Micro and Nano Electrodes Prepared by Patterning SiO_x Thin Films on Au Planar Surfaces

by Marcos Jose Leite Santos

SiO_x thin films have been used for applications in electronic devices and platforms for reflection-based optical spectroscopy. The presence of silanol groups at the surface of SiO_x films makes possible their functionalization with organic compounds such as dyes, polymers, and biomolecules. Due to this property, SiO_x thin films have also been used for applications in biological and chemical sensing, as an immobilizing surface in surface plasmon resonance (SPR).[1,2] Meanwhile, micro and nanoscale patterned chips have been developed for application in solar cells, optoelectronics, and various sensors for biodiagnostic detections.[3-8]

In this work, we present an alternative technique for the preparation of SiO_x thin films on a planar gold substrate by using a chemical precipitation method. This approach has been previously used to encapsulate gold nanoparticles.[9,10] The advantage of this procedure over other schemes for SiO_x deposition is that it does not require gas handling or low pressure (vacuum conditions). We also present micro and nanoscale patterning of the SiO_x films by photolithography and focused ion beam (FIB) milling. The patterned films expose the gold surface only in the patterned area, yielding arrays of micro- and nano-electrodes. This approach is the foundation for further applications in micro-, nano-electrochemisty, and biosensing applications.

Arrays of micro-sized holes on the SiO_x film were fabricated by applying photolithography and HF etching, as shown in the fabrication (Fig. 1). After coating the planar gold surface (100 nm-thick gold film deposited on a glass slide) with a 40 nm layer of SiO_x,[10,11] a layer of the photoresist SU-8 was deposited on the top of the SiO_x layer. Standard photolithography was used to pattern the SU-8 film with 40, 60, and 100 µm holes. The SiO_x film exposed through the photoresist layer was etched by HF. In the last step, the photoresist was removed by acetone revealing the patterned microholes in the SiO_x layer. Due to the isotropic nature of the HF etching, the microholes in the SiO_x are actually larger than the holes in the photoresist layer (see Fig.1).

Several deposition times were investigated, aiming to obtain homogenous and nonporous films with efficient blocking effect. The film thicknesses were dependent on the deposition time (varied from 1 to 120 h). After 120 h the layer thickness remains constant (the film obtained after 10 days of deposition presents about the same thickness as the film obtained after 120 h (50 nm thick). AFM images of the films were obtained after 48, 72, and 120 h of deposition (not shown). After 48 h the SiO_x film is rough and the gold surface is not completely covered; after 72 h the SiO_x layer is denser and it seems to cover most of the gold surface; and finally after 120 h of deposition a 50 nm thick, homogenous, and smooth SiO_x surface was obtained.

Cyclic voltammetry (CV) blocking experiments using 1 mM $K_3[Fe(CN)_6]$ in 0.1 M $NaClO_4$ was applied to evaluate the blocking efficiency of the SiO_x films and the behavior of the planar gold micro-electrodes (Fig. 2). Figure 2a shows the voltammograms of $K_3[Fe(CN)_6]$ at the SiO_x films deposited on a planar gold substrate obtained after varying the SiO_x deposition times. The CVs agree with the results obtained by AFM showing a more efficient blocking effect as the deposition time and the thickness of the film increase, with maximum blocking effect observed after 120 h of deposition.

As shown in Fig. 2b, at the bare gold electrode, the redox of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ pair displays an oxidation peak at 0.34 V and a reduction peak at 0.18 V. After the formation of a 50 nm thick SiO_x film (b) the current decreases dramatically due to the limited diffusion of the electroactive species toward the gold surface. It is interesting to point out that the curve (b) in Fig. 2b does not present waves of sigmoidal form as earlier reported in the literature.[8,11] Curve (b) in Fig. 2b seems to imply that the redox process has been almost completely blocked by the SiO_x layer. The small capacitance effect in this curve has been attributed to the stray capacitance formed between the gold and the electrolytic solution. The voltammogram (c) in Fig. 2b shows the redox process of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ pair, and a sigmoidal wave form characteristic for the diffusion of electroactive species toward microelectrodes is observed. The integration of the CV curves was carried out in order to determine the size distribution of the holes by means of the electrical charge involved in the redox process. The integration of the curve (a) in Fig. 2b corresponds to the total charge involved in the redox process taking place at the bare gold electrode. The curve (c), however, corresponds to the total charge involved in the redox process that occurs under limited diffusion taking place inside the micro-holes. The ratio between the areas calculated for the curves (a) (6.08×10^{-5} C) and (c) (9.95×10^{-6} C) divided by the number of the holes in the SiO_x layer (100 holes – determined by the mask used in the photolithographic step) was employed to evaluate the average diameter of the holes, and it was found as 400 µm. The difference in hole diameter between the holes in the photoresist layer (100 µm) and the values calculated by the CVs (400 µm), is in part related to the isotropy of the HF etching process. Due to lateral etching, the size of the holes in the SiO_x layer are actually larger than in the photoresist layer. The result obtained from integration of the voltammetric curve was found to be consistent with the size distribution measurements obtained by AFM.

After an efficient blocking of the gold surface by the SiO_x was confirmed (Fig. 2), we also prepared a nano-scale patterned film. The arrays of holes were then fabricated by FIB milling all the way through both the 50-nm thick SiO_x film and the 100-nm thick gold film (see fabrication scheme in Fig. 3a). A scanning electron microscope image of an array of nanoholes prepared in this work is shown in Fig. 3b. Figure 3c

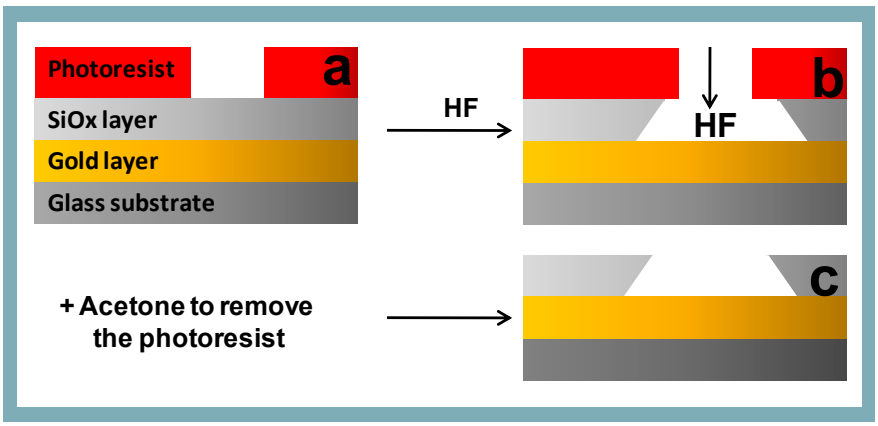

Fig. 1. *Fabrication scheme of the microholes by photolithography and HF etching.*

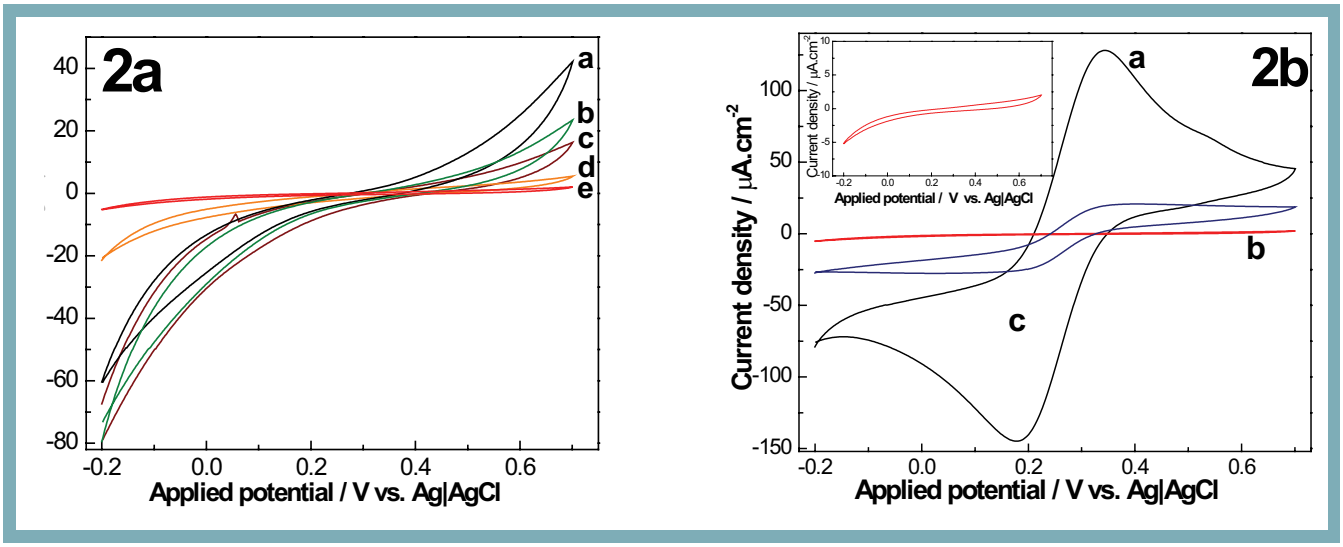

Fig. 2. *Cyclic voltammograms of 1 mM of $K_3[Fe(CN)_6]$ 0.1 M $NaClO_4$ scan rate 20 mV/s. Fig. 2a shows SiO_x film on planar gold obtained after 24 (a), 48 (b), 72 (c), 96 (d), and 120 (e) h of SiO_x deposition. Fig. 2b shows bare gold electrode (a), SiO_x film obtained after 120 h of deposition (b), and patterned micro-electrode (c). Inset shows the curve (b).*

is an expanded view of the full 14 µm x 14 µm array of 170 nm holes with 500 nm of periodicity.

The next step of this project will be performing nanoelectrochemistry measurements in the nanopatterned sample toward species detection at the single molecule level. Further, nanohole arrays have been shown to be useful for SPR-based biosensing. The chip will be used for application in biosensing where this structure would be of value in exploring in-hole based SPR detection.

This work demonstrates that a planar gold electrode can be coated by homogenous 50 nm thick SiO_x films obtained by chemical precipitation method. The SiO_x films are stable and display efficient electrochemical blocking capabilities. We also presented a straightforward method to obtain arrays of microscale electrodes by using photolithography and HF etching techniques. The micro-holes were in the range between *ca.* 40 and 100 µm. Nanoscale electrodes were also prepared and they seem promising for application in nanoelectrochemistry and biosensing.

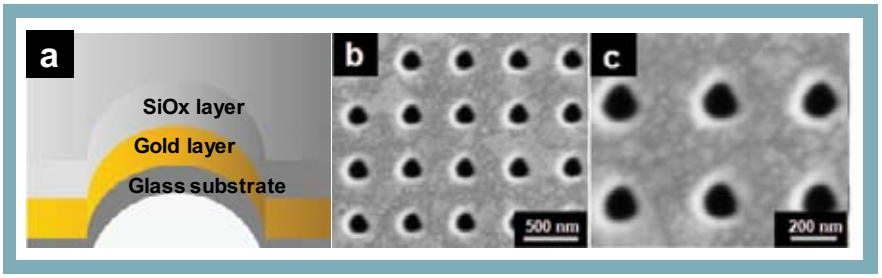

Fig. 3. *Scheme of the array of nanoelectrodes (a). SEM images of the array of sub-wavelength holes (b and c).*

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