removal (VII) and finally, annealing with Ar/H\(_2\) (VIII).

### 3.2 Experimental details

#### 3.2.1 Preparation of the wafer

First, we have to prepare the Si wafer for the succeeding processes. Given the fact that they are very susceptible to pollution and imperfections, we start cleaning the wafer. This can be performed through different means.

- **Standard cleaning:**
  - 5 min soak in acetone with ultrasonic agitation
  - 5 min soak in 2-propanol with ultrasonic agitation
  - Rinse in deionized water
  - Dry with a N\(_2\) gun or a centrifuge

- **Piranha etch:**
  This process is useful to remove organic contaminants
  - 10 min soak in a H\(_2\)SO\(_4\):H\(_2\)O\(_2\) (2:1) solution (piranha solution)
  - Rinse in deionized water
  - Dry with a N\(_2\) gun or a centrifuge.

- **Hydrofluoric dip:**
  This solution removes the native SiO\(_2\) film from the surface, the wafer becomes hydrophobic when the oxide is etched
  - 10 s dip in a 5% HF solution
3.2 Experimental details

We shall mention that the two last solutions contain strong acids and, thus, we have to take the convenient precautions. For these and all the following chemical processes we will use chemical resistant gloves, a lab coat, a gas mask and safety glasses, together with the usual clean room suit.

3.2.2 Photolithography

Photolithography is developed in order to transfer a given geometric pattern to the wafer. Particularly, square apertures of widths ranging from 1 to 10 \( \mu m \) and varying separations are obtained according to the different photomasks used. The following is a general description of the process.

First, a photosensitive material, a photoresist, is deposited on the silicon substrate via spin coating, which allows the formation of an almost-uniform film. The thickness of this layer depends on the viscosity of the resist and the angular velocity during the spin coating. We will usually coat a film of 1.2 \( \mu m \), which is thin enough to allow the desired resolution. It is followed by a pre-bake in a hot plate at 115 °C in order to enhance the adhesion to the substrate and remove the solvent photoresist. Next, we align the wafer to a glass photomask using the lithography aligner and we expose the resist to UV light, which permits its transmission across the apertures of the mask. Therefore, only some parts of the sample are directly exposed. Finally, a post-exposure bake is performed equally to the previous one and the wafer is chemically treated with a developer. Depending on the type of photoresist, the developer becomes soluble with the exposed portions (positive photoresist) or with the unexposed ones (negative photoresist) (figure 3.2). An additional post-bake can be performed in order to increase the adhesion of the resist. In our case, we omit this step as we want it to be easily removable.

![Figure 3.2: Main scheme of the photolithography process.](image-url)

A negative photoresist causes that the final pattern transferred is the inverse of the one from the mask. Therefore, in the case of the micropillars, it could act directly as a mask for the successive reactive-ion etching process. After that, the remnant photoresist could be easily removed through different methods, such as \( O_2 \) plasma or acetone. Nonetheless, this type of photoresist was not available, thus we
have performed a different procedure: we use a positive photoresist and we obtain the inverse pattern through an alternative method.

We have used three different photomasks in order to have varying pillar arrangements and widths. The desired pattern corresponds to the apertures of all of them instead of the inverse, which would be another method of using the resist as the RIE mask. Next we review the main features of the three available masks:

- A varied mask with 36 different regions in total, 9 corresponding to each quarter of the wafer. Each array contains a specific arrangement of the apertures, which have a certain width. The latter varies, depending on the region, from 2 to 10 µm, and there are four basic types of orderings: squared, triangular, hexagonal and squared with dislocations of the axis. In addition to these arrays, each side of the mask contains a group of long rectangular apertures, with different widths. These will be used to obtain 2D trenches.
- A mask with a squared array of holes and pitch of 4 µm, i.e., apertures of 2 µm with a distance of 2 µm between them.
- A second mask with a squared array but pitch of 2 µm. The lithography with this mask is more critical, as the feature size (1 µm) is close to the resolution limit of our lithography system.

**Technical details:**

1. **Photoresist:** Megaposit SPR-1.2 (positive)
2. **Developer:** Megaposit MF 24-A
3. **Optical lithography system:** SÜSS Microtec MJB4
4. **Pre & post-bake:** 115 °C, 90 s
5. **Exposure parameters:**
   - Hard contact time: 30s
   - Exposure time: 2s

### 3.2.3 Chromium deposition

After the lithography step, we deposit a chromium layer on the wafer. Cr is an excellent masking material for the subsequent processing steps, as described in the section about the RIE process. A thin (≈100 nm) film of Cr is built on the already patterned wafer via sputtering, which is a type of physical vapor deposition technique that relies on the ejection (sputtering) of atoms from a target and their following deposition on the substrate. This is possible because of the presence of plasma in the chamber. The generation of this plasma can be achieved through different means, with ours being a RF generator. First of all, we need vacuum conditions (≤ 10^{-5} mbar) to avoid the presence of any undesired gas and enhance the plasma formation. Next, we introduce an inert gas, usually argon, into the chamber and a voltage is applied between the cathode, where the target is placed, and the anode, which is below the sample. Argon atoms are ionized due to the produced electric discharge \((Ar + e^- \rightarrow Ar^+\rangle\) and accelerated towards the cathode,
3.2 Experimental details

resulting in the bombardment of the target and the ejection of Cr atoms. These atoms are subsequently deposited on the sample, yielding to the formation of a thin chromium layer.

A final remark regarding this process shall be done. In our case, it is important that the Cr is deposited only on the top of the wafer and not on the walls of the photoresist. Otherwise, it will be difficult to be removed during the lift-off process. In our case, the target is small and is placed far from the wafer in order to diminish this lateral deposition.

The thickness of the deposited Cr layer depends on the sputtering time. In our case, this duration is of 33 min and allows the formation of a layer of approximately 100 nm. We have measured this thickness using a profilometer, which relies on a tip that moves across the surface and evaluates its profile. However, the typical apertures of the photomasks are too small and the tip does not fit in it. Because of that, we have used the rectangular apertures placed at the lateral of the varied photomask, which are wider and allow an accurate measure of the Cr layer.

Technical details:

1. Sputtering system: Leybold Systems Vacuum Univex 350
   RF-Generator PFG 300 RF
2. Target material: Chromium
3. Power: 100 W
4. Duration: 33 min
5. Base pressure: $10^{-5}$ mbar

3.2.4 Lift-off

Once the wafer is covered with a film of Cr, a lift-off process is developed. This technique permits the creation of a pattern inverse from the one obtained through photolithography. We remove th photoresist, which acts as the sacrificial layer, with a soluble product, in this case acetone. The wafer is immersed in this product during the whole night and, despite of that, we usually need to agitate it for 5 min in ultrasounds in order achieve its complete removal. As a result, all the regions with resist and a film of Cr on the top are extracted, while the chromium that is directly on the Si remains thanks to the excellent adhesion between these two material. Therefore, we obtain a final pattern of chromium apertures which is inverse to the initial one.

After the lift-off, we cleave the wafer with a diamond pen, obtaining samples of approximately 2x2 cm. Taking into account that each of these samples can contain of the order of $10^7$ micropillars, a single one is enough for each annealing test.
3.2.5 Reactive-ion etching

The resulting Cr pattern acts as a mask during the reactive-ion etching (RIE) process, a dry etching technique used to form the micropillars. Plasma from a selected gas mixture is created, which attacks the atoms of silicon, thus removing part of the material from the wafer. We use a C₄F₈ with SF₆ recipe, which allows the anisotropic etching of the silicon.

We have chosen chromium as the RIE mask because of several reasons. As it has already been mentioned, the photoresist from the photolithography step cannot be used as a mask because the inverse image is needed. Moreover, the etch selectivity, i.e., the ratio of etch between the mask and the substrate, is not very high in these cases. Instead, metals have large selectivities and, consequently, can be used to etch considerable depths. Even though gold and aluminium are some of the most common materials for deposition, they are quite easily sputtered and redeposited in nearby regions, producing defects on the substrate. On the contrary, chromium can support higher energies with almost being unaffected.

Samples do not need much elaboration before etching for the RIE. The only problem arises when the size of our sample is smaller than a 4-inch wafer. In these cases, we have to fix it at the center of a Si wafer. For this purpose, we use a specific oil that enables adhesion with the substrate and improves the thermal contact. Nevertheless, this substance is arduous to remove, thus we have to develop a piranha etch in order to clean the sample. However, there might still remain some rests of this oil, which can produce the contamination of the furnace. In addition to this, we usually perform an oxygen plasma after each etching, in order to remove contaminants on the sample, from the same oil or other sources, that may arise during the process.

Etch rates cannot be obtained easily as there are many parameters affecting every process. Taking into account that we wanted to achieve different depths, we reckoned a relation between the time of the process and the obtained profundity. From different samples, were the depth was verified using a SEM microscope, we obtained a linear regression. Results are shown in figure 3.3. Note that depending on the type of wafer, and, more specifically, their doping, the rates vary considerably.

<table>
<thead>
<tr>
<th>Technical details</th>
<th>Si etching</th>
<th>Technical details</th>
<th>O₂ plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SF₆: 45 sccm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Pressure:</td>
<td>15 mTorr</td>
<td>2. Pressure:</td>
<td>10 mTorr</td>
</tr>
<tr>
<td>3. RF Fwd Power:</td>
<td>15 W</td>
<td>3. RF Fwd Power:</td>
<td>50 W</td>
</tr>
<tr>
<td>4. ICP Fwd Power:</td>
<td>800 W</td>
<td>4. ICP Fwd Power:</td>
<td>100 W</td>
</tr>
<tr>
<td>5. He flow:</td>
<td>12 sccm</td>
<td>5. He flow:</td>
<td>20 sccm</td>
</tr>
</tbody>
</table>
3.2 Experimental details

Figure 3.3: Relation between the height of the micropillars after RIE and the time needed for the process. The two plots refer to different wafers.

3.2.6 Chromium removal

Once pillars are formed, the chromium mask must be removed. Even though at first it seemed a straightforward step, it has yielded some difficulties. First, some tests were made with samples before the etching process trying two different recipes at a relatively high temperature (details in table 3.1), but none of them gave any encouraging result. The main reason for this failure seems to be due to the passivation of the surface produced by a thin native chromium oxide film. Afterwards, a commercial product (Microposit Chromium etch 18), which also removes the oxide from the surface, was tested directly on RIE-etched samples for 5 and 20 min. In the first case, SEM images showed that there was still a thin film of Cr of about 50 nm (figure 3.4(a)), thus the sample was left more time with the solution. After 20 min, it seemed that the Cr layer had disappeared. Nevertheless, at the end samples were left during 40 min.

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Time (s)</th>
<th>Temperature</th>
<th>Before RIE</th>
<th>After RIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl : H$_2$O (1:1)</td>
<td>20 min</td>
<td>50 °C</td>
<td>No</td>
<td>Not tested</td>
</tr>
<tr>
<td>HCl : H$_2$O$_2$ (3:1)</td>
<td>15 min</td>
<td>50 °C</td>
<td>No</td>
<td>Not tested</td>
</tr>
<tr>
<td>Microposit Cr etch 18</td>
<td>5 min</td>
<td>Ambient</td>
<td>Not tested</td>
<td>No</td>
</tr>
<tr>
<td>Microposit Cr etch 18</td>
<td>20 min</td>
<td>Ambient</td>
<td>Not tested</td>
<td>Yes</td>
</tr>
<tr>
<td>Cr etchant Aldrich Chemistry</td>
<td>20 min</td>
<td>Ambient</td>
<td>Not tested</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 3.1: Different solutions tested to remove completely the Cr layer.

The Cr etch rate that we achieved, which can be roughly approximated to 0.08 nm/sec, is significantly far from the theoretical 4 nm/sec stated from the manufacturer, both considered at room temperature. Moreover, a SEM image revealed that the Cr film remained in some pillars, even after 40 min with the etching solution (fig.
We thought that these difficulties could arise from the RIE process itself. During this step, the surface is bombarded with the chosen plasma, a mixture of C₄F₈ and SF₆, which could produce alterations on the surface of the Cr layer hence making it more difficult to remove. An oxygen plasma was applied to the samples after the usual RIE recipe, in order to clean possible material or plasma remainders, but it did not modify the difficulty in Cr removal. Moreover, we tried to soak the samples in the Cr etchant product with ultrasonic agitation, but it produced the fracture of most of the pillars. The effects of this incomplete etching are discussed in section 4.2.7.

![Cr layer](image)

Figure 3.4: Remainders of Cr even after removal. The first image (a) corresponds to a micropillar after 5 min of Cr etching with the commercial product, thus an entire layer (in a brighter colour) can be seen. The second one, (b), was taken after 40 min of etching. It is shown that Cr remains at random micropillars, thus making the complete etch very difficult.

3.2.7 Annealing with Ar/H₂

Before starting the annealing procedure, we clean the samples with a piranha etch and we remove the oxide from the surface with a dip in HF. Both processes are identical to the ones used to prepare the wafer before lithography.

As it has been previously seen (chapter 2), exposure of Si structures at a high temperature but below their melting point can lead to surface reorganization. Nonetheless, this supposition does not include the effects of the surrounding ambience of the sample. Annealing processes in a furnace can be performed in vacuum or in a chosen gas atmosphere. The first option ensures that the results are due to the sample itself instead of any effect coming from the interaction with the environment. However, this method was not accessible during the development of the project, except from some tests performed in Valencia (details in section 4.2.5). Therefore, a proper atmosphere had to be chosen.

Several gases or gas mixtures can work as the furnace environment. H₂, N₂, O₂ and Ar are common atmospheres used in annealing processes. Despite of that, the effects on the surface vary depending on the chosen gas. Both O₂ and N₂ ambiences are not convenient, as they prevent the atoms from migrating and, thus, the initial
shape remains unaltered\textsuperscript{29}. Moreover, a thick film of silicon dioxide (SiO\textsubscript{2}) can be observed after annealing with oxygen. In contrast, hydrogen and argon atmospheres show better performances, as they allow the reorganization of the silicon surface\textsuperscript{30,23}. This improved behaviour is due to the fact that at high temperatures they can remove the oxide present on the Si surface. This oxide usually hinders the activation of surface diffusion, thus its etch in H\textsubscript{2} and Ar atmospheres enhances this mechanism. Moreover, both gases, and specially H\textsubscript{2}, promote the formation of dangling bonds\textsuperscript{29}, which accelerate the movement of atoms. Even though H\textsubscript{2} seems to be more convenient, argon is a less hazardous gas and, thus, can be easily used in a conventional furnace without major problems. In fact, the selected gas for the development of this project has been argon with a 5\% of hydrogen.

A horizontal furnace is used and samples are loaded on a quartz boat at 400 \degree C. After that, temperature is increased at a rate of 15 \degree C/min up to 1150 \degree C with a flux of the argon composite. After the desired time interval, the furnace is left to cool down freely down to 400 \degree C and the sample is unloaded. The annealing time is considered to start when temperature begins to increase and ends at the moment when it is set to diminish, thereby the duration of the process includes the rise of temperature from 400 \degree C to 1150\degree C and the time spent at that point. This condition comes from the fact that samples cannot be introduced at a high temperature such as 1150 \degree C. Hence, when taking into account the time duration of the surface reorganization, there will always be an uncertainty as it cannot be exactly determined at which temperature the migration starts.

\textbf{Technical details:}

\begin{itemize}
\item[1.] \textbf{Temperature slope:} \hspace{1cm} 15 \degree C/min
\item[2.] \textbf{Gas mixture:} \hspace{1cm} Inoxline H5 (Ar with 5\% H\textsubscript{2})
\item[3.] \textbf{Temperature:} \hspace{1cm} 1150 \degree C
\item[4.] \textbf{Time duration:} \hspace{1cm} 1-2 h
\end{itemize}
30

3 Experimental method
4 | Results

In the previous chapters we have revised the theory of reorganization by surface diffusion and shown that, for the right dimensions, a Si pillar can develop into a quasi-spherical shape connected to the substrate. We have also presented the fabrication techniques in order to obtain Si pillars and the annealing conditions to favour its reorganization. This chapter is devoted to present and discuss the results of the different experiments realized. With this purpose, first we introduce the characterization techniques used to study both the initial pillars and annealed structures. Then we will analyse their general morphology and we will study the effect of different process parameters, together with the discussion of some unexpected problems. Finally, the results will also be compared with theory.

4.1 Characterization

The morphological characterization of the samples has been performed through imaging techniques. In particular, samples are characterized in detail right before and after the annealing treatment with a cross-beam workstation (Zeiss Neon 40) equipped with a high-resolution scanning electron microscope (SEM), a focused-ion-beam (FIB) and energy dispersive X-ray spectroscopy (EDS). This set-up allows us to acquire high-resolution images of the structures, carve them in order to reveal its cross-section, and analyse and identify materials and contaminants all in the same place. In the following we will describe with brief detail these techniques and summarize the main features arising from them.

4.1.1 Scanning electron microscopy (SEM)

The central part of the physical characterization is developed through a field emission scanning electron microscope (FESEM, even though we will always refer to it as SEM), which forms an image from the interaction between a beam of electrons and the sample. Electrons are accelerated through an applied voltage and they are focused on the sample by condenser lenses. The interaction between these e\(^-\) and the atoms from the samples produces different types of signals, which include secondary e\(^-\) (SE), back-scattered e\(^-\) (BSE), Auger e\(^-\) and characteristic X-rays. In particular, this SEM is equipped with four detectors: SE, SE in-lens, BSE and STEM, i.e., scanning transmission electron microscope. Our images have only been
obtained using the two first ones, unless otherwise stated. SE is a conventional detector placed at the lateral of the lens that allows a 3D perception of the sample. The SE in-lens detector, instead, is located inside the electron column and offers higher contrasts on the surface, specially for low voltages and small working distances. Figure 4.1 shows the difference between both detectors. As it can be seen, surface details become more visible for the in-lens detector (image b). Moreover, in this case we have to take into account an additional phenomenon: edge effects. More secondary electrons are detected at the edges, as the emitted beam has less surface to interact with the sample. Therefore, the contours appear notably brighter.

![Figure 4.1: Same image taken with SE (a) and SE in-lens (b) detectors. Whereas SE produces a higher 3D perception, SE in-lens display higher contrast images. Moreover, surface details become more visible with it, specially for higher magnifications.](image)

### 4.1.2 Focused ion beam (FIB)

Part of the morphological characterization includes the analysis of profiles, thus we will need cross section images. The focused ion beam (FIB) technique, which is incorporated together with the SEM, allows the etching of a material through its bombardment with a focused beam of ions, which is usually gallium, Ga$^+$. When these ions hit a surface, sputtering occurs, and material from the sample is ejected. Moreover, their focusing permits the removal of individual spots and, thus, selective milling in the desired direction and with different depths can be achieved. In our case, we will obtain images of the cross sections of the profiles. Nonetheless, during this process, part of the ejected material redeposits on the surroundings of the etching spot, causing the deformation of the profiles. In order to avoid this effect, a thin layer of platinum, Pt, is deposited on the structure, previous to the ions bombardment. Therefore, the profile remains unaltered and, besides, a higher contrast is achieved. The deposition of this Pt film is developed via ion beam-induced deposition, which parts from the injection of a given gas containing Pt in the atmosphere. The focused beam of ions decomposes this gas, from which the volatile components remain on the atmosphere, while the non-volatile fall on the surface, inducing the formation of a film.
Figure 4.2 shows the profile of two different samples. The first one, with initial aspect ratio \( \sigma_0 = 2.6 \), was not covered with Pt before the etching. Even though in this case the deformation is not very noticeable, from adjacent structures it can be seen that some material has redeposited on the vicinities. Instead, in sample b (\( \sigma_0 = 2.2 \)) a layer of Pt (in the image with a brighter colour) has been deposited before the milling, inducing a notable enhancement in contrast. It will be specially useful when measuring the angles of some planes, as the ones on the top become significantly visible with this technique.

Finally, we should mention an additional remark regarding the images obtained with the SEM. In general, samples are inclined a certain angle with respect to the horizontal. This angle is usually 54°, as it corresponds to the angle between the e\(^-\) and the Ga\(^+\) column. This set-up allows a 3D perspective of the structures, hence samples will be usually presented from a bird’s-eye view. Nevertheless, we have to take into account that the dimensions that we see (in height) are in fact projections of the sample with respect to the e\(^-\) column axis. This effect becomes significant in two cases: when measuring heights and when considering frontal images, such as the profiles obtained using the FIB. The same software from the equipment allows to apply the tilt correction, that provides cross-sectional images with the correct dimensions. If nothing else stated, we will present all the profiles that are milled with the FIB with this correction already applied.

4.1.3 Energy-dispersive X-ray spectroscopy (EDS)

A secondary tool that has been used in some cases is the energy-dispersive X-ray spectroscopy (EDS or EDX), useful to determine the chemical composition in a given spot of the sample. The EDS technique relies on the fact that when a high-energy beam, for example of electrons, is focused on the sample, it results in the excitation of an e\(^-\) from an inner shell, and the consequent occupation of this hole by an outer e\(^-\). The energy released during this latter event can be detected and is characteristic
of each element, allowing the identification of the composition of a given material. In our case, it has been useful as a way to evaluate if chromium had been properly removed (after the RIE step) and in some other cases were unknown defects and layers were observed, as it will be seen in following sections. As an example, figure 4.3 shows the spectrum of a spot from a sample before the annealing process.

![SEM image of micropillars with some remainders of Cr](image1)

![Spectrum obtained with the EDS technique](image2)

**(a)**

**(b)**

**Figure 4.3:** SEM image of micropillars with some remainders of Cr (a) and its corresponding spectra obtained with the EDS technique. The spot in (a) shows the exact point where the analysis is performed.

### 4.2 Annealing results

The annealing treatment is the focus of this section, where we will present and discuss the obtained results. First, we will provide a general view of the main features arising from this process, followed by a discussion of some specific characteristics and dependence on different parameters. The latter will be important, as the more we know about how a given profile evolves and the variables that affect it, the more control we will have over the resulting structures. In addition to that, we dedicate a final subsection to the problems that have arisen from this treatment, with a discussion about the possible causes and solutions.

Before starting the discussion, it is convenient to specify the sets of samples that have been prepared. We have designed each of these series according to the specific purpose that we had to study. In what follows, a brief summary of the samples is presented. Notice that, unless otherwise stated, the annealing conditions are the ones explained in the experimental section (3.2.7), i.e., temperature of 1150 °C, atmospheric pressure and annealing ambience of Ar/H₂.

1. We prepared a first set of samples using the photolithography mask with varying aperture sizes and arrangements. They were used to start making some annealing tests, thus we could experiment with different pillar dimensions. Moreover, we also used these first samples to calibrate the relation between height and time of the RIE.
4.2 Annealing results

2. After the first tests with different sizes and pillars distributions, we used the squared photomask with a pitch of 4 \( \mu \text{m} \) to study some dependences. First, we prepared a set of samples with varying aspect ratio, which were annealed during the same time. This will allow us to analyse how micropillars with different \( \sigma_0 \) change.

3. A second series of the 4 \( \mu \text{m} \)-pitch photomask were prepared, in this case with the same height, i.e., equal \( \sigma_0 \). We annealed these samples for different time durations in order to examine how a given micropillar evolves in time.

4. A new set of samples with the squared mask of pitch 2 \( \mu \text{m} \) and different aspect ratios was fabricated. They were annealed with the same conditions as the previous ones, which will permit us to study the effects for lower feature dimensions.

5. Finally, we also prepared and annealed a set of trenches, which will be treated as 2D structures in order to examine their evolution.

4.2.1 Morphology of pillars and annealed structures

We will start the discussion of the annealing results by giving an overview of the effects that can be seen at first sight. Figure 4.4 provides a group of images, all from the same sample, which will make this general review more visual. Even though we are aimed to study the effect of the heat treatment, first we will introduce a brief comment on the initial micropillars.

1. Concerning the pre-annealing micropillars, SEM images (4.4(a) and 4.4(b)) show that they are approximately cylindrical, despite of the fact that the initial pattern from the photomask, during the photolithography step, was composed by squared-apertures. This phenomenon is due to the fabrication process, mainly the photolithography. Nevertheless, this result is in agreement with the assumption made in the simulation program, which supposes an initial cylindrical configuration.

2. From the post-annealing images (4.4(c) and 4.4(d)), we can see that a neck is formed between the substrate and the microstructure, similar to what occurred in the simulation program when only surface diffusion was taken into account (section 2.2.1). Hence, it supports the assumption that it is the principal mechanism driving changes in the surface. Moreover, according to the simulation, the width of this neck depends on time and, thus, it can be controlled with the annealing process and the initial aspect ratio.

3. In spite of the general change of the structures towards a more rounded shape, complete spherical shapes cannot be achieved. Instead, a faceted surface is observed. Even though it can seem unexpected, it is in accordance with the theory. As it has already been seen, surface diffusion is, in the ultimate case, driven by the changes in surface energy: depending on its value, a given atomic
Figure 4.4: SEM images of a sample before (a,b) and after (c,d) annealing at 1150 °C for 1h 30min. Their initial dimensions were 2 μm width and 4.6 μm height and were arranged in an hexagonal array.

arrangement is more or less favourable. Accordingly, our material is not amorphous but crystalline, meaning that its structure is ordered in planes, each of them having different surface energies. Therefore, the migration of atoms takes place following the crystal directions. A deeper study on this effect is developed in section 4.2.2.

4. Finally, some defects are detected on the surface of the substrate after annealing. Grooves emerge at apparently random positions of the sample, which suggest that some kind of contamination or imperfections was present before or during the treatment. Besides, some of the Ω-spheres also show imperfections on their surface, which probably have the same origin as the ones from the substrate. The main hypothesis of the source of these phenomena is the presence of some kind of contamination in the furnace, possibly from the sample itself. In section 4.2.7 we will discuss about the potential causes and solutions of this effect.

4.2.2 Crystallinity

One of the aims of this project was to achieve monocrystalline Si microspheres (mono-Si or commonly named directly c-Si), in contrast to the previously reported polycrystalline and amorphous ones. Monocrystallinity implies that the entire solid,
the wafer in this case, is formed by a single continuous crystal lattice. Opposite to polycrystalline Si (poly-Si), c-Si materials are free of grain boundaries, which can be beneficial in some applications, as these boundaries are usually a focus of recombination and reduce the mobility of electrons. In the case at hand, the initial material was a c-Si wafer, and none of the following experimental processes should alter this atomic organization. SEM images show that the obtained structures are not completely smooth but they display a faceted surface, supporting the assumption that crystallinity is not affected during the procedure.

This faceted behaviour was not predicted by the Mullins model, and we did not either take it into account in our simulation, as we assumed an isotropic surface of Si. Conversely, in a crystalline material, atoms are arranged differently depending on the direction, thus forming different crystallographic planes. The density of atoms is not the same for all of these planes, hence the chemical potential will vary according to the plane where the atom belongs. As a consequence, surface diffusion will be promoted or hindered depending on the crystal planes.

**Figure 4.5:** SEM image of a profile etched with FIB with the most visible planes. At the left, there is depicted the chosen coordinate system (top) and a scheme of how angles are considered (down).

Silicon has a diamond cubic crystal structure with a lattice constant of 5.43 Å. From SEM images and the profiles obtained using the FIB technique, the most visible planes can be recognized parting from the angles they form with already known ones. Our reference plane will be (100), the one corresponding to the top of the wafer, and the <110> family indicated by the flat of the wafer. All angles will be referenced to (100) (figure 4.5). The chosen coordinate system and how angles are taken into account are specified at the left of figure 4.5. First, the planes on the left of the profile (a, b, c and d) have been examined: given the same plane, the angle with respect to (100) is measured from different images, and their arithmetical mean is reckoned. The theoretical values for each plane intersection have been extracted from reference works and they have been compared to the one obtained. Table 4.1 shows this information, together with the proposed matching plane, which has to fulfill angle requirements and, moreover, it has to fit with the selected coordinate system. For planes on the right, a rotation of 180° with respect to the x axis has been performed, as symmetry is considered. If angles are also
measured in these cases, the results match with the ones from the rotation.

<table>
<thead>
<tr>
<th>Plane</th>
<th>Measured angle</th>
<th>Candidate plane</th>
<th>Theoretical angle</th>
<th>Plane</th>
<th>Candidate plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>24.0</td>
<td>(311)</td>
<td>25.2</td>
<td>a’</td>
<td>(3 T T)</td>
</tr>
<tr>
<td>b</td>
<td>55.0</td>
<td>(111)</td>
<td>54.7</td>
<td>b’</td>
<td>(1 T T)</td>
</tr>
<tr>
<td>c</td>
<td>90.0</td>
<td>(011)</td>
<td>90.0</td>
<td>c’</td>
<td>(0 T T)</td>
</tr>
<tr>
<td>d</td>
<td>53.8</td>
<td>(111)</td>
<td>54.7</td>
<td>d’</td>
<td>(T T T)</td>
</tr>
</tbody>
</table>

Table 4.1: Data with the most visible planes, the measured angle, the possible matching plane and its theoretical angle. All angles are measured with respect to the (100) plane.

The data presented in table 4.1 has been gathered and treated in order to identify planes on the images, as seen in figure 4.14. Data not included in the table has been extracted by means of rotations with respect to the $x$ axis in steps of 90°. In image $b$ only some planes are perceptible, thus it has not been possible to complete the planes recognition. We have also taken into account the orientation of the wafer. It was a n-type, thus its flat corresponds to the $<110>$ family, which agrees with our results. In particular, at the bottom of figure 4.14(a), the plane following (1T1) should be (0T1), which belongs to the family planes $<110>$.

![Figure 4.6](image1.png)  ![Figure 4.6](image2.png)

Figure 4.6: Identified planes with images from a sample seen from above (a) and from a bird’s-eye perspective (b). In the latter view, only some planes are visible, hence only they have been marked.

Even though the main objective was to achieve monocrystalline $\Omega$-spheres and, consequently, they display a faceted surface, for some applications it might be interesting to achieve smoother structures. For instance, if we wanted to use our $\Omega$-spheres as spherical resonators, the presence of planes instead of a perfect globular shape could produce a decay in the resonance behaviour. A possible way to avoid, or at least diminish this effect is an after-annealing treatment. For instance,
we made a test shown in figure 4.7. After the time of the heat treatment, the temperature was decreased with a $N_2 + O_2$ atmosphere, instead of doing it with the $Ar/H_2$ mixture as usual. Hence, we oxidised the surface of the $\Omega$-sphere, resulting in its smoothening. The oxidation of Si, i.e., formation of $SiO_2$, is nearly isotropic, which means that the outer faceted behaviour will disappear. In fact, it will only happen with the exterior, as the structure is still crystalline and crystallographic planes remain under the $SiO_2$ layer. Nevertheless, we should do more tests in case we wanted to achieve this more spherical shape and see if it exhibits an enhancement in the resonating behaviour.

![Figure 4.7](image)

Figure 4.7: Difference between samples annealed with the usual procedure (a) and ended with a $N_2+O_2$ atmosphere (b). In the second case, facets from the surface tend to smooth.

4.2.3 Effect of the aspect ratio

From the theory we have seen that the aspect ratio of the initial micropillar is critical to the evolution of the profile. Whereas structures with $\sigma_0$ tend to flatten, high $\sigma_0$ allows the creation of a neck and the formation of the final $\Omega$-sphere, which will be more or less spherical depending both on $\sigma_0$ and the time.

We have studied experimentally this phenomenon by fabricating a set of samples with different $\sigma_0$, ranging from 1 to 3.5. They have all been annealed during 1h 30min and, afterwards, we have characterized them through SEM. Figure 4.8 shows the images of samples corresponding to initial aspect ratios $\sigma_0 = 1, 2.2, 2.6$ and 3.5 (a, b, c and d respectively). The results are not surprising as they follow the same tendency as predicted by the simulation: for low aspect ratios (a) a neck between the substrate and the structure is not even formed. Moreover, if the annealing was kept for a longer time, it would probably end up being absorbed by the substrate and the pillar would disappear, as predicted by theory. Contrary to this behaviour, samples with higher initial aspect ratio (b, c and d) do exhibit the formation of a neck. Besides, we can clearly distinguish that the $\sigma_0=2.2$ sample presents a more spherical profile, even though the neck is still quite thick. As an additional remark, we shall notice that the longer structures ($\sigma_0=3.5$) are far from the expected $\Omega$-spheres, but could resemble the shapes from the fovea centralis.
Such structures have already been studied as an enhancement in light trapping\textsuperscript{15}.

\begin{figure}[h]
\centering
\begin{subfigure}{0.4\textwidth}
\centering
\includegraphics[width=\textwidth]{a.png}
\caption{(a)}
\end{subfigure}
\begin{subfigure}{0.4\textwidth}
\centering
\includegraphics[width=\textwidth]{b.png}
\caption{(b)}
\end{subfigure}
\begin{subfigure}{0.4\textwidth}
\centering
\includegraphics[width=\textwidth]{c.png}
\caption{(c)}
\end{subfigure}
\begin{subfigure}{0.4\textwidth}
\centering
\includegraphics[width=\textwidth]{d.png}
\caption{(d)}
\end{subfigure}
\caption{SEM images of different samples annealed at identical conditions during the same time (1h 30min). Initial aspect ratios are $\sigma_0 = 1, 2.2, 2.6$ and 3.5 respectively.}
\end{figure}

### 4.2.4 Effect of annealing time

The next parameter studied is the time duration of the annealing treatment. According to the theory, surface diffusion starts transforming the regions with higher curvature, the corners in this case. Therefore, we should expect that both the bottom and the top of the initial micropillar will become more rounded. From this, two possible results can take place, depending on the initial aspect ratio: the transformation of the profile into a total flat plane and the narrowing of neck, ending with the \textit{pinch-off}, i.e., the separation of the $\Omega$-sphere from the substrate.

In order to test experimentally how this evolution actually occurs, we have annealed a set of samples with equal $\sigma_0$ during different times. After that, we have obtained the cross-section of each of them using the FIB. Figure 4.9 displays the results, all corresponding to $\sigma_0=2.1$. The samples were annealed during 1h, 1h 30min and 2h, respectively. At first sight, these results agree with what expected from the theory: sharper regions start rounding, which produces the formation of a neck at the bottom of the profile. The diameter of this neck decreases as time increases, with values of around 1.6, 1.3 and 1 $\mu$m, respectively (we have measured...
this length at the point where the neck is narrower in each case).

![SEM images](image)

**Figure 4.9:** SEM images of samples with equal $\sigma_0=2.1$ that have been annealed during different times (1h, 1h 30min and 2h, correspondingly). The cross-sections have a Pt layer on the top, deposited during the FIB milling.

In addition to this scanning in time of equal samples, we have tested other micropillars with different aspect ratios. We obtained an interesting result for two samples of $\sigma_0=2.4$, showed in figure 4.10 for corresponding annealing times of 1h 30min and 2h. Even though there is only a variation in aspect ratio of 0.3 with the previous ones, the result is surprisingly different. We can observe that these new profiles exhibit a much thinner neck, $\sim 920$ and 300 nm. From these results arise two interesting facts. Firstly, the comparison with the earlier profiles suggests that the critical aspect ratio ($\sigma^*$) belongs to the interval (2.2, 2.4). This result does not agree with the one extracted from the theory, thus either there is an experimental error or the theory does not exactly correspond to the experiments. This comparison is developed in a following section (2.2.1), hence we will leave this question unsolved for the moment. Secondly, the diameter of the neck reduces much rapidly for the last set of samples. In the 2.2-case, the diameter for 2h is around 25% thinner than that for 1h 30min. In contrast, for the 2.4-profiles, the reduction is around 70%. We can explain this important difference if we consider that the profile is near the pinch-off, which accelerates the evolution of the neck. Instead, the 2.1-samples are not close to the separation, thus the width of the neck does not vary that rapidly.

### 4.2.5 Annealing temperature, atmosphere and pressure

In addition to the aspect ratio and the annealing time, the evolution of the profiles might also have strong dependences on other variables. In the following we will discuss the effects of the temperature, pressure and atmosphere during the annealing treatment. In this case, the experiments have been restrained to the limitations of the equipments, such as the impossibility of changing the pressure or the lack of specific equipment to deal with gases like H$_2$. In spite of this, we have been able to test the evolution of some samples in a vacuum conditions.
Figure 4.10: SEM images of samples with equal \(\sigma_0=2.4\) that have been annealed during 1h 30min and 2h, correspondingly. The notable different among the previous ones suggests that the critical point is between \(\sigma_0=2.2\) and 2.4.

Surface reorganization takes place at high temperatures, when atoms acquire enough energy to become movable. In addition, in order to occur in solid phase, this atomic migration has to take place at temperatures below the melting point, which is 1414 °C for Si at atmospheric pressure. We have performed all the annealing processes at 1150 °C, which has been proved to be high enough to activate surface diffusion. We have not been able to try higher temperatures, as the furnace would possibly not withstand them. Instead, we have performed a few tests at lower temperatures, which revealed that the time needed to achieve the same morphology varies significantly. Images in figure 4.11 correspond to samples with the same aspect ratio, \(\sigma_0=2.4\), but different annealing treatments. We annealed micropillars from \(a\) in the same fashion as always: 1150 °C during 1h 30min. In contrast, we treated sample \(b\) at 1100 °C during 1h 30min, but we could not appreciate any change of the morphology. Therefore, we performed a succeeding annealing at the same temperature for 2h. Despite the fact that sample \(b\) was left more time in the annealing treatment, it still shows less changes in the morphology than \(a\). The profile is far from spherical and the neck is still thick, compared to the reference ones. Consequently, we can conclude that temperature is critical, as a reduction of 50°C implies an increase in time of more than 2h. This high dependence can be explained according to the expression for the constant \(B\) involved in the surface diffusion evolution: even though the dependence of \(B\) on the temperature is inversely proportional, the diffusion coefficient also varies highly with \(T\).

In addition to the temperature, the annealing atmosphere is crucial in the morphology changes. We have already discussed some of the effects of different ambiances in section 3.2.7, were we justified why we had chosen the Ar/H\(_2\) compound. Surface reorganization only occurs in the presence of non-reducing atmospheres, thus N\(_2\) and O\(_2\) gases cannot be used. Otherwise, the initial profile remains unaltered and the only visible modifications are the formation of a SiO\(_2\) and the presence of oxynitrides in the case of nitrogen. In contrast, H\(_2\) and Ar atmospheres are apparently more suitable, as they prevent the formation of an oxide film and reorganization succeeds. In fact, the most proper ambience seems
4.2 Annealing results

![SEM images of samples with equal $\sigma_0=2.5$ that have been annealed at 1150 and 1100 °C, respectively. Sample b was annealed during 3h 30min in total, but still shows a less spherical morphology.](image)

**Figure 4.11:** SEM images of samples with equal $\sigma_0=2.5$ that have been annealed at 1150 and 1100 °C, respectively. Sample b was annealed during 3h 30min in total, but still shows a less spherical morphology.

...to be H$_2$ as visible effects appear at shorter annealing durations. As an example, Sudoh$^{40}$ obtained Si voids with a similar shape of our $\Omega$-spheres after only 10 min of annealing in a H$_2$ atmosphere, even at a temperature of 1100 °C. Furthermore, according to some works, H$_2$ promotes the removal of any dioxide layer present on the surface. Therefore, in this ambience even samples with an initial oxide film would be reorganized without major problems. Nevertheless, H$_2$ is a hazardous gas and requires specific conditions that were not available in the laboratory.

Finally, a third important parameter that has to be taken into account is the pressure at which the heat treatment is developed. Most of the studies concerning the reorganization of surfaces are developed in low pressure conditions$^{23,24,40}$. These type of ambiences enhance surface migration of atoms and, therefore, the morphological changes occur more rapidly. Moreover, if a pressure of the order of the vapour pressure of Si (at the annealing temperature) is achieved, the mechanism of evaporation/condensation would become more important and it should have to be taken into account.

Thanks to the research group of F. J. Meseguer Rico, from the Universitat Politècnica de València, we have been able to perform an additional annealing treatment in vacuum. Therefore, in this case we have to consider both a change in the atmosphere, as now there is not any gas that can interact with the sample, and a low pressure ($P \approx 10^{-7} - 10^{-9}$ mbar), in addition to a lower temperature (1000 °C, which was the maximum they could achieve). We prepared samples with $\sigma_0=3.5$ and sent them to the research group. They developed some tests for different annealing durations because we did not know the time it would take in a vacuum atmosphere. Nevertheless, even though these tests ranged from 1 to 8h, we did not obtain any satisfactory result, as it can be seen in figure 4.12. The micropillars disappeared and only some small slopes can be seen. A possible justification of this can be related to the activation of the evaporation/condensation mechanism due to the low pressure conditions. The vapour pressure of Si is difficult to obtain for low temperatures such as 1000°C. Some possible estimations$^{45}$ reveal orders of magnitude around $10^{-6}$. Therefore, it is possible that in these conditions Si is evaporating and, thus, the evolution of the micropillars are not the expected ones. Nonetheless, we will...
have to develop more tests in order to discard any other possible source, such as pollution from the furnace or problems with the specific sample that was annealed.

![SEM images of samples annealed at 1000 °C in vacuum for 1h (a) and 2h (b).](image)

**Figure 4.12:** SEM images of samples annealed at 1000 °C in vacuum for 1h (a) and 2h (b).

### 4.2.6 Scaling of the structures

In general, we have fabricated pillars of 2 µm in diameter using the squared photomask with 4 µm pitch. Nevertheless, a scaling of these structures should in principle be possible if we had the appropriate photomask. Particularly, we have made some tests with 1 µm-width micropillars (pitch of 2 µm). The fabrication of these samples has been more delicate, as we have halved all the feature dimensions. The most critical step has been the photolithography process, as tiny defects and imprecisions of the wafer became of considerable importance in the final result. In fact, we are very close to the limit that can be achieved with our contact lithography aligner, which is of 0.7 µm. The annealed samples are displayed in figure 4.13, which correspond to $\sigma_0=4.2$, 3.2 and 2, respectively, and an annealing time of 1h 30min for all of them. The main feature that can be seen is the dispersion in morphology, despite of the fact that all the pillars were theoretically equal at the beginning of the annealing treatment. We hypothesize that these differences might be caused by tiny imperfections of the initial micropillars or even during the heat treatment, that become more noticeable at low dimensions. For instance, as we have already mentioned, from the photolithography step itself we could quite easily have some dispersion in width. The succeeding fabrication steps, specially the lift-off and RIE, can magnify these tiny differences, resulting in very critical structures.

In addition to the delicate nature of the micropillars and the obtained $\Omega$-spheres, we should mention a second visible effect. Many of the samples in figure 4.13 display a narrow neck, much smaller than that for their homologous $\Omega$-spheres of 2 µm-width, which suggests that the time dependence is stronger when dimensions are lowered. Moreover, in the last image we only found a few $\Omega$-spheres, and the rest of the surface presented smooth small hills. The most presumable reason is that $\sigma_0$ was too little to allow the formation of the neck and the subsequent pinch-off. Instead, pillars tend to flatten, as predicted by the theory, and are swallowed by the substrate itself. This result is not surprising: tinier features need shorter times to evolve, thus the time at which annealing is stopped becomes much
more critical. Otherwise, it results in very different outcomes, as the mentioned ones.

![Fig 4.13](image1.png)

**Figure 4.13:** 1 $\mu$m-width samples annealed during 1h 30min. The initial aspect ratios are 4.2, 3.2 and 2, respectively.

### 4.2.7 Defects on the surface

One of the most noticeable effects of the annealing process, besides the evident rounding of the structures, is the appearance of defects on the surface. In particular, grooves of considerable dimensions emerge on the substrate and, in less cases, even on the $\Omega$-spheres themselves. The source of this phenomena is still unknown, although we have some hypothesis. It seems quite evident that these grooves arise from imperfections on the surface, even though we do not know its exact origin. The presence of a given impurity or defect on the substrate can also activate the diffusion mechanism, causing the reorganization of atoms on their surface, in the same fashion as for the micropillars. In fact, Mullins$^{27}$ first developed his model to describe the evolution of a groove, thus it is not surprising that small changes on the surface such as these imperfections (compared to the micropillars) produce remarkable defects.

![Fig 4.14](image2.png)

**Figure 4.14:** Images of different samples with remarkably visible surface defects. Whereas on the left (a), the imperfections are more focused at the bottom of each $\Omega$-sphere, sample on the right (a) shows a high number of defects on the substrate and also on some structures.
One of the strongest hypotheses about the source of these phenomena is the contamination, both from the furnace and the sample itself. Even though SEM images show clearly these grooves, analysis with EDS did not give any conclusive result. This can be due to two reasons: the first, this technique has a limited resolution, as there has to be a significant amount of material in order to be detected. Thus, impurities, or their remainders, could be too small to be identified. The second motive, and the most probable one, is that any impurity could be dragged with the flow of Ar/H\(_2\) during the annealing process. Therefore, they would leave a small defect that becomes more pronounced due to the migration mechanisms. The ultimate source of these imperfections is thought to be the chromium that remains on the micropillars, even after specific wet etching, as seen in section 3.2.6. The presence of these Cr dots was difficult to control, given the fact that they seemed to appear at disperse random positions over the whole sample, hence they could easily produce the defects. Besides, we were unaware of them for some time. Moreover, after some annealing steps, the furnace might become polluted with the Cr itself, thus making more difficult the identification of this problem.

A second possible origin of the imperfections on the surface could arise from the same crystallographic nature of Si and its imperfections. Stacking faults are common defects on crystalline materials, specially in face-centered structures as the one in hand. They emanate from a dislocation of the atomic layers. In other words, in a given closed-packed structure, atoms arrange forming a set of layers, one of the top of the other, following a given pattern. When one of the layers is displaced with respect to the others, defects (stacking faults) appear in the crystallite. Therefore, due to the high mass transported, they could be a feasible source of imperfections in our case, which are amplified with the annealing of the samples, that activates the surface reorganization. Notice that the number of defects on the spheres, from where the mass is leaving, is less.

4.2.8 Other problems arising from the annealing treatment

In addition to the surface defects, that are present in all the annealed samples, in some cases we have had to deal with some additional problems. Specifically, we have obtained three different samples that did not evolve into Ω-sphere after the usual annealing times and conditions. Instead, micropillars were almost destroyed, as shown in figure 4.15. The first noticeable fact in the image is that micropillars are still formed, hence it suggests that surface diffusion was not activated despite of the high temperature. Moreover, these pillars are nearly destroyed due to unknown causes. We can observe that some of them have very thin layers, as if the silicon was being evaporated and a thin film of SiO\(_2\) remained. Nevertheless, the conditions (temperature, argon flow and time) are exactly the same as in the successful samples. Moreover, figure 4.15(b) displays the spectra resulting from an EDS analysis. Silicon, oxygen and carbon are the only recognized elements, thus it seems that contamination, at least from different materials, is not the source. The presence of carbon is not surprising, as it can easily come from the same SEM atmosphere. However, it could also come from the RIE process, which uses a
plasma containing C\textsubscript{4}F\textsubscript{8}. Even though it is not quite feasible, there could remain some rests of this compound on the sample and produce unexpected events when annealing.

The oxygen peak from the EDS spectra is higher than the typical due to the native oxide, thus it reveals the presence of a layer of oxide. Right before introducing the sample into the furnace, we always dip it in hydrofluoric acid (5%), which removes the oxide from the silicon surface, thus the origin of this SiO\textsubscript{2} is still unknown. Moreover, even if there existed a SiO\textsubscript{2} film before the heat treatment, the argon and, specially, the H\textsubscript{2} from the gas mixture should remove it\textsuperscript{29}. According to the references, for low oxygen partial pressures and high temperatures (\sim 1150 °C), the dominating reaction is $\text{Si}_1(s) + \text{SiO}_2(s) \rightarrow 2\text{SiO}_1(g)$, which produces the conversion of SiO\textsubscript{21}(s) into SiO\textsubscript{(g)}. Hence, this is still an unsolved issue.

\textbf{Figure 4.15:} SEM image of one of the problematic samples. Figure b shows the EDS spectra focused on one point of the same sample.

### 4.2.9 Anneling of 2D structures

We have prepared an additional set of samples based on long trenches, which allows us to consider the profiles as 2D structures. Theoretically, surface reorganization acts in the same fashion as for the 3D case, i.e., atoms tend to diffuse from high to low curvature. In figure 4.16 we show two images from a sample ($\sigma_0=3.5$) annealed during 1h 45min. The fabrication is exactly the same, with the only difference that the initial structures are rectangular long trenches instead of pillars. From these samples we can see that the evolution of a 2D structure is quite similar to the 3D one, as the corners become rounded and a neck is formed. In spite of this, the latter is less pronounced, which might imply that these structures have a more slowly evolution. This change in time dependence comes from the fact that a 3D structure such as a cylinder will exhibit changes in curvature higher than for the analogous 2D case and, thus, the evolution is faster. Moreover, for 2D trenches such as the ones discussed there is not the Rayleigh instability that accelerates this narrowing of the neck.
4.3 Adjustment with theory

The experimental results will be next compared to the ones predicted by the theory. In this way, we will be able to discuss the accuracy of the theoretical model and, in particular, of the simulation program. Moreover, we make a rough estimation of the constant (B) involved in the evolution of the profile through surface diffusion.

4.3.1 Adjustment of the profiles

In the following we will focus our discussion on the comparison between the profiles obtained via simulation and the experimental ones. In this manner we can evaluate the accuracy of the program when matching the SEM images with the simulation results. Figure 4.17 shows a set of SEM images corresponding to the cross-sections of profiles with $\sigma_0=2.1$ and annealed for different times. We have superposed each of the images with the profile obtained through the simulation. Calculations have been performed taking into account the same initial aspect ratio (2.1) and considering single micropillars, i.e., the distance between samples is long enough so that they do not interfere in the evolution of the neighbours.

This comparison shows that the theoretical profiles fit quite well when the process starts (a,b), but they become worse as time passes (c,d). The last profile (d, in red) corresponds to the minimum diameter of the neck that we can achieve using the simulation. In contrast, experimental results show that the neck continues narrowing in time. This difference becomes more evident in the case of $\sigma_0=2.4$. From experiments, we have already seen that we can achieve a very narrow neck after annealing samples with this aspect ratio during 2h. Futhermore, it seems that the pinch-off will take place if samples are left some more time in the furnace. Nevertheless, results from the simulation show a very different situation: profiles with this aspect ratio exhibit a thicker neck and end up evolving

Figure 4.16: SEM images from a bird’s-eye (a) and frontal (b) view of the same sample, with initial aspect ratio of approximately 3.5 and annealing time of 1h 45min. The trenches from b have been covered with a Pt layer before being melted with the FIB.
4.3 Adjustment with theory

Figure 4.17: Cross-section images of samples with equal initial aspect ratio, $\sigma_0=2.1$, annealed for different times. The results from the simulation have been superposed, showing that it only reproduces the evolution successfully at the start of the process.

into a flat surface. Figure 4.18 (a and b) depicts this problem, where it becomes clear that the simulation cannot reproduce the reality with these specific conditions.

Taking into consideration this behaviour, we have performed a second simulation test with a change in the assumptions. Because of the limitations of the code itself, we cannot impose the 3D real boundary conditions, i.e., each micropillar is surrounded by identical ones in a square lattice. Therefore, until now, we have always considered large distances between profiles, thus we have made the approximation that the evolution of a given micropillar is not influenced by nearby structures. Opposite to this, an alternative approach would be to consider that the profile does have neighbours and, hence, their influence has to be taken into account. Due to the restrictions of the program, we will in fact be assuming that there exist a neighbour profile in all directions (let us recall that we assume cylindrical symmetry). This approach is not an accurate representation of the reality and we should be careful when considering it in the simulation, but it might give an idea of how the surroundings affect each profile. The fitting in subfigures c and b in fig. 4.18 has been obtained assuming this condition and the results show that it reproduces more satisfactorily the real evolution. Moreover, with this new assumption, the critical aspect ratio above which pinch-off occurs becomes $\sigma_*=2.3$. This value agrees more with the behaviour seen from the experiments (4.2.4). Even though the latter approach is still far from the reality and the algorithm itself might yield some inaccuracies, at least we can conclude from it that the presence of nearby profiles does have a non-negligible impact on the morphological evolution.

4.3.2 Approximation of model constants

As we have already seen, the expression for the surface diffusion,

$$v_{n,\text{diff}} = B\nabla^2 H$$ (4.1)
Figure 4.18: Fittings of the results from the simulation with the experimental cross-sections. Whereas the single-profile approach (a,b) reproduces more poorly the time evolution, the assumption of having neighbours in all directions exhibits a better performance.

has an explicit dependence on the constant \( B \),

\[
B = \frac{D_s \gamma \Omega^2 \nu}{k_B T} \tag{4.2}
\]

which depends on parameters that are difficult to determine, as they depend on the specific conditions at which they are measured. An example of this is the diffusion coefficient, \( D_s \), that depends on the temperature, dimensions of the particle and viscosity, among others. Therefore, it is considerably complicated, if not impossible, to determine accurately its value from published data. In all the simulations, we have performed a normalization of the expression from 4.1, i.e.,

\[
\tau_B = Bt = \frac{D_s \gamma \Omega^2 \nu}{k_B T} t \tag{4.3}
\]

in order to avoid any dependence on this unknown constant. Hence, the simulation time, \( \tau \) is in fact a fictitious parameter related to the actual time through \( B \).

<table>
<thead>
<tr>
<th>Approach</th>
<th>Annealing time</th>
<th>Simulation time</th>
<th>Approximated B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Single profile</strong></td>
<td>60 min</td>
<td>7.16\cdot10^{-3}</td>
<td>6.46\cdot10^{-6}</td>
</tr>
<tr>
<td></td>
<td>90 min</td>
<td>1.80\cdot10^{-2}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120 min</td>
<td>3.04\cdot10^{-2}</td>
<td></td>
</tr>
<tr>
<td><strong>Surrounded profile</strong></td>
<td>90 min</td>
<td>4.38\cdot10^{-2}</td>
<td>7.85\cdot10^{-5}</td>
</tr>
<tr>
<td></td>
<td>120 min</td>
<td>1.85\cdot10^{-1}</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Data extracted from the different tested profiles and the corresponding value of \( B \). As it can be seen, the second approach is, once again, closer to the reality.

We can obtain a rough approximation of the \( B \) constant by considering the previous dependence between the simulation time and the actual one (expression 4.3). This relation is linear, thus we only need two values to estimate the constants. We have developed this approximation by using data from the previous profiles (figures 4.17 and 4.18). In fact, we would only need a point (real time and
4.3 Adjustment with theory

simulation time) and we could consider the zero (0,0), as when the real time is zero the simulation one should also be. Nevertheless, taking into account that we do not know in depth the exact phenomena that takes place at the beginning of the surface reorganization, we have used two points obtained experimentally. Thus, two exact profiles were annealed during two different times and the corresponding $\tau$ values have been approximated. Moreover, we have developed this estimation following the two already mentioned approaches: assuming a single profile and a surrounded one. The data that we have used and the obtained values of B are presented in table 4.2. In order to have a first idea of the magnitude of this value, we can compare it to a value taken from Sudoh\textsuperscript{40}, $B \approx 3 \cdot 10^{-5}$ $\mu m^4/s$, who estimated the constant from gathered data. Nevertheless, we should always take into account that the annealing conditions might have a strong influence on this result, hence the comparison is only in general terms. Regarding the obtained data, first of all, we notice that the second approach yields a result closer to the one expected, which is not surprising as we have already seen that it reproduces results that are more similar to the reality. Secondly, even though the obtained value, $B = 7.85 \cdot 10^{-5}$ $\mu m^4/s$ is still different from the reference one, it is only an order of magnitude lower, meaning that this method is reliable. Finally, we shall comment a final remark. We should not be confused by the units of $\tau$: even though we have considered it a sort of simulation time, the proper proper units are of length\textsuperscript{4}. The exact units depend on the data that we insert in the simulation: our profiles are always measured with $\mu m$, thus the units of B become $\mu m^4$. 
Results
In this project we have reported on the fabrication of monocrystalline quasi-spherical Si microstructures connected to the substrate through a neck, which we have named Ω-spheres due to its resemblance with this letter. It has been developed through a high-temperature annealing treatment of initial sharp structures, micropillars, that evolve towards a more spherical shape because of surface reorganization. Moreover, we have studied the parameters involved in the process in order to determine the optimal conditions. The experimental results have been compared with the theory through a simulation program, exhibiting a high level of agreement between both approaches.

This work has essentially been an experimental development of a technological process. Although there was a limited previous experience in the department on the reorganization process, this was the first time that this method, the production of sphere-like particles through reorganization, was attempted. Therefore, we have had to propose and perform the fabrication of the micropillars and the annealing treatment using the materials and processes already accessible in the laboratory. These initial sharp structures have been successfully obtained through the transfer of a pattern to the wafer through photolithography. The subsequent deposition of a metal, chromium, and the lift-off process has allowed us to obtain an inverse template of the mask, which was what we needed in order to fabricate the micropillars. Finally, we used a dry etching technique (reactive-ion etching, RIE) to achieve three-dimensional structures, concretely pillars of a few micrometers width and aspect ratio ranging from 1 up to 5.

The annealing treatment has showed satisfying results when the samples are exposed to a temperature of 1150 °C in an Ar/H\textsubscript{2} atmosphere during different times, usually between 1 and 2h. This set of conditions induces morphological changes on the surface, tending to smooth regions with high curvature and forming a neck between the microstructures and the substrate. In particular, we have studied the effects of the initial aspect ratio and annealing time on the final results in order to estimate the optimal ones. We have seen clearly that the critical aspect ratio which enables both the narrowing of the neck and the formation of a highly-spherical microstructure lies between $\sigma_0=2.1$ and 2.4. Besides, the ideal annealing time is between 1h 30min and 2h. Even though structures annealed during 2h exhibit very narrow necks, they are close to the pinch-off and their control becomes difficult. Therefore, the optimal Ω-spheres would be with an aspect ratio of approximately
2.3 and annealed for around 1h 45min. The final Ω-spheres obtained using these parameters are shown in figure 5.1, from which we can see that we have achieved our purpose, i.e., quite-spherical structures with a narrow neck. Besides, all the fabricated Ω-spheres exhibit a faceted surface that evidences their monocrystalline nature, proving that none of the fabrication steps alter this property.

![SEM images of Ω-spheres](image)

*Figure 5.1: SEM images of Ω-spheres obtained from initial micropillars of aspect ratio $\sigma_0=2.3$ that were annealed in an Ar/H$_2$ atmosphere for 105 min. The images have been taken from a bird’s-eye perspective (a, b and c) and from above (d).*

We have also compared these experimental results to the theoretical predictions. This comparison has been performed through a simulation program developed *ab initio* in this department. We have proved that the mass-transport mechanism responsible of the formation of our Ω-spheres is surface diffusion, in contrast to evaporation/condensation that has a minor effect in the given experimental conditions (temperature and pressure). Moreover, we have verified that the proximity of other micropillars near the considered one has non-negligible effects on final shape. Finally, we have obtained a rough estimation of the value of the constant involved in the evolution of an arbitrary profile due to surface diffusion. Even though it is only an approximation, it allows us to know its order of magnitude without having to deal with very specific physical parameters.

**Future work**

Taking this work as a starting point, several lines of research can emerge, both regarding the improvement of the fabrication method and the obtained Ω-spheres.
and its further optical characterization and applications.

Even though we have obtained quite satisfying $\Omega$-spheres, there still remain some unsolved problems and issues. First of all, we should determine the source of the defects that appear on the surface and avoid it. A possible way of doing it is trying an alternative RIE mask, as chromium is probably the main origin of the contamination of the sample and, thus, the development of these defects. We could test the performance of a negative photoresist and, hence, we would not need to obtain the inverse pattern. Therefore, the resist itself could act as the RIE mask and could be later removed with less difficulty than in the case of Cr. In addition to all this, we should clean deeply the furnace where all the annealing tests have been developed, as it is probably already contaminated at least with chromium from the samples. In fact, a new quartz tube to use exclusively for this process is being currently installed.

A second natural line of study arising from these $\Omega$-spheres is their optical characterization, as we shall remember that the final purpose of these structures was to mimic the ones obtained by M. Garín et al.. Therefore, their optical performance has to be studied in order to see if the same resonance behaviour and light harvesting can be obtained from them. The characterization of ordered arrays of $\Omega$-spheres, as the ones we have fabricated, can be developed through Fourier transform infrared spectroscopy (FTIR). Nevertheless, in order to perform a complete optical characterization, we should need single $\Omega$-spheres, to study the resonating modes, and arrangements with only a few of them, for the study of multiple scattering effects. Hence, the fabrication of these concrete structures would be an additional track of research.

Finally, further studies on this topic could be developed by implementing the 3D behaviour to the simulation code. In this manner, we could reproduce the evolution of a profile by considering the appropriate boundary conditions, without the simplifications that we have assumed. This would allow the study of new profiles such as a micropillars with very high aspect ratio, which could end up forming a column composed by microspheres one of the top of the other and connected through a neck.
Conclusions & future work
Bibliography


[34] Lee, M-C. M. & Wu, M. C. Thermal Annealing in Hydrogen for 3-D Pro-


