SUPPORTING INFORMATION FOR "Fabrication of porous silicon-based optical sensors using metal-assisted chemical etching"

R. F. Balderas-Valadez,[a] V. Agarwal[a] and C. Pacholski[b†*]

[a] CIICAp, UAEM, Av. Universidad 1001 Col. Chamilpa, Cuernavaca, Morelos 62210, México.

[b] Department of New Materials and Biosystems, Max Planck Institute for Intelligent Systems, Heisenbergstr. 3, 70569 Stuttgart, Germany. Pacholski@is.mpg.de

[†] Present address: University of Potsdam, Institute of Chemistry, Am Mühlenberg 3, 14476 Potsdam, Germany. cpachols@uni-potsdam.de

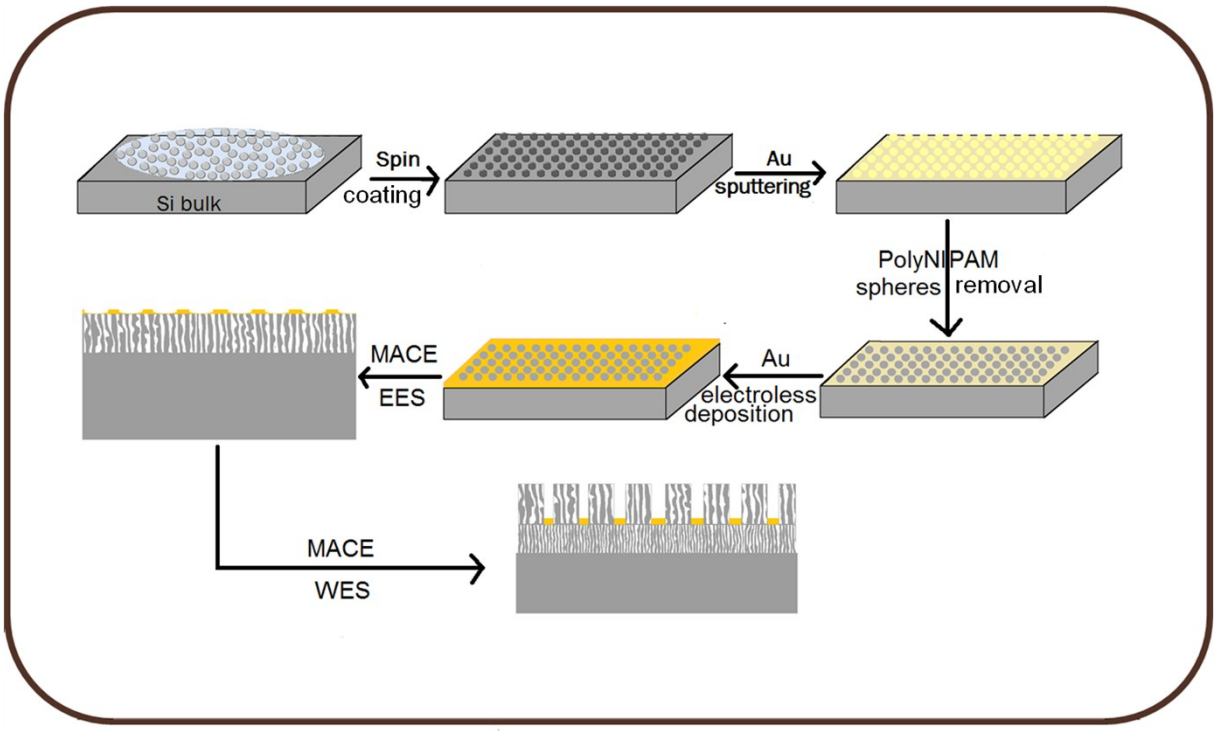
Materials & Methods.

Silicon wafers (p-type, boron doped, <100 > orientation, resistivity 0.001-0.005 Ω cm) were purchased from Cemat Silicon S.A. (Warszawa, Poland). Hydrofluoric acid (HF), ethanol, protein A and H_2O_2, were supplied by (Merck KGaA, Darmstadt, Germany). N-isopropylacrylamide (NIPAM), hydroxylamine hydrochloride, $HAuCl_4$ $3H_2O$ and 3-aminopropyltriethoxysilane (APTES) were purchased from Sigma-Aldrich Chemie GmbH (Munich, Germany). HCl, H_2SO_4 and HNO_3 were received from Carl Roth (Karlsruhe, Germany). Water was deionized to a resistance of at least 18.2 MΩ (Ultra pure water system (TKA, Niederelbert, Germany)) and then filtered through a 0.2-μm filter. Some solutions were prepared: PBS buffer pH 7.4, 0.1 M acetic acid, 20% sucrose in PBS buffer and 0.25 mg/mL protein A in PBS buffer.

Scanning electron microscopy (SEM) images were obtained with a Zeiss Ultra 55 'Gemini' scanning electron microscope (Carl Zeiss, Inc., Oberkochen, Germany) using an acceleration voltage of 5 keV and an in-lens detector. Reflectance spectra were recorded at normal incidence using an Ocean Optics charge-coupled device (CCD) spectrometer (Ocean Optics GmbH, Ostfildern, Germany) fitted with a microscope objective lens connected to a bifurcated fiber optic cable. A tungsten halogen light source was focused on the sample surface with a spot size of approximately 2 mm^2. Reflectance data were collected with a CCD detector in the wavelength range of 500 to 1000 nm. Experimental reflectance spectra were analyzed by applying a fast Fourier transform (FFT) using the software IGOR Pro (http://www.wavemetrics.com). Details of the analysis can be found in [1].

Sensing experiments were carried out in a custom-made flow cell (Plexiglass). Solutions were pumped through the flow cell with a flow rate of 5 μL/min. For recording reflectance spectra the light beam was focused onto the sensor surface through the Plexiglass cover. The biomolecules protein A and sucrose were used as received and dissolved in PBS buffer. To support the removal of protein A from the porous silicon sensor, a solution of 0.1 M acetic acid was flown over the sensor surface. Details can be found in literature.[2]

A Bal-Tec MED 020 sputter coater (Bal-Tec AG, Balzers, Liechtenstein) was used for depositing a thin gold film onto the polyNIPAM decorated Si substrate (instead of covering the sample with gold nanoparticles as described in [3]). The gold film was grown to a thickness of approximately 100 nm by electroless deposition. For this purpose the samples were placed face down on a aqueous solution containing $HAuCl_4$ * $3H_2O$ (5%, w:w) and 0.65 mM hydroxylamine hydrochloride. Electroless deposition of gold was carried out for 25 min on an orbital stirrer. Afterwards the samples were rinsed with dest. water and blown dry with N_2.



Scheme 1. Fabrication steps of double layered porous silicon structures consisting of porous pillars with large pores on top of a porous silicon layer with smaller pores.

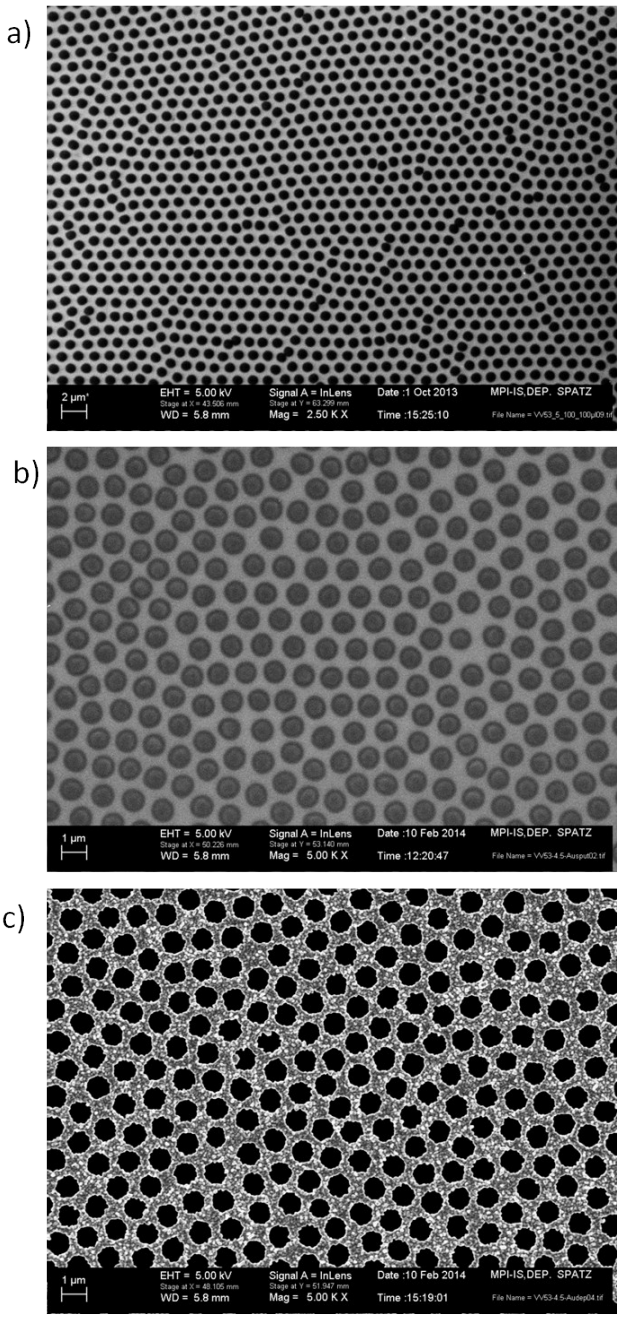


Figure S1. SEM images (inlens detector) of the fabrication steps for the deposition of a nanostructed gold film onto the Si substrate. **a)** Hexagonal array of polyNIPAM microspheres on Si substrate; **b)** gold film deposited onto microsphere mask by sputtering; **c)** gold film with periodic array of holes after removal of the polyNPAM microspheres using ultrasonication.

Additional functionalization of the silicon substrate with Au nanoparticles

After etching the gold decorated Si substrate consecutively in EES and WES the top of the porous silicon pillars was found to be blocked by an unidentified material (no more than 10 nm (Figure S2)). This 'blocking' layer was observed in all the samples fabricated by the double etching method and its composition could not be determined by EDX investigations without any doubt.

In order to obtain porous silicon pillars with open pores, gold nanoparticles were deposited in the holes of the periodic hole array composed of gold, i.e. on the exposed Si which is not covered by the perforated gold film. For this purpose gold patterned silicon substrates were functionalized with APTES (vapor deposition) a second time. Thereby the adhesion of gold nanoparticles (Au-NPs) over

the circular spaces generated after the removal of polyNIPAM microspheres was ensured. After baking the samples at 110 °C for 1 h, the patterned silicon substrates were incubated in a Au-NPs solution (diameter 15 nm ± 2nm, prepared according to Turkevich et al. [4]) for 30 min at 40 °C. Then the samples were rinsed with deionized water and dried in a stream of N_2.

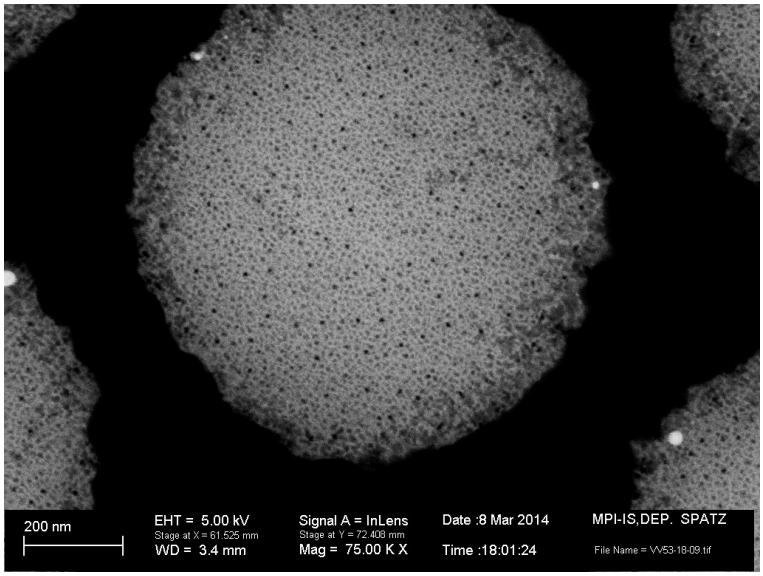


Figure S2. Top view SEM image of porous silicon pillars covered with an unidentified material after etching the gold decorated Si substrate with EES and WES.

In figure S3 a representative SEM image of the samples after Au-NP deposition is displayed. The exposed Si surface is now sufficiently covered with Au-NPs.

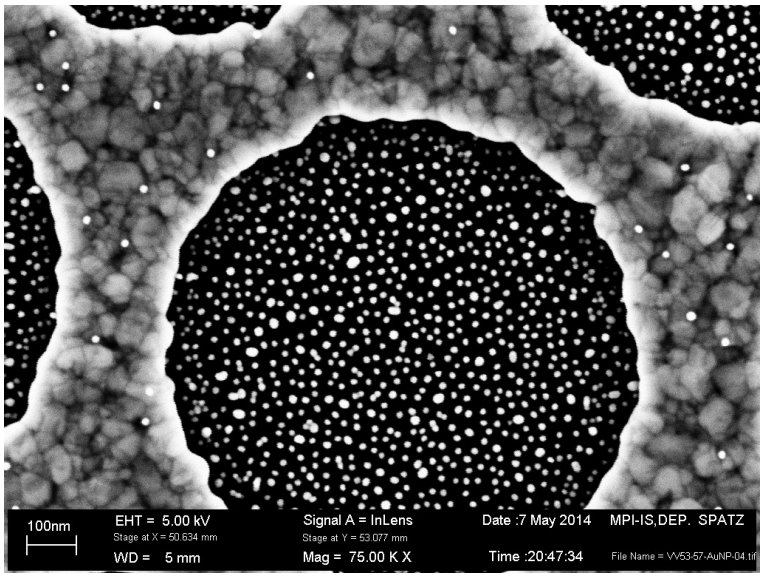


Figure S3. Top view SEM image of the exposed silicon surface on the gold patterned silicon substrate after functionalization with Au-NPs. Au-NPs (bright spots) were preferentially deposited on the uncovered silicon surface.

MAE of gold patterned silicon substrates with additional Au-NPs (shown in figure S3) with EES and consecutively WWS lead to the formation of porous silicon sensors composed of a porous silicon layer with small pores underneath porous silicon pillars with larger and now unblocked pores (figure S4 a)). Due to the presence of the Au-NPs deposited on the uncovered silicon surface, the etching rate was accelerated and relatively rough pillar structures were obtained in comparison to the porous silicon structures etched without additional Au-NPs (Figure S4 b)).

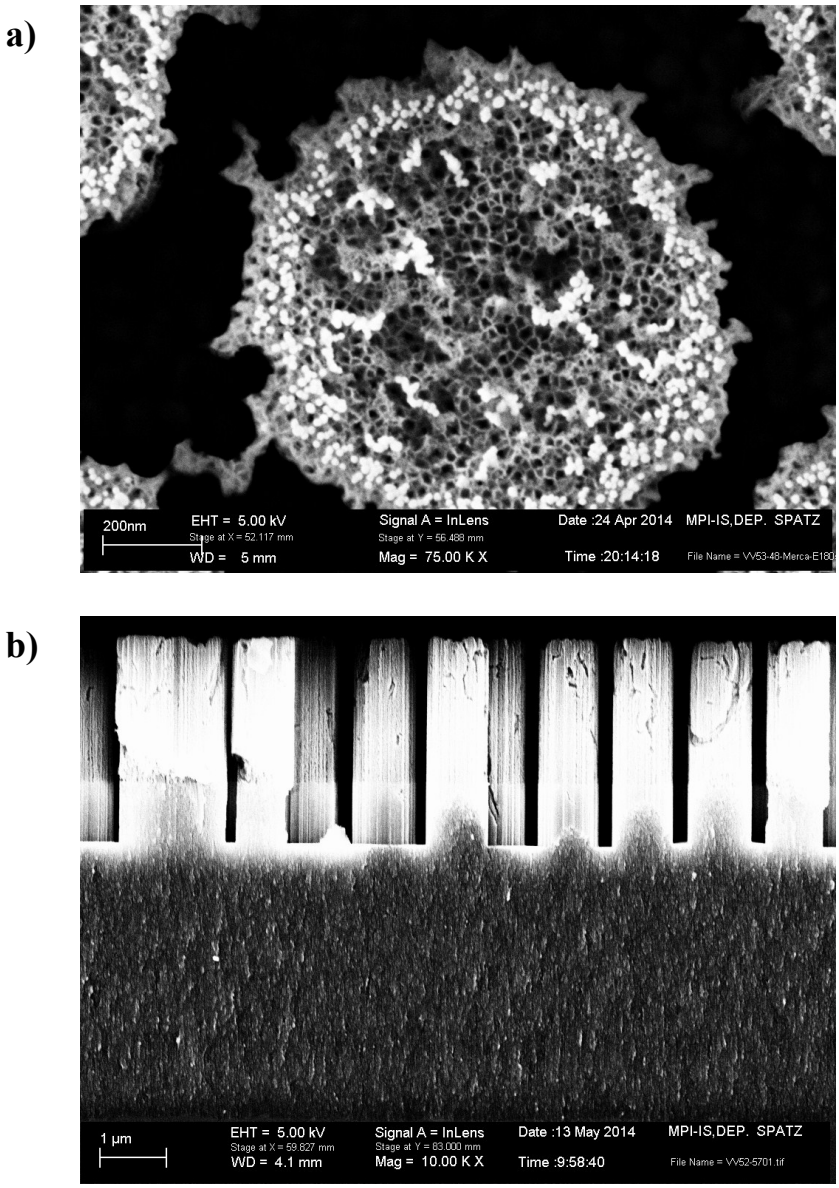


Figure S4. SEM images of porous silicon sensors fabricated by etching a gold patterned silicon substrate with additionally deposited gold nanoparticles in EES (40 s) etching and WES (60 s). a) Top view SEM image of the porous silicon sensor with unblocked pores. (b) Cross sectional SEM image porous silicon sensor.

References

1. M. J. Sailor, in *Porous Silicon in Practice*, Wiley-VCH Verlag GmbH & Co. KGaA, 2011, pp. 133-187.
2. C. Pacholski, C. Yu, G. M. Miskelly, D. Godin and M. J. Sailor *Journal of the American Chemical Society*, 2006, **128**, 4250-4252.

3. S. B. Quint and C. Pacholski, *J. Mater. Chem.*, 2009, **19**, 5906-5908.
4. J. Turkevich, P. C. Stevenson and J. Hillier, *J. Phys. Chem.*, 1953, **57**, 670-673.