

# Electrochemically Patterning Sol-Gel Structures on Conducting and Insulating Surfaces

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## Supporting Information

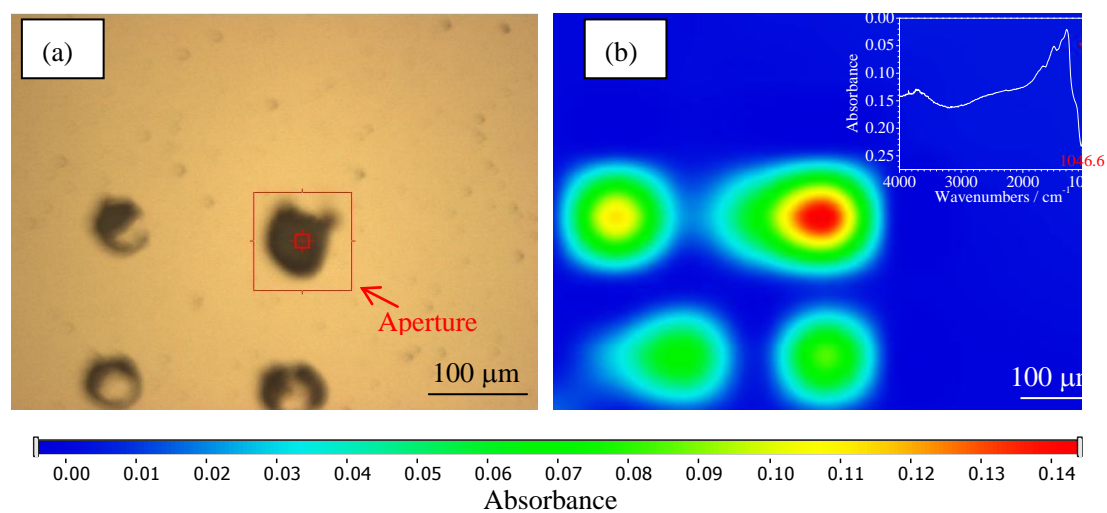
### Experimental details:

For the feedback mode patterning, a commercial SECM (CHI 920C, CH Instruments, USA) at room temperature ( $\sim 20$  °C) was employed where a Pt microelectrode (10 or 25  $\mu\text{m}$  diameter biased vs. Ag wire) was used as a working electrode and another Pt wire served as the counter electrode. First, the tip-surface distance was calibrated from an approach curve using 2 mM ferrocene and 0.1 M  $\text{Bu}_4\text{NPF}_6$  in acetonitrile. The Pt tip was held at ca. 7 and 25  $\mu\text{m}$  above insulating and conductive substrates, respectively. After positioning the tip the ferrocene solution was replaced by the silane precursor. The latter consisted of 1 mL tetramethoxysilane (TMOS) 10 mL ethanol, 10 mL 0.1 M  $\text{NaNO}_3$  (adjusted to pH 3 by HCl). This solution was hydrolysed by stirring at room temperature ( $\sim 20$  °C) for at least 2 hours before use. After the hydrolysed silane solution was poured into the SECM electrochemical cell, desired negative potential was applied to the Pt tip. Spots or lines of silane microstructures were deposited by holding the SECM tip for 120 s or linearly moving it across the surface at a speed of 1  $\mu\text{m}/\text{s}$ . Finally, the substrates were dismantled from the cell, washed with DI water, blow-dried and cured at 70 °C overnight.

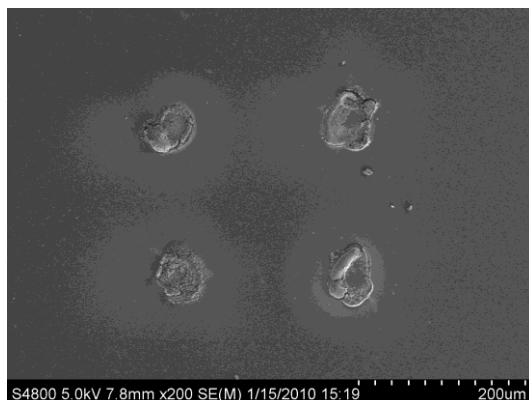
The direct mode patterning was carried out on a home-made SECM. The deposition solution which consisted of 0.125 mL TMOS, 5 mL ethanol, 5 mL buffer phthalate pH 3.5, was hydrolysed for one hour at room temperature. The approach to an ITO surface was carried out using the feedback mode by recording the reduction of oxygen with a 25  $\mu\text{m}$  diameter Pt microelectrode ( $E_{\text{tip}} = -0.8$  V vs. Ag/AgBr). Once the negative feedback current (due to reduction of oxygen) decreased by ca. 70%, the tip was stopped and the direct mode was applied in the same solution ( $E_{\text{surface}} = -0.8$  V vs. Ag/AgBr) for different times. Approaching the surface was performed in the deposition solution, however in the feedback mode ( $-0.8$  V vs. Ag/AgBr was applied to the tip to cause the reduction of oxygen). It is worth mentioning that after approaching we moved the microelectrode laterally to another area before deposition.

The structure of the silane patterns was inspected by SEM (Hitachi S4800, JEOL JSM-6400). AFM and TUNA measurements were carried out by a Nanoscope Dimension 3100 scanning probe microscope equipped with a Nanoscope IVa controller (Veeco). A magnetic etch silicon probe (MESP) was used in the AFM

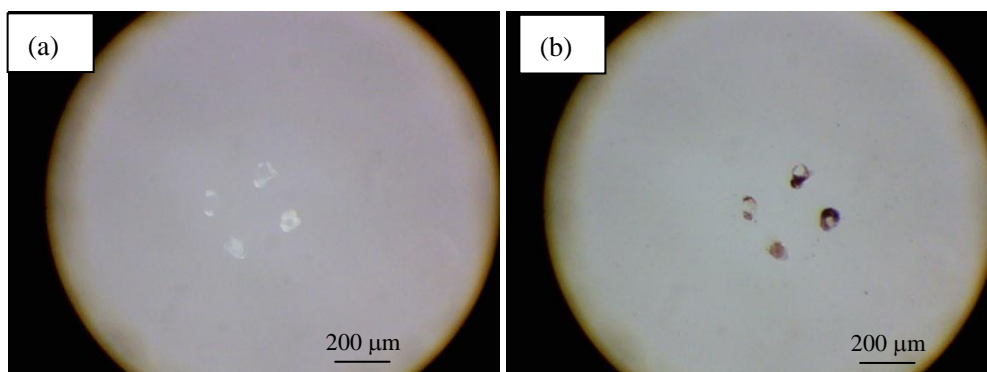
measurements while a tapping etch silicon probe (TESP) was used for the TUNA measurements. The FTIR-IR measurement and IR mapping was performed with a Nicolet 6700 spectrometer. The spectra were collected with bare silicon wafer as the background at  $8\text{ cm}^{-1}$  resolution and average of 64 scans. The aperture used for IR mapping was  $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ .



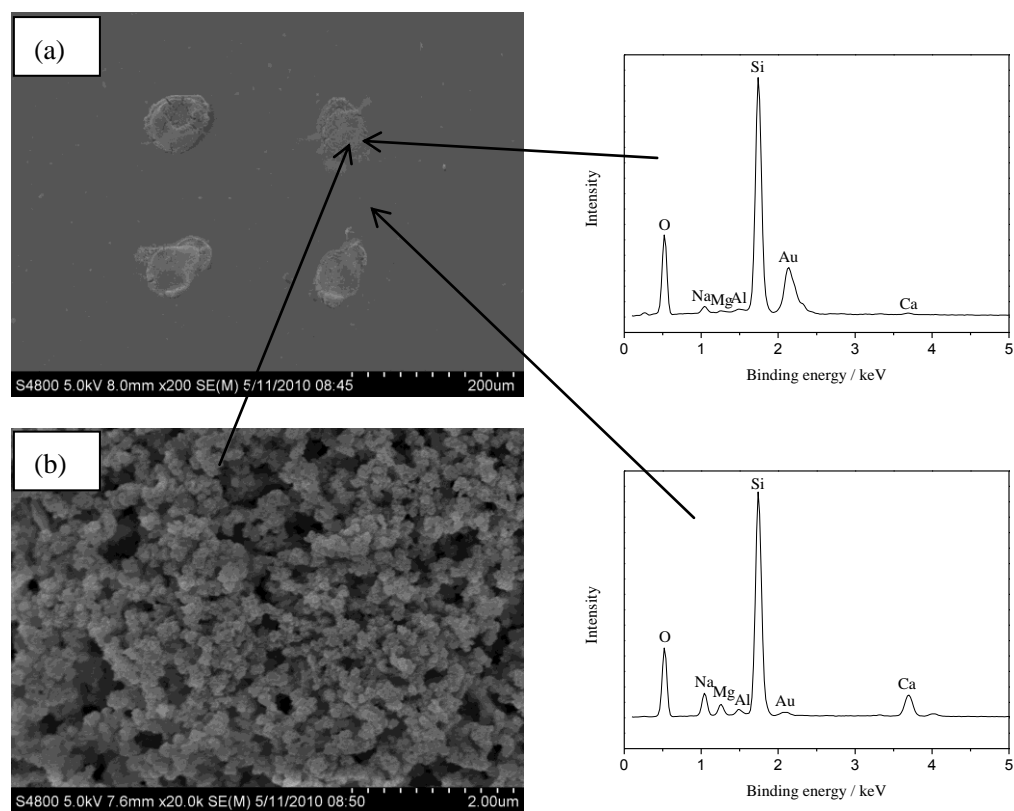
**Figure S1.** Stereomicroscopic image (A) and FTIR mapping at 1046.6 cm<sup>-1</sup> (B) of the four deposits on silicon wafer (-1.5 V/Ag, 200 μm × 200 μm, deposition time 120 s, tip-substrate distance ~7 μm). Inset of (B) is the FTIR spectrum collected where the aperture is focused on a spot (shown in (A)).



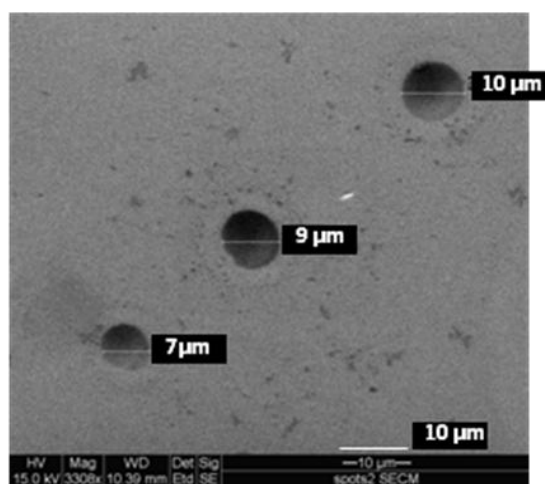
**Figure S2.** SEM image of the locally deposited TMOS films on ITO (4 spots,  $200\ \mu\text{m} \times 200\ \mu\text{m}$ ,  $25\ \mu\text{m}$  Pt tip, tip potential:  $-1.5\ \text{V/Ag}$ , deposition time: 120 s, tip-substrate distance:  $\sim 25\ \mu\text{m}$ ).



**Figure S3.** Stereomicroscopic images of the locally electrodeposited silane structures on glass before (a) and after (b) loading gold nanoparticles. The change of the color is due to nanoparticles attachment as was confirmed by EDX (see Figure S4).



**Figure S4.** SEM images and EDX spectra of the locally electrodeposited silane structures on glass after loading gold nanoparticles: 200× (a), 20000× (b).



**Figure S5.** SEM image of the locally electrodeposited TMOS structures on ITO surface upon applying different negative potentials for 20 s (from left to right: -0.8 V, -1 V, -1.2 V, vs. Ag/AgBr)