Propuesta de Trabajo Fin de Grado en Física

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Título del Trabajo:	Characterization and engineering of the stick-slip behavior during the deposition of self-assembled microgel monolayers on silicon wafers.

Tipología del Trabajo: *(Segun punto 3 de las Directrices del TFG aprobadas por Comisión Docente el 10/12/14)*	*(Marcar con X)*	*1. Revisión bibliográfica*		*4. Elaboración de nuevas prácticas de laboratorio*	
		2. Estudio de casos teórico-prácticos		*5. Elaboración de un proyecto*	
		3. Trabajos experimentales	*x*	*6. Trabajo relacionado con prácticas externas*	

Breve descripción del trabajo:

Nanoscale surface patterning constitutes a powerful way to modify materials and impart new properties or functions that go beyond the ones of the unstructured bulk material, including wetting, adhesion, mechanical or optical properties. **Spatial positioning** of the features, together with their **geometry**, holds the key for future technological applications. Our main objective is to develop the colloidal lithography technique [1]. Colloidal lithography consists in the controlled deposition of nano or microparticles onto a solid substrate, which act either as a direct mask or are used to produce metal masks complementary to the particle arrangement. The advantages are manifold: the large availability of highly monodisperse particles allows precise control over the feature size and the process is inherently parallel and scalable to large samples. The main limitation lies in the accurate control of the spacing between the features and in the architecture of the patterns. Self-assembly processes at the base of colloidal lithography in fact basically only lead to hexagonal close packing of monodisperse spheres. Partial control on separation can be achieved by self-assembly and deposition of charged colloids at fluid-fluid interfaces [2] but this approach carries limitations in terms of the size range and separation of the colloids due to attractive capillary forces during drying overcoming adhesion to the substrate.

These obstacles can be completely overcome by using **microgel** particles to fabricate soft colloidal lithography masks. Microgels are soft, compressible nanoparticles (10↔1000 nm) made of crosslinked, water-soluble polymers. During synthesis, they develop a core structure with a less dense shell. This is enhanced when adsorbed at interfaces, where the shell stretches**¡Error! Marcador no definido.** [3]. Their softness and steric repulsion give tremendous potential for the tuneable assembly of monolayers at interfaces and deposition on silicon substrates, controlling their microstructure. After deposition, the height of the dried microgels is of few nm, giving little material contrast to use them as lithography masks. Nevertheless, they can be swollen with photoresist, enabling their use as soft colloidal masks for etching [1].

Moreover, novel non-hexagonal patterns have been obtained by combining different sizes of microgels with sequential deposition of microgel monolayers [4] and even with sequential depositions of the same microgel, thanks to their softness and deformability [5] as can be seen in Figure 1.

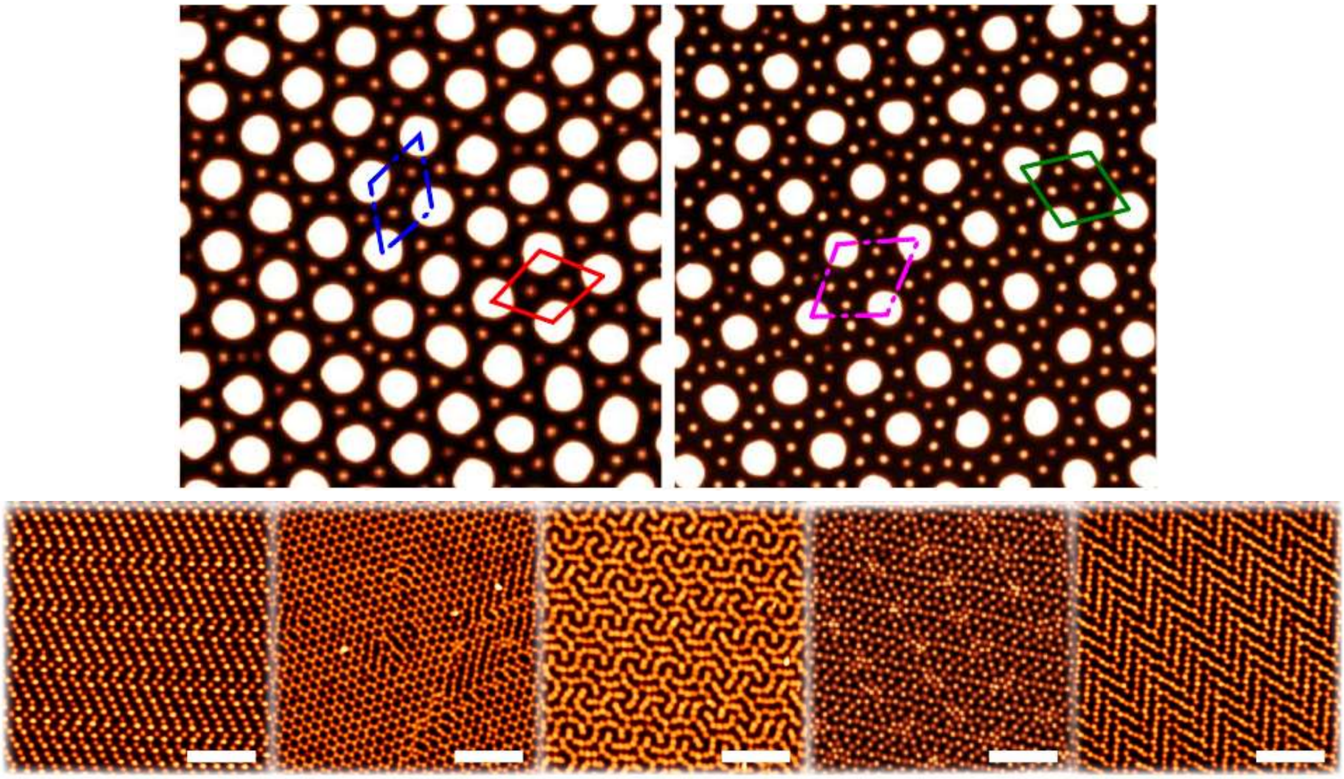


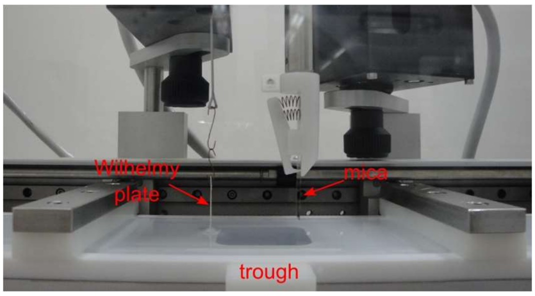
Figure 1. Top row: AFM images (10x10 μm^2) of silicon substrates showing different 2D binary colloidal arrays of deposited microgels with varying interparticle distances between the big and small microgels [4]. Bottom row: AFM image (scale bar, 5 μm) of rectangular lattices, honeycombs, interlocking-S structures, hexagonal superlattices, and herringbone superlattices obtained by the sequential deposition of the same microgel twice [5].

The deposition of microgel monolayers from water/air and water/oil interfaces onto a silicon substrate involves a receding liquid meniscus over the substrate. Therefore, the stick-slip behaviour of the receding meniscus [6] which produces local variations in the microgel density needs to be taken into account for the development of this soft colloidal lithography technique.

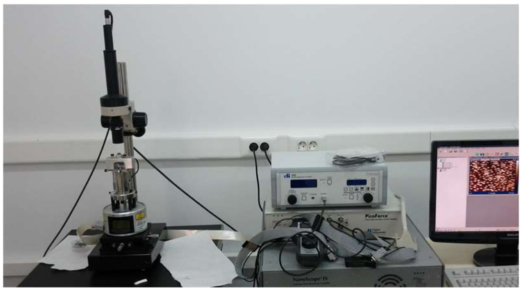
Objetivos planteados:
The main goal of this project is to characterize the stick-slip behaviour of a receding meniscus during the deposition of a microgel monolayer on a silicon substrate, and the engineering of such behaviour by surface treatments of the substrate, involving plasma and UV-ozone hydrophilization, perfluorosilane functionalization and mechanical functionalization with direct laser patterning.

Metodología:
The methodology will involve the diamond cutting and cleaning of the silicon substrates from silicon wafers, and the preparation of the microgel spreading solutions with 4:1 isopropanol, used as a spreading agent [1]. A sequential deposition in a Langmuir trough (see Figure 2a) to obtain a honeycomb pattern [5] will be used as a benchmark structure to characterize the stick slip behaviour, as slight changes in the microgel density will be easily distinguished and characterized on the substrate in a regular and an atomic force microscope (AFM, Figure 2b).

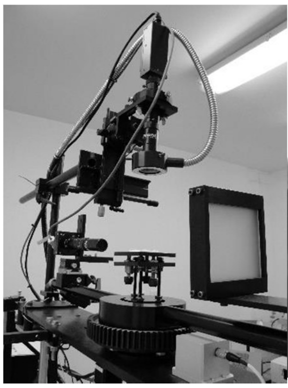
Once the benchmarck experiment reproducing the honeycombs is achieved, two model experiments with a silicon wafer and a receding microgel-laden meniscus will be performed by i) controlled withdrawing of water from a microgel-laden water droplet, with a microsyringe pump, and ii) by controlled tilting of the substrate to induce the receding of the meniscus over the substrate (Figure 3c-d). In both cases the contact angle will be obtained in real time with a camera and a homemade software, and the stick-slip behaviour will be captured and analyzed.
Furthermore, the wettability and therefore the stick-slip behaviour of the silicon substrate surface will be engineered and tuned by argon and ozygen plasma, UV-Ozone treatment, perfluorosilanization, and topographical marks induced by dynamic laser patterning. With these treatments we aim to control the stick-slip behaviour to both understand better this process and to produce better soft colloidal lithography patterns.



(a)



(b)



(c)

(d)

Figure 2. Equipment present and at the Laboratory of Surface and Interface Physics, in UGR. **(a)** Langmuir trough setup for the assembly of microgels at interfaces and deposition on solid substrates. **(b)** Atomic Force Microscope capable of measuring in water. **(c)** Set-up for tilted angle drop experiments, and image of tilted droplet.

Bibliografía:

[1] Rey et al. Fully Tunable Silicon Nanowire Arrays Fabricated by Soft Nanoparticle Templating. Nano Lett. **2016**, 16(1):157-163.
[2] Isa et al. Particle Lithography from Colloidal Self-Assembly at Liquid-Liquid Interfaces. ACS Nano **2010**, 4(10):5665-5670.
[3] Camerin et al. Microgels Adsorbed at Liquid-Liquid Interfaces: A Joint Numerical/Experimental Study. ACS Nano **2019**, 13(4):4548-4559.
[4] Fernandez-Rodriguez et al. Tunable 2D binary colloidal alloys for soft nanotemplating. Nanoscale **2018**, 10(47):22189-22195.
[5] Grillo et al. Self-templating assembly of soft microparticles into complex tessellations. Nature **2020**, 582(7811):219-224.

[6] Noguera et al., Transition from Stripe-like Patterns to a Particulate Film Using Driven Evaporating Menisci. Langmuir **2014**, 30(25), 7609–7614

A rellenar sólo en el caso que el alumno sea quien realice la propuesta de TFG	
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Granada, 19 de Junio de 2020