Local Functionalization of Surfaces by EBL and CVD and AFM characterization

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Local chemical modification of surfaces has attracted the interest of many research groups in the last years because it allows a selective surface functionalization for a wide range of applications. Hydrophilic and hydrophobic surfaces, as well as areas reactive to a specific entity, can be patterned in the same sample. Locally modified surfaces can be applied to define a fairly large range of structures and devices, covering a wide field of applications, like biomedical, biological or microelectronic devices (controlled cell growth, DNA biosensors, molecular devices, etc).

In this work we present a versatile, simple, robust and fast method of local functionalization by lithography and deposition of thin film of silanes. The whole process consists on Electron Beam Lithography (EBL), Chemical Vapor Deposition (CVD) and lift-off, as shown in the drawings of figure 1. First, the sample, coated with a 100 nm film of PMMA, is patterned by EBL, and the resist is developed. Then, the sample is introduced into a small recipient and kept under nitrogen atmosphere. A small liquid droplet of silanes is dropped inside the recipient. After few minutes (the required time depends on the silanes nature), the silanes evaporate, saturating the atmosphere, and a layer of silane molecules is deposited in the patterned features of the sample. The last step is a conventional lift-off process: the sample is rinsed for 5 minutes in acetone at 50ºC, and 5 more minutes in ultrasounds, to remove the resist. Figure 2 shows examples of nanometer scale patterns defined by 3 different types of silanes: an amine-silane, an acrilate-silane, and fluorinated-silane. The first type is interesting because its high reactivity to DNA, the second one because of its high hydrophilicity, and the third one because of its high hidrophobicity.

AFM characterization has been performed. When silanes form a self assembled monolayer, topographical images have to be complemented with lateral force/friction images, as shown in figure 3(a), as it is the case for a fluorinated silane (F13-TCS). Topographical images show that the mean height of the lines is 1nm, and friction images reveal that in the functionalized areas, friction decreases significantly, as it corresponds to the highly hydrophobic nature of this fluorinated silanes. This hydrophobic behavior is demonstrated also in force versus distance curves made with contact mode AFM tips (figure 3(b)). In these curves, the difference in the adhesion force is due mainly to capillarity forces. The adhesion force is minimized in the hydrophobic areas, as can be observed in figure 3(b).

Acknowledgment

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References:

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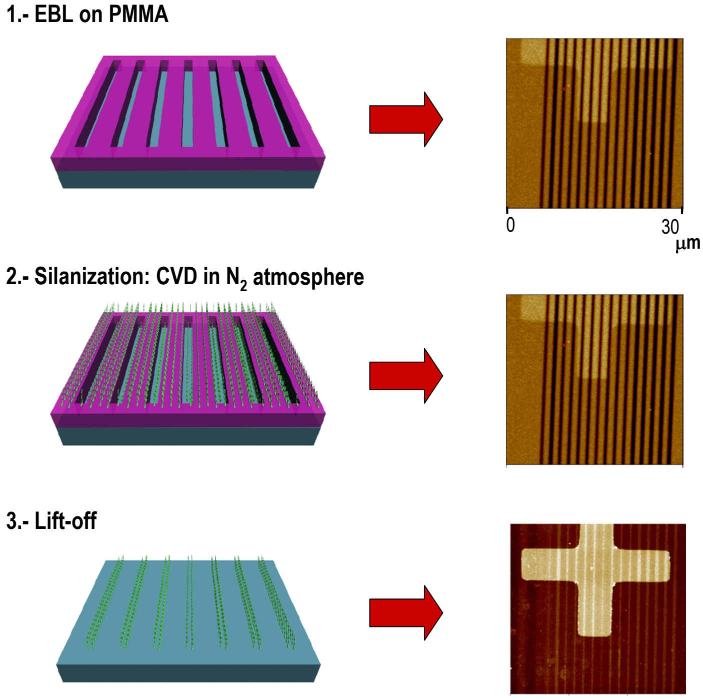

Figure 1. *Scheme of the selective functionalization process (drawings in the left) and AFM images of the resulting patterns for an amino-silane deposition (right). First step: EBL patterning of the PMMA and exposed resist development. Second step: Deposition of silanes [(3-Aminopropyl)TriMethoxySilane] in gas phase, in a controlled nitrogen atmosphere, at room temperature, for 24 hours. Last step: lift-off to remove the remaining resist, with a hot acetone (50ºC) bath during 5 minutes, and ultrasounds, for 5 minutes. Resulting silane lines have a pitch of 1,5 µm and a height of 7nm (not a monolayer, due to the long CVD time).*

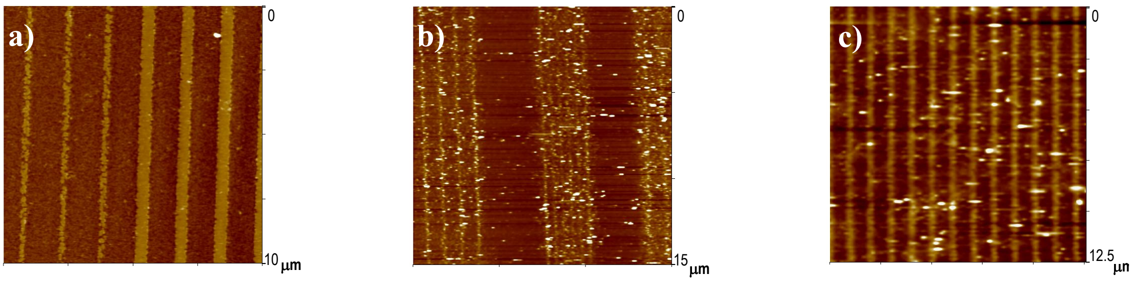

Figure 2. *Examples of patterned surfaces with different types of silanes:* ***(a)*** *Patterns of (3-Aminopropyl)TriMethoxySilane, deposited as described in Figure 1. The average width is 220 nm for the lines in the left, and 450 nm for the lines in the right.* ***(b)*** *Arrays of lines with different pitch of 3-(Trimethoxysilyl)PropylMethacrylate: 1µm, on the left, 500 nm in the middle, and 1.2 µm on the right. Average line with is 200 nm and measured height is less than 1 nm, corresponding to a monolayer, achieved for a CVD time of 24 hours.* ***(c)*** *Lines of 1µm pitch and 200 nm wide of TridecaFluoruro-(1,1,2,2)-tetrahydrooctyl-triChlorosilane (F_{13}-TCS). Deposition time is 5 minutes, resulting in a monolayer of 0.7 nm in height.*

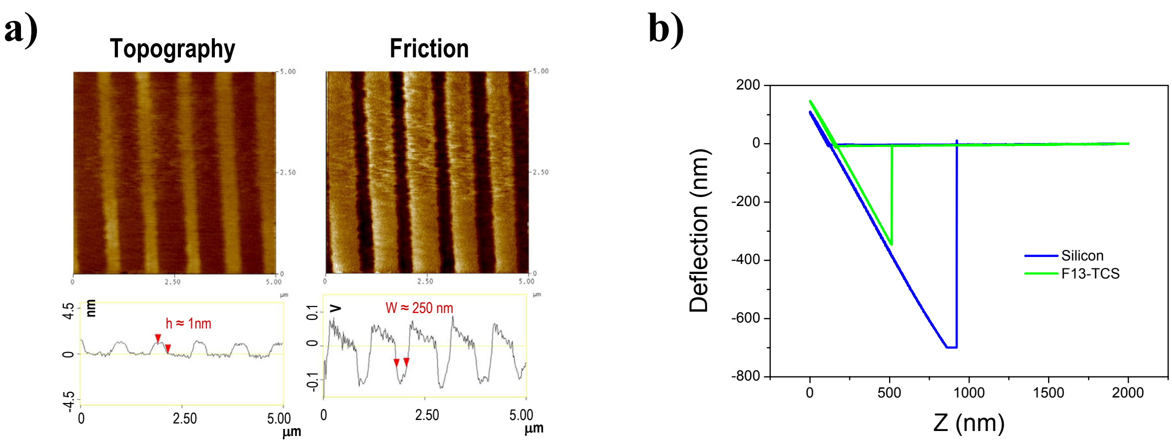

Figure 3. ***(a)****, AFM images of topography in contact mode (left) and lateral friction (right) of a lines pattern (1µm in pitch) of fluorinated silane, deposited during 5 minutes. Lines height is less than 1nm. A high contrast can be observed in the friction image: silicon surface shows a higher value than the silane-covered one.* ***(b)*** *AFM Curves of Force/Deflection vs Distance in silicon and in a functionalized area. The difference in the traces is an evidence of the high hydrophobic nature of the fluorinated silanes.*