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Flow-through self-standing porous silicon sensor†

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Abstract: A self-standing porous silicon (PS) multilayer structure detached from the substrate by lift-off method and integrated with a microfluidic cell is presented. Experiments of refractive index changes sensing flowing through open-ended pores are reported. We have recorded continuously the reflectance spectra of the PS membrane each 30 seconds and measured the shift while flowing different substances. Experimental sensitivity values are in good agreement with the theoretical simulations performed. .

Keywords: porous silicon; membrane; lift-off; flow-through; self-standing film; sensing

1. Introduction

Porous silicon (PS) [1] is a good host for fabricating high sensitivity optical sensors. Its sponge-like structure is very sensitive for detecting changes in the refractive index of the medium filling the pores or the adsorption of analytes on its surface. A high aspect ratio between surface and volume can be achieved [2], which results in a high sensitivity, allowing the miniaturization of the sensor and the reduction of the limit of detection.

Formation of PS occurs under anodization of silicon in hydrofluoric acid (HF) solutions, known as electrochemical etching [3]. Etching conditions, such as anodization current or solution composition, define the porosity of the PS layer. Likewise, etching time determines its thickness. Pore size also can be tuned from less than 5 nm (micropores) to more than 1 μm (macropores) [4]. However, the highest sensitivity is reached for small pore sizes [5].

P-type silicon wafers have some advantages concerning PS formation e.g. better surface and vertical uniformity [6], linear etching rates [7, 8] and lack of need of backside illumination [9]. For heavily doped p-type silicon, micropores are formed with most HF solutions [4]. However, certain applications in which pore walls are going to be biofunctionalized [10, 11] or some molecules must penetrate the pores [12] require a bigger pore diameter. For this purpose, some organic solvents, such as dimethylformamide (DMF), are combined with HF to increase pore size during anodization [13, 14].

Close-ended PS structures used for sensing purposes e.g. Fabry-Pèrot interferometers [15] and distributed Bragg reflectors [16] have reported good results. Nonetheless, they may suffer some effects like air entrapment and bad flow diffusion that can lower the sensitivity and threaten performance [17, 18]. It has been demonstrated that flowing through open-ended PS films reduces the time of detection, optimises the sensitivity and avoids mixture of different substances [19]. There are several methods for obtaining open-ended pores but lift-off is the easiest and fastest method [20]. In this method, the PS structure is detached from the substrate in a single step by electrochemically etching with a current close to electropolishing. The self-standing PS membrane can be integrated in a microfluidic cell in order to perform sensing experiments.

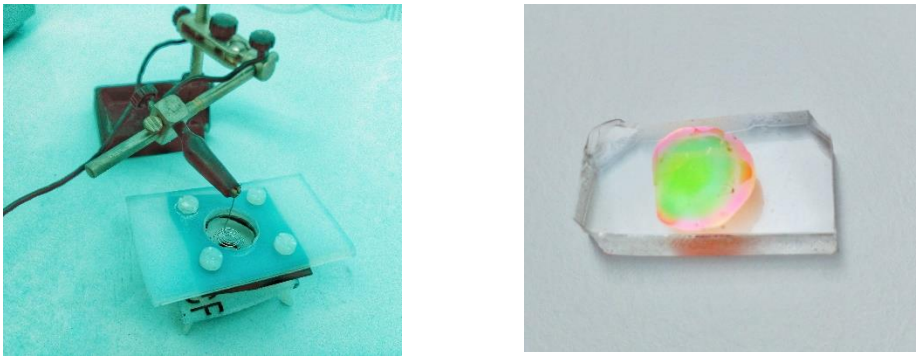
2. Methods

PS was prepared by electrochemically etching highly doped p-type silicon (boron doped, <100> oriented, 0.01-0.02 Ω·cm resistivity) purchased from MicroChemicals GmbH (Germany). Ethanol (EtOH) and 2-Propanol (IPA) were obtained from Scharlab S.L. (Spain) and N,N-Dimethylformamide (DMF) from Sigma-Aldrich (USA). Hydrofluoric acid (HF) (48% solution in water), Hydrogen Peroxide (H_2O_2) and Sulfuric acid (H_2SO_4) were purchased from BASF (Germany). Deionized water (DIW) was produced in house by a Millipore water purification system.

All silicon samples were pretreated for 30 min in a 3:1 volumetric mixture of H_2SO_4 and H_2O_2 for cleaning organic residues off the substrate. Afterward, they were dipped into a solution of <5% HF for 30 s to remove the native oxide layer.

PS films were fabricated under galvanostatic conditions with a Pt electrode using an electrolyte solution of HF:DIW:DMF in a 1:1:4 volumetric ratio (see electrochemical cell in Figure 1 (a)). A multilayer alternating regions of high (H) and low (L) porosity was formed using anodization current densities of 22 mA/cm^2 (82% porosity) and 8 mA/cm^2 (62% porosity), respectively. The etching times were of 27.5 s and 24 s for H and L layers to have a photonic bandgap (PBG) in the visible region of the spectrum.

After the formation of 8 periods of H and L layers, an anodization current of 45 mA/cm^2, close to electropolishing, was applied to allow later lift-off of PS film from the substrate. Then, samples were oxidized in an oven at 800 ℃ for 15 min in oxygen atmosphere. Figure 1 (b) shows an example of how the PS multilayer looks like after detachment.



(**a**) (**b**)

Figure 1. (**a**) Electrochemical cell used in this work for fabricating PS samples; (**b**) PS multilayer detached from the substrate.

A microfluidic flow cell was design to facilitate sensing with the PS film while flowing over and through the pores. First, membranes were detached from the substrate using a PDMS layer with holes for the tubes already assembled. A microchannel was then attached between the PS film and a glass slide. Together, this cell forces the liquids to pass from the inlet tube through the pores to the microchannel and again through the PS film to the outlet tube.

All measurements were performed using a Fourier-Transform Infrared Spectroscopy (FTIR) (Bruker, USA) in the range between 500 and 910 nm. Reflectance spectra of the PS film was collected every 30 s with an acquisition time of 20 s. For the experiments, three different liquids were flown, i.e., DIW, EtOH and IPA. Recorded data was processed with a MATLAB (vR2016b) program and the shift of local maximum at approximately 850 nm was measured. Sensitivity, described as spectral shift divided by refractive index increase, was calculated considering the refractive index of DIW, EtOH and IPA, being 1.329 [21], 1.3555 and 1.3718 [22] respectively.

3. Results and Discussion

A simulation program based on the Transfer Matrix Method (TMM) [23] has been used to compare the theoretical response of the sensor with the experimental one of the fabricated PS film. Figure 2 (a) shows the simulated reflectance spectra of a multilayer of 8 periods with 82% and 62% of porosity in each layer and 320 and 240 nm of thickness, for different medium filling the pores, i.e., DIW, EtOH and IPA. Figure 2 (c) shows the local maximum position for each substance, what leads to a theoretical sensitivity of this structure of 358.6 nm/RIU.

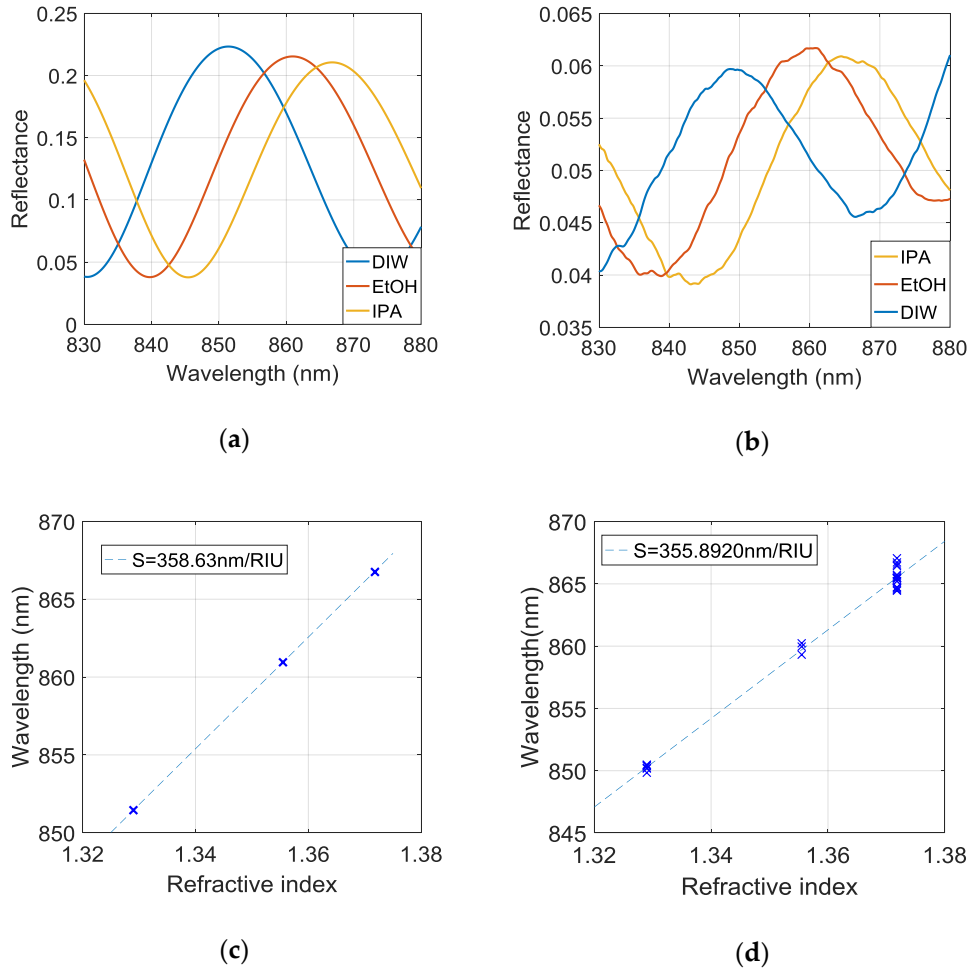


Figure 2. (**a**) Simulated reflectance spectra of the sensor for different medium filling the pores; (**b**) Experimental reflectance spectra of the fabricated sensor; (**c**) Theoretical local maximum position and sensitivity; (**d**) Measured local maximum position and experimental sensitivity.

Figure 2 (b) shows the reflectance spectra registered with FTIR for the fabricated PS sample while flowing through the pores different substances. Only a group of three are represented for a better understanding. The position of the local maximum for all recorded data during the experiment is represented in Figure 2 (d). An experimental sensitivity of 355.9 nm/RIU was achieved. Therefore, the experimental results are in perfect agreement with the simulations.

4. Conclusions

In this work, we have presented the fabrication of a PS membrane detached from the substrate by the lift-off method and its use as a sensor for the detection of refractive index changes. Flowing through open-ended pores optimizes the sensitivity and allows reaching the design value. A sensitivity of 355.9 nm/RIU has been achieved in the visible range of the spectrum.

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References

1. Pacholski, C. Photonic crystal sensors based on porous silicon, *Sensors*, **2013**, 13, 4697-4713, DOI: 10.3390/s130404694.
2. Bisi, O.; Ossicini, S.; Pavesi, L. Porous silicon: a quantum sponge structure for silicon based optoelectronics, *Surf. Sci. Rep.*, **2000**, 38, 6-21, DOI: 10.1016/S0167-5729(99)00012-6.
3. Kolasinski, K.W. Etching of silicon in fluoride solutions, *Surf. Sci.*, **2009**, 603, 1904-1911, DOI: 10.1016/j.susc.2008.08.031.
4. Zhang, G.X. Porous silicon: morphology and formation mechanisms, In *Modern Aspects of Electrochemistry*, Vayenas, C.; Gamboa-Adelco, M.E., Springer, Boston, USA, 2006, 39, 65-133, ISBN 0076-9924.
5. Suárez, I., Chirvony, V., Hill, D., Martínez-Pastor, J. Simulation of surface-modified porous silicon photonic crystals for biosensing applications, *Photonic Nanostructures: Fundam. Appl.*, **2012**, 10, 304-311, DOI: 10.1016/j.photonics.2011.04.014.
6. Agarwal, V. Porous silicon multilayers and superlattices, In *Handbook of porous silicon*, Canham, L.T., Springer International Publishing, Switzerland, 2014, 153-162, ISBN 978-3-319-05744-6.
7. Halimaoui, A. Porous silicon formatin by anodization, In *Properties of porous silicon*, Canham, L.T., IEEE INSPEC, London, UK, 1997, 12, ISBN 0852969325.
8. Frohnhoff, S.; Berger, M.G.; Thönissen, M.; Arens-Fischer, R.; Munder, H.; Lüth, H.; Arntzen, M.; Thei, W. Formation techniques for porous silicon superlattices, *Thin Solid Films*, **1995**, 255, 59-62, DOI: 10.1016/0040-6090(94)05604-C.
9. Föll, H.; Christophersen, M.; Carstensen, J.; Hasse, G. Formation and application of porous silicon, *Mater. Sci. Eng. R.*, **2002**, 39, 93-141, DOI: 10.1016/S0927-796X(02)00090-6.
10. Mariani, S.; Strambini, L.M.; Barillaro, G. Femtomole detection of proteins using a label-free nanostructured porous silicon interferometer for perspective ultrasensitive biosensing, *Anal. Chem.*, **2016**, 88, 8502-8509, DOI: 10.1021/acs.analchem.6b01228.
11. Arroyo-Hernández, M.; Martín-Palma, R.J.; Pérez-Rigueiro, J.; García-Ruiz, J.P.; García-Fierro, J.L.; Martínez-Duart, J.M. Biofunctionalization of surfaces of nanostructured porous silicon, *Mater. Sci. Eng. C*, **2003**, 23, 697-701, DOI: 10.1016/j.msec.2003.09.159.
12. Karlsson, L.M.; Tengvall, P.; Lundström, I.; Arwin, H. Penetration and loading of human serum albumin in porous silicon layers with different pore sizes and thicknesses, *J. Colloid Interface Sci.*, **2003**, 266, 40-47, DOI: 10.1016/S0021-9797(03)00595-2.
13. Lehmann, V.; Stengl, R.; Luigart, A. On the morphology and the electrochemical formation mechanism of mesoporous silicon, *Mater. Sci. Eng. B*, **2000**, 69-70, 11-22, DOI: 10.1016/S0921-5107(99)00286-X.
14. Haldar, S.; De. A.; Chakraborty, S.; Ghosh, S.; Ghanta, U. Effect of dimethylformamide, current density and resistivity on pore geometry in p-type macroporous silicon, *Procedia Mater. Sci.*, **2014**, 5, 764-771, DOI: 10.1016/j.mspro.2014.07.326.
15. Hutter, T.; Horesh, M.; Ruschin, S. Method for increasing reliability in gas detection based on indicator gradient in a sensor array, *Sens. Actuators B*, **2011**, 152- 29-36, DOI: 10.1016/j.snb.2010.09.058.
16. Kovacs, A.; Malisauskaite, A.; Ivanov, A.; Mescheder, U.; Wittig, R. Optical sensing and analysis system based on porous layers, Proceedings of the 17th International Conference on Miniaturized Systems for Chemistry and Life Sciences, Freiburg, Germany, 2013, 275-277.
17. Zhao, Y.; Gaur, G.; Mernaugh, R.L.; Laibinis, P.E.; Weiss, S.M. Comparative kinetic analysis of closed-ended and open-ended porous sensors, *Nanoscale Research Letters*, **2016**, 11, 395, DOI: 10.1186/s11671-016-1614-3.
18. Kumar, N.; Froner, E.; Guider, R.; Scarpa, M.; Bettotti, P. Investigation of non-specific signals in nanoporous flow-through and flow-over based sensors, *Analyst*, **2014**, 139, 1345-1349, DOI: 10.1039/c3an01996a.
19. Zhao, Y.; Gaur, G.; Retterer, S.T.; Laibinis, P.E.; Weiss, S.M. Flow-through porous silicon membranes for real-time lable-free biosensing, *Anal. Chem.*, **2016**, 88, 10940-10948, DOI: 10.1021/acs.analchem.6b02521.
20. Solanki, C.S.; Bilyalov, R.R.; Poortmans, J.; Celis, J.P.; Nijs, J.; Mertens, R. Self-standing porous silicon films by one-step anodizing, *J. Electrochem. Soc.*, **2004**, 151, C307-C314, DOI: 10.1149/1.1688797.
21. Hale, G.M.; Querry, M.R. Optical constants of water in the 200-nm to 200-µm wavelength region. *App. Opt.* **1973**, *12*, 555-563, DOI: 10.1364/AO.12.000555.

22. Sani, E.; Dell'Oro, A. Spectral optical constants of ethanol and isopropanol from ultraviolet to far infrared, *Opt. Mater.*, **2016**, 60, 137-141, DOI: 10.1016/j.optmat.2016.06.041.
23. Balili, R.B. Transfer matrix method in nanophotonics, *Int. J. Mod. Phys.*, **2012**, 17, 159-168, DOI: 10.1142/S2010194512008057.