



Collaborative project

Project acronym: SNM

Project full title: "**Single Nanometer Manufacturing for beyond CMOS devices**"

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Deliverable: <D3.3> ("Template growth of organic and biological molecules onto nanopatterns")

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<p style="text-align: center;">SNM Work Package 3 Deliverable: D3.3 “Template growth of organic and biological molecules onto nanopatterns”</p>										
Lead beneficiary number	7	Nature			R	Dissemination level				PU
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Person-months by partner for the Deliverable	CSIC									
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Criteria and Achieved Results	Criteria			Achieved result						
	Optimal conditions to generate patterns of different chemical compositions and sizes			The creation of highly efficient guiding patterns for the directed self-assembly of block copolymers by resistless nanolithography using atomic force microscopy (AFM) is demonstrated.						
	o-SPL patterns with sub 10 nm features			Single lines of 6.8 nm (FWHM) were fabricated by o-SPL on a polymer brush layer						
	Sub-20 nm pattern resolution (half pitch)			Ordered polymer patterns were fabricated by directed self-assembly of block copolymers with a 14 nm half-pitch . The initial guiding nanopattern was made by o-SPL.						
Reduction of the lithography steps			The number of lithographic steps of the present method has been reduced with respect to the state-of-the-art methods for creating BCP guiding patterns by chemical surface modification							



**Description
of the
Deliverable**

- **Introduction**

This deliverable will describe the optimal conditions to obtain arrays of patterns of different chemical compositions (silicon dioxide, polymeric structures, biological molecules), with the target to approach the sub-20 nm pattern resolution (half pitch)

The activity has been focused on the creation of guiding patterns for the directed self-assembly of block copolymers (polymeric structures). It is shown that chemical patterns consisting of arrays of lines defined on a brush layer by AFM allow the alignment of the blocks of lamella-forming polymers. The main advantage of this method relies on the capability to create high resolution (sub-10 nm line-width) guiding patterns and the reduction of the number of process steps compared to the state-of-the-art methods for creating guiding patterns by chemical surface modification. It is found that the guiding patterns induce the block alignment very efficiently, allowing the achievement of an unprecedented density multiplication factor of 7 for block copolymers of 14 nm half-pitch, which is attributed to the combined effect of topographical and chemical modification.

In addition, electrostatic interactions have been applied to direct the organization of proteins. This process involves the functionalization of a silicon surface to control at a given pH the electrostatic interaction with proteins.

- **Directed self-assembly of block copolymers**

Directed self-assembly (DSA) of block copolymers (BCP) is becoming a well-established method with a potential of gaining industrial relevance because it has a high throughput and simplifies processing when DSA is compared to other approaches. BCPs are macromolecules which are formed by two (or more) chemically distinct polymer chains (blocks) joined by inter-block covalent bonds. In order to minimize the contact area between them, the blocks tend to separate due to a balance between repulsive intermolecular and attractive forces. This segregation leads to a regular nanometer arrangement of different structural configurations (plates, cylinders, spheres or other more complex shapes) depending on the ratio of molecular weights of the blocks forming the copolymer. The special interest of the study of these materials lies on the fact that they have the intrinsic property of forming dense nanoscale structures whose length scales are not accessible using traditional lithographic techniques.

Highly oriented and ordered patterns can be achieved by conveniently creating guiding patterns on the surface, either by graphoepitaxy (R. Segalman, H. Yokoyama and E. Kramer, *Adv. Mater.* 13, (2001)). or chemical epitaxy (S. Kim, H. Solak, M. Stoykovich, N. Ferrier, J. de Pablo and P. F. Nealey, *Nature* 42 (2003)). Graphoepitaxy is based on creating topographic patterns (usually holes or trenches) and confine the BCP on them.



Graphoepitaxy is commonly used in combination with cylinder-forming BCPs in order to shrink the size of contact holes or to achieve contact-hole multiplication.

Chemical epitaxy consists on creating chemical patterns on a neutral surface, so the modified areas of the surface would present larger affinity to one of the blocks, determining the position and orientation of the molecules. Density multiplication is defined as the ratio between the period of the guiding pattern with respect to the period of the directed self-assembled pattern. As a consequence, high density multiplication lowers the requirements of the lithography method used for creating the guiding pattern.

Chemical guiding patterns are usually created on neutral polymer brush layers which present equal affinity for both blocks of the copolymer. The procedure for defining the chemical guiding pattern consists on creating a mask on top of the brush layer and using this mask for a selective etching or exposure process. The mask is created by means of a lithography process that requires high resolution accuracy, and in consequence, either DUV optical lithography or electron beam lithography are commonly used.

In the SNM project we have developed a method to fabricate guiding patterns for directing the self-assembly of BCPs by means of oxidation scanning probe lithography (o-SPL). The resulting process is much simpler than using DUV or EBL based processing, since the pattern is directly created on the neutral layer without the need of spinning a resist and further chemical development. Moreover, the unique capabilities of AFM in terms of resolution and position accuracy makes its use highly convenient for the investigation of the guiding behavior of novel polymer materials, in particular those that are of very small block size, in view of obtaining a half-pitch resolution around 10 nm or below.

We report on the application of o-SPL for the fabrication of guiding patterns for lamella forming BCPs, which induces the formation of aligned arrays of parallel lines, with density multiplication factors of up to 7. We show that such patterns can be created very efficiently, precisely and routinely using commercial equipment.

- **Directed self-assembly of block copolymers by using o-SPL**

The overall process for DSA using guiding patterns created by o-SPL on top of brush layers made of hydroxyl-terminated polystyrene (PS-OH) consists on three step process: (i) grafting a brush layer on top of a silicon surface, (ii) formation of the guiding patterns by o-SPL, (iii) block copolymer self-assembly. The whole process becomes much simpler than the usual methods to create chemical guiding patterns, since the sequence of resist, exposure, development and resist removal is substituted by the single process of o-SPL nanopatterning. Figure 1 illustrates, the scheme of the process for DSA of BCP by o-SPL. The AFM tip creates chemical patterns by local anodic oxidation on a PS-OH brush layer.

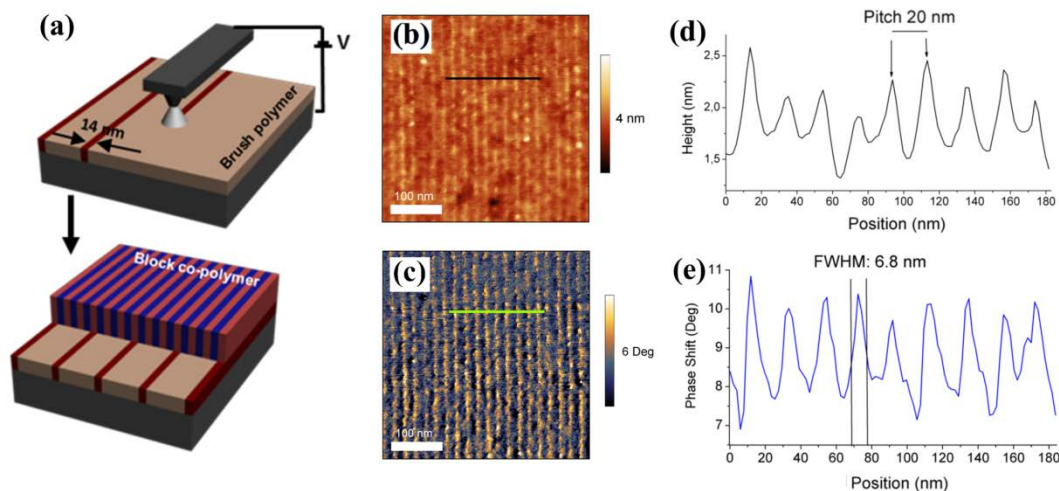


Figure 1. (a) Scheme of the process for DSA of BCP by o-SPL. The AFM tip creates chemical patterns by local anodic oxidation on a PS-OH brush layer. After creation of the guiding pattern, the block copolymer is deposited and annealed. The two phases of the lamella forming block copolymer (PS and PMMA) become oriented in the way dictated by the guiding patterns. (b) Topographic AFM image of an array of lines of 20 nm pitch ($\Delta z = 4$ nm). The o-SPL patterning conditions: bias voltage: 32.5 V, tip speed 20 $\mu\text{m/s}$. (c) AFM phase image acquired simultaneously with (b) ($\Delta z = 6^\circ$). (d) Profile extracted from (b). (e) Profile extracted from (c).

Grafting of the PS-OH brush layer

The brush layer is created from hydroxyl terminated polystyrene (PS-OH, M_n (molar mass) = $4.5 \text{ kg}\cdot\text{mol}^{-1}$, Polydispersity index (PDI) = 1.09) grafted on p-type silicon wafers with resistivity of 4-40 $\Omega\cdot\text{cm}$. The grafting process starts by coating the silicon surface with the polymer brush. Previously, the silicon surface has been cleaned and activated by O₂ plasma for 10 minutes, in order to allow the reaction between the hydroxyl groups from the PS-OH and the native oxide of the surface. A 40 nm thickness PS-OH brush layer is deposited and subsequently, the sample is annealed either in air or in a nitrogen environment. Annealing in air is performed using a pre-heated hot-plate at 190°C for 2 minutes while annealing in nitrogen is performed in an atmospheric furnace at 260 °C for 5 minutes with a continuous nitrogen gas flow. After annealing, the unreacted PS-OH is rinsed away with toluene by ultrasonication at 40 °C for 5 min leaving a brush layer of approximately 5 nm.

Block copolymer self-assembly

Poly(styrene-*b*-methacrylate) (PS-*b*-PMMA 50:50, $M_n = 35 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.12), has been used as a block copolymer. The PS-*b*-PMMA powder is dissolved in a 1.15 % (w/w) toluene solution. After o-SPL the block copolymer is spin-coated onto the brush layer at 2750 rpm, obtaining a 36 nm film thickness. Afterwards, the samples are annealed on a pre-heated hot-plate at 200 °C for 20 min, in order to self-assemble the



block copolymer. Finally, PMMA domains are removed by O₂ plasma.

- **o-SPL fabrication of guiding patterns**

Guiding patterns are created on the grafted PS-OH brush layers by o-SPL under non-contact mode operation. The AFM instrument has close-loop correction of X, Y and Z displacement, what facilitates to fabricate patterns of good dimensional quality. Standard non-coated silicon AFM probes have been used (OTESPA, Bruker). The control humidity system works by introducing dry or wet nitrogen air into the AFM chamber to set it in the range 20% - 60 % relative humidity (RH).

The sequence for creating a guiding pattern is as follow: (1) The AFM is operated in soft tapping mode, at oscillation amplitude around 15 nm. (2) The AFM tip is moved to the selected position to start the nanopattern. (3) The feedback-loop is disconnected and a positive bias voltage is applied to the sample through the AFM chuck. (4) The tip is moved along the line at the selected speed. (5) When the tip reaches the end of the line, the bias voltage is switched to zero and the feedback loop is connected. (6) The tip is moved to the new position to create the next line. In order to maintain tip-surface separation constant, the lines are fabricated following the direction where the lateral movement of the tip is parallel to the surface.

The whole process is highly simplified compared with usual methods, since the sequence of resist deposition, exposure, development, selective functionalization and resist removal is replaced by the single process of o-SPL nanopatterning. The AFM is operated in non-contact mode and it requires the formation of a water meniscus connecting tip and surface (R. Garcia, M. Calleja, F. Perez-Murano, Appl. Phys. Lett. 72, (1998)). Under the application of a positive voltage to the sample with respect to the tip, the water meniscus is ionized and OH⁻ ions are accelerated towards the surface, where the electrochemical reaction takes place. The resolution of the pattern is determined by the AFM tip radius, the size of the water meniscus (which depends on the air humidity), the applied voltage and the relative velocity of the tip with respect to the surface. Patterns of small line-width are achievable by using high tip-speed (above 10 μm/s) and low ambient humidity.

Figure 1b-c shows an example of a high resolution pattern, consisting on an array of lines with a 20 nm pitch and a linewidth resolution below 10 nm. The patterns created by o-SPL are highly effective for guiding of BCPs. As o-SPL can easily produce high resolution patterns, the oxidation conditions are set to obtain a linewidth similar to the half-length of the BCPs (14 nm), and a pattern pitch equal to an integer multiple of the BCP characteristic length.



Figure 2 shows an example of density multiplication obtained by a guiding pattern fabricated by o-SPL. In Fig. 2a we show a comparison between the guiding pattern (top, AFM image) and the resulting aligned BCP (bottom, SEM image). The guiding pattern is made of a set of lines with a varying pitch in multiples of the block copolymer length L_0 (28 nm), resulting in density multiplication factors from $3L_0$ to $5L_0$. The frontier between aligned and not aligned areas can be observed in the SEM image (Fig. 2b). It demonstrates the effectiveness of the o-SPL nanopattern for BCP alignment.

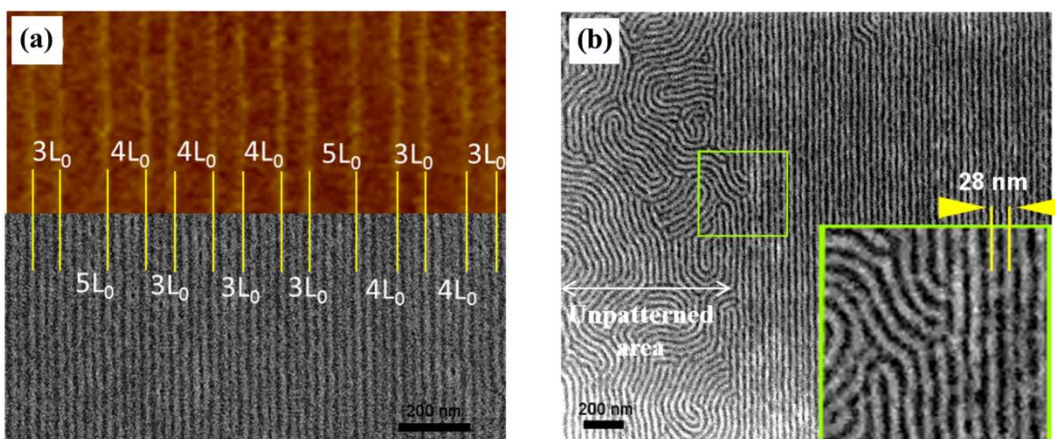


Figure 2. Density multiplication in DSA of PS-b-PMMA block copolymers induced by a guiding pattern defined by o-SPL ($V = 36$ V; tip speed = $3 \mu\text{m/s}$; RH=23 %) (a) Comparison between the guiding pattern (top, AFM image) and the aligned BCP pattern (bottom). SEM images are taken after removing the PMMA block by oxygen plasma etching. (b) SEM image showing the aligned block-copolymer on top of the guiding pattern and the non-aligned polymer on top of the un-patterned area.

Figure 3a shows an array of lines covering an area of $15 \times 15 \mu\text{m}^2$. A zoom in the array (Figure 3b) and the cross-section (Fig. 3c) reveals that the patterns consist of lines of 15 nm in width and roughly 1 nm of height. The modified regions protrude from the background. This indicates the oxidation of the underlying substrate (see discussion below). Figures 3d and 3e show the influence of the relative humidity (RH) on the line width. These patterns have been obtained under the same conditions (voltage=32.4 V (sample positive), tip speed = $5 \mu\text{m/s}$) except for the RH, which was raised from 20% to 40 %. A closer inspection of the patterns reveals that its roughness is basically dictated by the surface roughness of the brush layer, which is the limiting factor for the present pattern resolution.

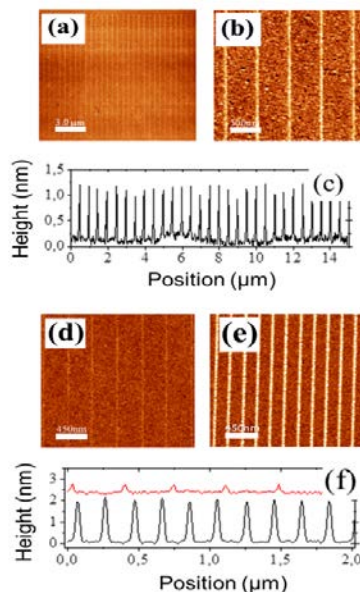


Figure 3. AFM images and profiles of guiding patterns created by o-SPL. (a) Array of lines covering an area of $15 \times 15 \mu\text{m}^2$. The o-SPL patterning parameters were, 45 V (voltage, sample positive), $1 \mu\text{m/s}$ (tip speed), 35 % (RH). (b) A zoom in the array and the profile extracted from Fig. 3a (c) reveal that the pattern consists of lines of 15 nm width and roughly 1 nm of height.. (d) Array of lines performed at relatively low humidity of 20 %. (e) At RH of 40 %. In panels d and e, the patterns are created under the same conditions (bias voltage: 32.4 V, tip speed $5 \mu\text{m/s}$). (f) Profile extracted from images (d, red) and (e, black) to highlight the effect of relative humidity

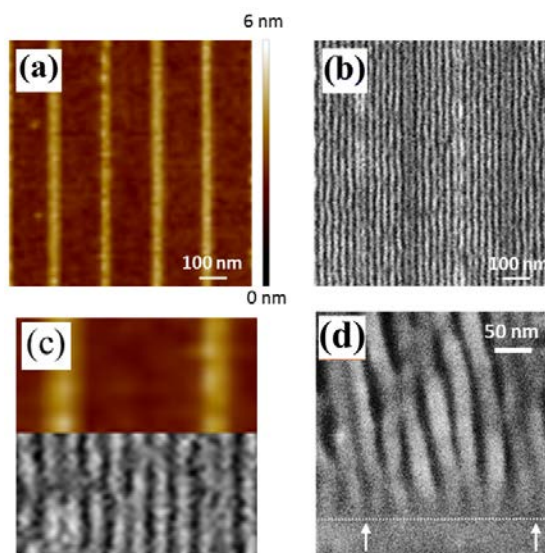


Figure 4. (a) AFM image of a guiding pattern defined by o-SPL ($V=34.2 \text{ V}$; Tip speed = $2 \mu\text{m/s}$; RH = 38%). (b) SEM image of the BCP aligned pattern. (c) Comparison between the guiding pattern (top, AFM image) and the aligned block-copolymer pattern. (d) Tilted SEM image of a cross-section performed on the pattern of image (b) by focused ion beam, showing the interface between the PS lines of the copolymer and the substrate (dashed line). The arrows indicate the position of the guiding pattern lines. SEM images are taken after eliminating the PMMA block.



Some attempts have been made to obtain larger density multiplication factors. We have observed that patterns made of very thin lines, like the one shown in Figure 1c, are not effective to obtain large density multiplication factors. Increasing the local oxides results in a larger guiding effectiveness, even taking into account that the linewidth of the pattern increases. Figure 4a shows an example of a pattern formed by an array of lines with a separation of 168 nm (6 x 28 nm). The lines that form the pattern are thicker and wider than the ones shown in Figure 1d.

The SEM image of the BCP pattern in Figure 4b shows good alignment after DSA. Remarkably, as the line-width of the guiding line is larger than half of the period of the BCP, a density multiplication factor of 1.5 is also occurring on top of the chemically modified areas, resulting in a total multiplication factor of 7. Figure 4c shows a comparative zoom-in of the data shown in panels 4a and 4b. It is observed that the guiding pattern sets the position of the PMMA-block at the center of the guiding pattern, while two polystyrene domains are positioned also on top of the guiding lines. Figure 4d shows a tilted SEM image of a cross-section performed by focused ion beam on the pattern from Figure 4b. The position of the substrate/copolymer interface is depicted by the dashed line, and the two arrows indicate the position of the center of the guiding lines. As the thickness of the oxide is lower than 2 nm, the guiding lines cannot be appreciated in the SEM image.

The guiding patterns formed by o-SPL on the brush layer can have a diverse chemical/physical nature: (i) chemical surface modification of the top groups of the brush layer polymer molecules, similar to what it has been reported on tip-induced electro-oxidation for constructive nanolithography (R. Maoz et al. "Constructive Nanolithography: Inert Monolayers as Patternable Templates for In-Situ Nanofabrication of Metal-Semiconductor-Organic Surface Structures. A Generic Approach" *Adv. Mater.* 2000, 12, 725–731); (ii) chemical modification of the brush and oxidation of the underlying silicon; and (iii) oxidation of the underlying silicon together with degradation of the brush polymer layer. The actual co-existence of these three situations is demonstrated by performing on-purpose experiments. Situations (ii) and (iii) require that the local oxidation process proceeds through the brush layer. Actually, it has been previously reported that the silicon surface can be oxidized through thin polymer layers (K. Kodera et al., *SPIE Adv. Lith.*, 9049, (2014)). The oxidation of the underlying substrate is induced by the transport of OH⁻ ions through the polymer layer, enhanced by the large electrical field originated from the voltage applied between tip and surface. Discrimination between situations (ii) and (iii) is achieved by performing patterns at different voltages, followed by a process consisting in immersing the sample in a 5% HF solution for 10 seconds to remove the silicon oxide (see Figure 5).

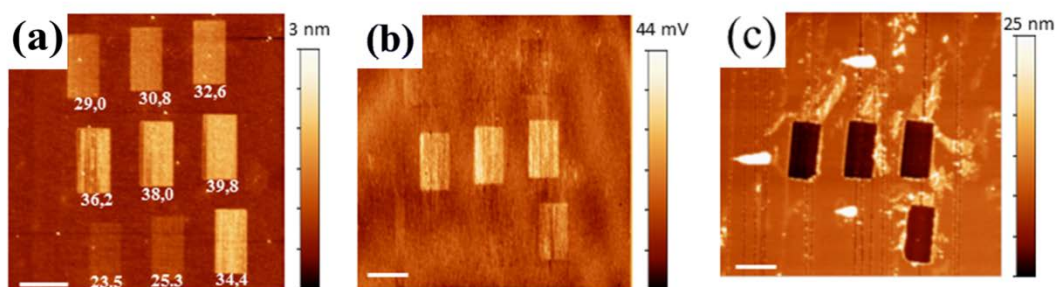


Figure 5. (a) Contact mode AFM images of chemical patterns performed on a PS-OH brush layer by o-SPL. The oxidation voltages are depicted in the figure. Units are Volts. (b) Friction image obtained simultaneously to the topographic image (a). (c) Tapping mode AFM image obtained after immersing the sample in an HF solution for 10 seconds. Scale bar is 1.8 μm for the three AFM images.

The un-degraded PS-OH brush layer is resistant to an HF etch, thus, it protects the silicon oxide to be etched. We have found that, at high voltages, the polymer brush layer degrades. These experiments indicate that the simple chemical modification of the brush layer surface alone is not sufficient to guide the alignment, while patterns showing at least 0.5 nm of topographic height contrast efficiently induce the guiding of the BCP.

A closer inspection of the aligned BCP patterns (Figure 4) indicates a larger affinity of the modified areas to the PS block. A possibility for the nature of the chemical modification in the case of PS-OH brush layers is that the o-SPL patterning process causes a partial degradation of the PS molecules, increasing its affinity to the PS-block.

The experiments indicate that the simple chemical modification of the brush layer surface alone is not sufficient to guide the alignment, while patterns showing at least 0.5 nm of topographic height contrast efficiently induce the guiding of the BCP. The influence of topography-induced alignment on chemical patterns has been recently studied (K. Kodera et al., SPIE Adv. Lith., 9049, (2014)). This is very relevant for the understanding of the DSA process of future, small size BCP. When employing low weight (small length) polymers in order to obtain DSA patterns of higher resolution, the future requirements for guiding patterns are going to be more stringent. In this context, the unique capabilities of o-SPL to create patterns of resolution below 10 nm that, in addition, combine topographic and chemical contrast will provide unprecedented possibilities for expanding the present limitations of DSA to smaller feature sizes. Moreover, this method can be extended to other polymer material combinations, facilitating the investigation of their self-assembly behavior.

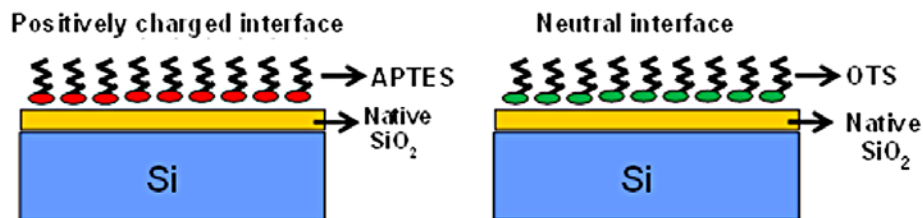


Figure 6. Scheme of silicon functionalization. (a) A self-assembled monolayer APTES provides a positive charge surface for neutral or acid pH values. (b) A self-assembled OTS monolayer provides a electrically neutral interface.

- **Template growth by controlling electrostatic interactions**

This approach is based on controlling the electrostatic interactions between biomolecules and/or nanoparticles and the nanopatterns. Biological molecules are charged in solution, in addition, their charged could be modified by tuning the pH of the solution below or above the isoelectric point of the molecule. On the other hand, the electrostatic interactions of a silicon substrate could be modified by functionalizing the surface with suitable molecules. For example, amino-functionalized silicon surfaces will be protonated at a pH below 7, this is, they will show a net positive surface. On the other hand, silicon surfaces functionalized with a self-assembled monolayer of octadecyltrichlorosilane (OTS) will show charge neutrality over a wide range of pH values. In the SNM project we have studied the ability to pattern proteins by controlling the electrostatic interactions. Figure 6 shows an scheme of the functionalization steps applied in the SNM project. Silicon surfaces were functionalized with either a self-assembled monolayer of octadecyltrichlorosilane (OTS) or self-assembled monolayers of aminopropyltriethoxysilane (APTES).

We illustrate the potential of the method by patterning ferritin molecules. Ferritin is a cage-shaped protein that accommodates an iron oxyhydroxide nanoparticle. The protein is formed by a polypeptidic hollow shell of about 12 nm in diameter that encapsulates the iron-based core (about 7 nm in diameter). Figure 7a shows a Si surface after being functionalized with APTES. The AFM image shows the presence of ferritin after a 20 μ l drop of a buffer (pH=6.5) containing ferritin (250 μ g/ml) was deposited on the surface (Fig. 7b). A similar deposition was performed on a Si surface functionalized with OTS (Fig. 7c), however, in this case no ferritin molecules were observed (Fig. 7d). This comparison indicates that the electrostatic interaction between the negatively charged ferritin and the positively charged APTES favours the adsorption of the ferritin to the surface. In the above experiments, after the deposition protocol the samples were rinsed in distilled water to remove loosely adsorbed proteins and/or other elements from the buffer.

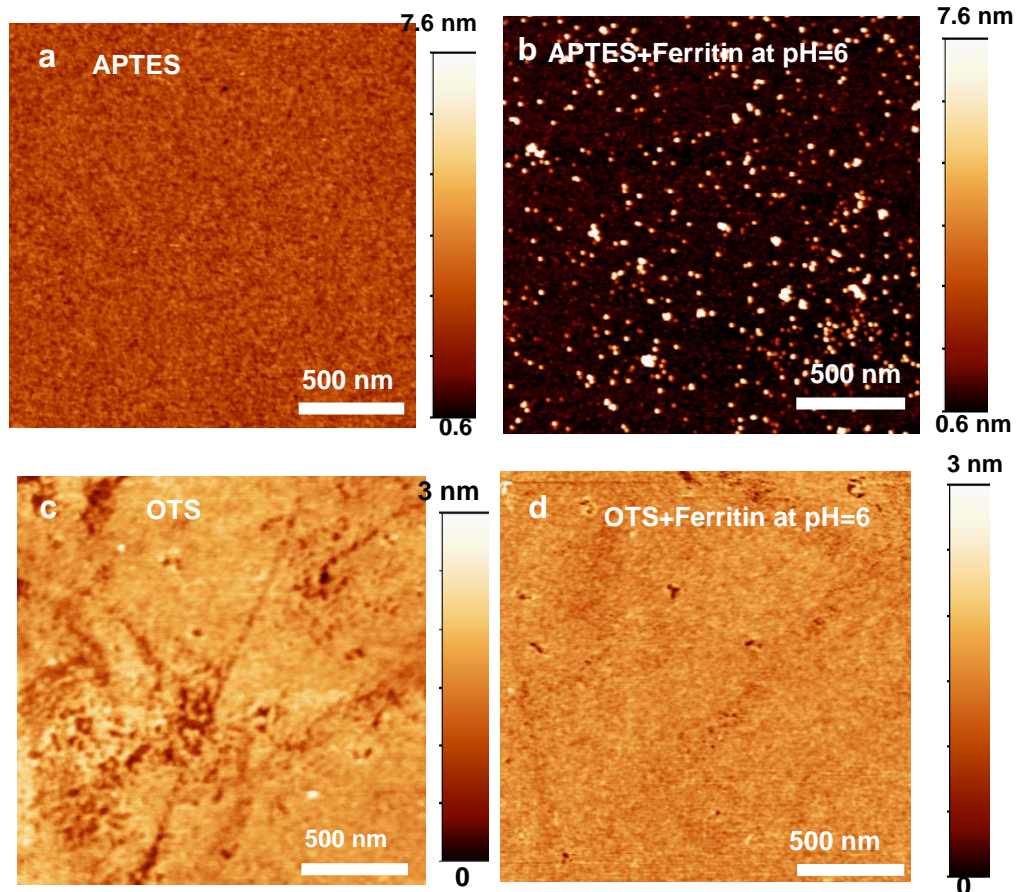


Figure 7. (a) Silicon surface functionalized with APTES. (b) Ferritin adsorption on a Si+APTES surface at pH=6. (c) Silicon surface functionalized with OTS. (d) No ferritin molecules are observed after following a similar deposition and rinsing protocol as in (b).

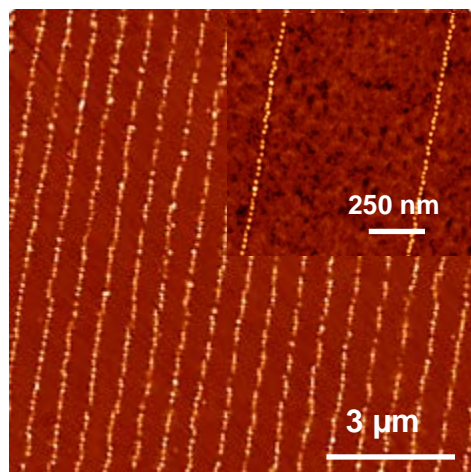


Figure 8. Patterning of proteins (ferritin) achieved by lithography controlled dewetting. First a PMDS stamp was inked with ferritin then the inked stamp was gently pressed against a APTES functionalized Si surface at pH=6.5. The AFM images show the parallel lines of ferritin molecules. Each line has the width of a ferritin (12 nm). The inset shows a high resolution image of the pattern showing the single ferritin lines.



	<p>Figure 8 shows the process to form parallel lines of ferritin molecules. A soft-stamp (see Milestone MS6 for fabrication details) inked with the proteins is gently pressed against an APTES functionalized Si surface. The formation of nanoscale liquid meniscus between the ridges of the patterns on the stamp and the surface together with the electrostatic interaction between the negatively charged ferritin and the positively charged APTS surface leads to the selective deposition of the ferritin. The AFM image (inset) shows the presence of single proteins along the lines.</p>
Explanation of Differences between Estimation and Realisation	<p>The deliverable has been achieved by demonstrating the organization of polymers on top of o-SPL nanopatterns. The patterns of the block copolymers have a half-pitch of 14 nm.</p>
Metrology comments	<p>Block copolymers nano-phases have characteristic sizes that mainly depend on their molecular weight and the annealing process. These samples could be used for metrology studies at the nanoscale due to the well-defined XY periodicities</p>