Electronic Supplementary Material (ESI) for Nanoscale.


# Supplementary information

## Direct etching at the nanoscale through nanoparticle-directed capillary condensation.

M. Garín,[1,2]* R. Khoury,[3] I. Martín,[1] E.V. Johnson[3]

*[1] Grup de recerca en Micro i Nanotecnologies, Departament d'Enginyeria Electrònica, Universitat Politècnica de Catalunya, c/ Jordi Girona Pascual 1-3, Barcelona 08034, Spain*
*[2] GR-MECAMAT, Department of Engineering, Universitat de Vic – Universitat Central de Catalunya, c/ de la Laura 13, 08500 Vic, Spain*
*[3] Laboratoire de Physique des Interfaces et des Couches Minces (LPICM), CNRS. Ecole Polytechnique, Institut Polytechnique de Paris, 91128 Palaiseau, France.*

** Corresponding author: moises.garin@uvic.cat*

## 1 Inverted pyramid formation.

### *Process details*

Inverted pyramids were formed through anisotropic etching of c-Si in tetramethilammonium hydroxide (TMAH) water solution (25%) at 85 ºC using the patterned $SiO_2$ layer as a mask. This step was performed in a glass beaker covered with a Teflon lid and using one liter of TMAH solution. The temperature of the TMAH solution was automatically controlled using a hot plate and a teflon-protected temperature prove introduced in the solution. Right before the etching, the samples were dipped in HF 5% solution for 10 seconds, in order to remove the native oxide from the opened areas, rinsed for 10 seconds in deionized (DI) water (18.2 MΩ·cm), and introduced in the hot TMAH solution for 5 minutes. After the etch, the samples were thoroughly rinsed in DI water and introduced again in HF 5% solution to remove the $SiO_2$ mask layer. Finally, the samples were rinsed in DI water and blow-dry with $N_2$.

### *Discussion*

TMAH is a an organic alkaline solution with excellent anisotropic silicon etching characteristics. Its non-toxicity and full CMOS-compatibility makes TMAH preferable over other classical alkaline solutions, such as KOH and NaOH, with similar silicon anisotropic etching features. The etching rate of Si in TMAH solution heavily depends on the crystalline direction, being the etching rate of the <111> direction the slowest [1]. For 25% TMAH at 85ºC, the etching rate at the <100> direction is, roughly, 0.36 µm/min [2], while the etch ratio <111>/<100> is 0.04. [1,3] Also, the etching rate of thermal $SiO_2$ is extremely low, around 1.25 Å/min [2], what makes $SiO_2$ an excellent mask for TMAH etching.

Inverted pyramids are created through anisotropic wet etching of <100> oriented crystalline silicon through the small openings defined by a mask. The characteristic pyramidal shape is a result of the slow etching rate in the <111> direction, the confined silicon area exposed to the solution, and the crystal orientation of the wafer. Notice, therefore, that inverted pyramids do not form when using <110> or <111> oriented silicon wafers [4,5]. During the process, silicon is quickly etched in the exposed <100> direction leaving only the slow etched {111} planes, creating the sharp pyramidal shape and forming the characteristic angle of 54.7 º between the {111} walls and the {100} surface (See Fig. S1a,b). Once the pyramid is formed the etching progresses very slowly (almost stops), since the slow etched {111} planes are the only surfaces in contact with TMAH. This makes the process very robust and low sensitive to the total etching time, although a small undercut is introduced (See Fig. S1a). As the pyramidal shape is formed by {111} planes, the shape is always square (or rectangular) irrespective of the shape of the mask. In other words, the process always form the smaller pyramid (either square or rectangular) that contains the opening plus the small undercut (See Fig. S1c—e). Any mask island within the opened region, as it happens in our case, will also by etched away (Fig. S1e).

Another important aspect of the inverted pyramid formation is that the sides of the pyramids are aligned with the crystalline orientation of the wafer (*i.e.* they align with the wafer flats); however, the alignment of the self assembled monolayer is, in general, random. As a result, the pyramids show a random rotation angle, $\theta$, with respect to the monolayer (see Fig. S2a), which can also change between different monolayer grains. Relatively large pyramids can overlap for certain rotation angles leading to full etching of the surface and, therefore, destroying the sample in that region. This limits the largest pyramid size, in order to ensure that the process works for any random monolayer orientation, to a size $d=a/\sqrt{2}$ , where *a* is the diameter of the particles (see Fig. S2b).

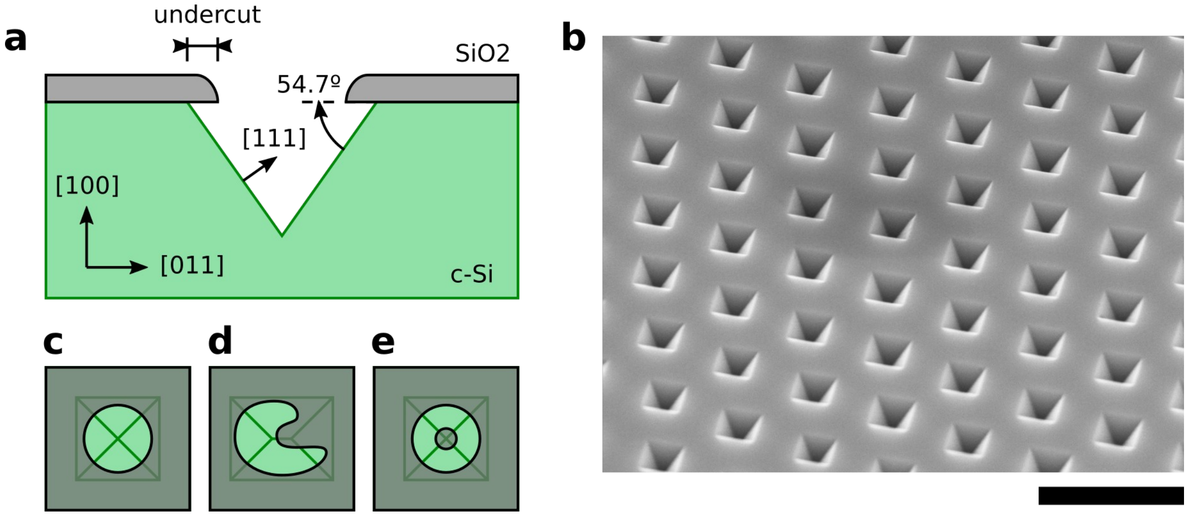


**Figure S1.** (a) Schematic of final inverted pyramid geometry obtained after TMAH etching. (b) SEM image, bird's eye view, of inverted the pyramids obtained with the process using a monolayer with 600nm PS spheres. The scale-bar represents 1 µm. (c—e) Schematic of the inverted pyramidal structure formed for different opening shapes in the $SiO_2$ mask layer.

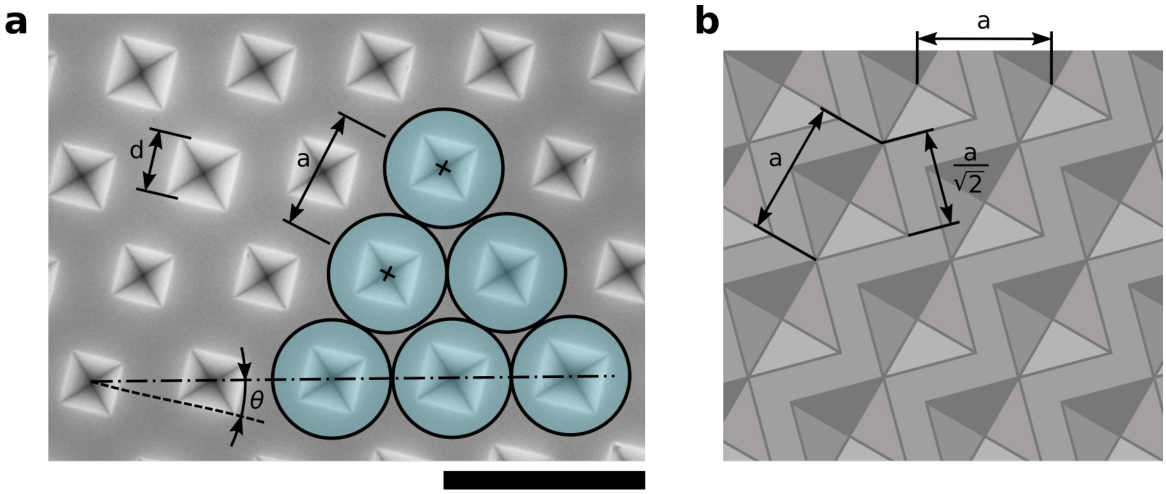


**Figure S2.** (a) SEM image, top view, of a pattern of inverted pyramids highlighting the misalignment between the silicon crystalline directions and the monolayer orientation. The blue circles represent the original particle positions, with a diameter *a*=600 nm. The scalebar represents 1 µm. (b) Schematic of the worst case scenario for the critical pyramid size $d = a/\sqrt{2}$ .

## 2 References


1. K. Satoa, M. Shikidaa, T. Yamashiroa, K. Asaumib, Y. Iriyeb, M. Yamamoto “Anisotropic etching rates of single-crystal silicon for TMAH watersolution as a function of crystallographic orientation”, Sens. Actuator A Phys., 1999, **73**, 131–137.
2. P.-H. Chena, H.-Y. Penga, C.-M. Hsieha, M. K. Chyub “The characteristic behavior of TMAH water solution for anisotropicetching on both Silicon substrate and $SiO_2$ layer”, Sens. Actuator A Phys 2001, **93**, 132–137.
3. J. S. You, D. Kim, J. Y. Huh, H. J. Park, J. J. Pak, C. S. Kang, “Experiments on anisotropic etching of Si inTMAH”, Sol. Energy Mater. Sol. Cells, 2001, **66**, 37–44.
4. A. Hölke and H. T. Henderson “Ultra-deep anisotropic etching of (110) silicon” J. Micromech. Microeng., 1999, **9,** 51–57.
5. R. E.n Oosterbroek, J. W. Berenschot, H. V. Jansen, A. J. Nijdam, G. Pandraud, A.t van den Berg, and M. C. Elwenspoek “Etching Methodologies in <111>-Oriented Silicon Wafers”, J. Microelectromech. Syst., 2000, **9** 390–398.