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Soft photo structuring of porous silicon in water

M. Juan[*], **J. S. Bouillard, J. Plain, R. Bachelot, P. M. Adam, G. Lerondel,** and **P. Royer**

ICD – Laboratoire de Nanotechnologie et d'Instrumentation Optique, CNRS FRE 2848,
Université de Technologie de Troyes, 12 rue Marie Curie, BP 2060, 10010 Troyes, France

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We report on local photo-induced patterning of porous silicon in water. Scanning probe microscopy images of the sample surface after illumination show that the emission properties as well as the topography are modified according to the interferometric illumination pattern. Local photo-oxidation is believed to be at the origin of these modifications.

1 Introduction

Silicon thermal oxidation in wet atmosphere has been extensively used in microelectronics. It is also well known that after formation in hydrofluoric acid (HF), porous silicon (PSi) slowly oxidises in air leading to a modification of its emission properties [1] as well as its refractive index. In addition, under illumination, the ageing of the material was found to be much faster. Previous works [2] have shown the possibility to locally photo dissolved PSi in HF. As far as only photo-oxidation is concerned, these different results suggest that the soft photo structuring of PSi in water should be possible. Demonstration of this soft photo structuring is the subject of the present paper.

2 Experimental set-up

PSi samples were obtained by anodisation of p-type Si substrate in HF. Several anodisation currents and times were used to obtain samples with different porosities, 51 and 61%, and thicknesses in the 200 nm – 15 µm range.

To photo induce oxidised PSi structures, two kinds of illumination have been used; a focused laser beam and an interferometric set-up consisting in two coherent overlapping laser beams.

3 Results and discussions

3.1 Preliminary study

First, the study of the oxidation of PSi without any photonic excitation was necessary to predict the kinetics of the oxidation that will occur outside of the illuminated regions. We used a p-type 51% porosity and 15 µm thickness PSi sample, the solution was water : ethanol (1 : 1). The ethanol enhances the wettability of the sample allowing a better penetration of the water into the pores. The time-evolution of the oxidation process was then studied by measuring the refractive index change using an ellipsometer.

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[*] Corresponding author: e-mail: mathieu.juan@utt.fr, Phone: +00 33 3 25 71 80 01, Fax: +00 33 3 25 71 84 56

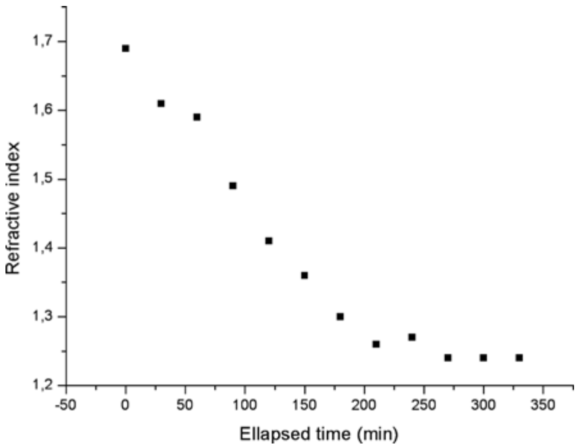

Fig. 1 Oxidation of PSi sample in a water : ethanol (1 : 1) solution without illumination.

Even if the oxidation in water is quite slow, a significant decrease of the refractive index (about 0.5) was found during the first 200 minutes (Fig. 1). Then, for longer elapsed time (>250 minutes) appears a saturation induced by the formation of an oxide layer which passivates the sample. Thus the sample oxidation in water without illumination is important enough to be taken into account in further experiments.

3.2 Photo generated structures

3.2.1 Focused LASER beam

To obtain the first photo generated structure, a PSi sample (p-type, 51% of porosity and 200 nm of thickness) was exposed to a focused laser beam. The laser used was an Argon laser at 514.5 nm. Several ex-

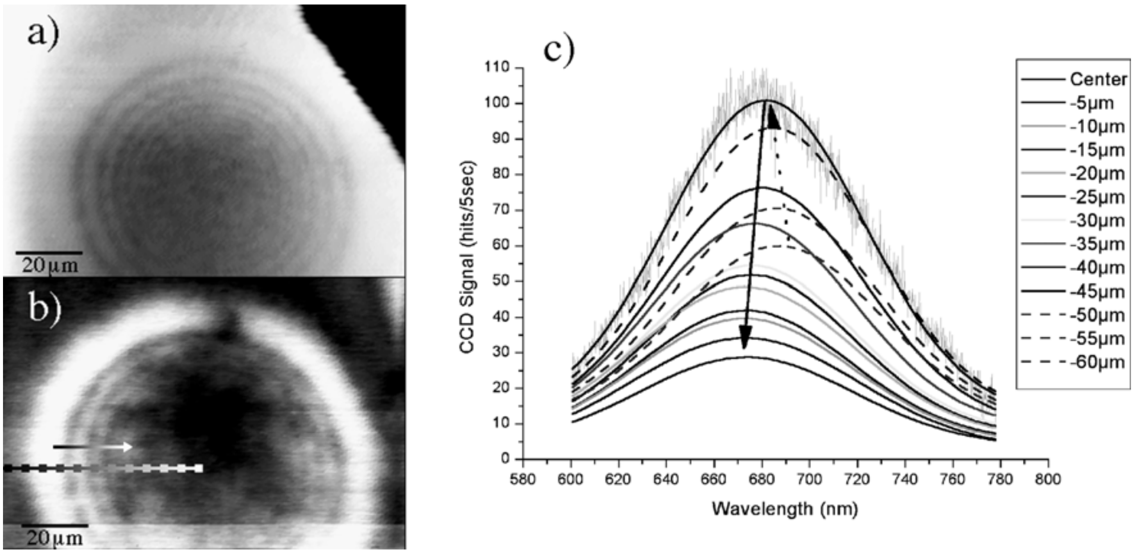

Fig. 2 (a) AFM image, (b) SNOM image and (c) local photoluminescence spectra of a photo-generated structure obtained using a focused laser beam after a 15 minutes exposition time at 1 mW. The graph shows gaussian fit of the photoluminescence spectrum obtained on several points of the structure symbolised on (b) by the squares. The arrows in (b) and (c) are guide for the eye to emphasise the evolution of the photoluminescence spectra. A raw photoluminescence spectrum has been plotted to show the good agreement of the fit.

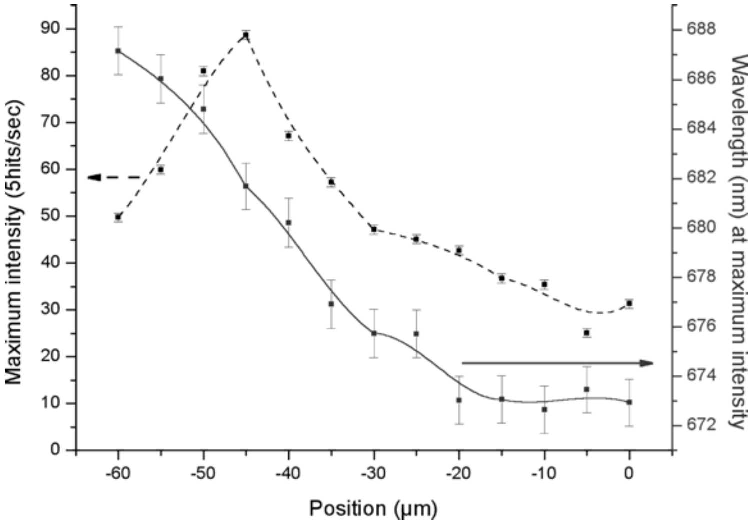

Fig. 3 Maximum intensity (black squares, dashed line) and wavelength at the maximum intensity (grey squares, solid line) versus the position. Lines are guides for the eyes.

posures have been made with illumination times ranging from 5 to 25 minutes. Only the structure obtained for an exposition time of 15 minutes is presented here. The focalisation system involved strong diffraction phenomena leading to annular fringes which can be clearly observed.

An Atomic Force Microscope (AFM) and a Scanning Near field Optical Microscope (SNOM) [3] was used to characterise both the topography (Fig. 2a) and the photoluminescence (Fig. 2b) of the structure. Using a spectrometer on the SNOM, we got the local photoluminescence spectrum on several points of the structure. The spectra were fitted by Gaussian functions (Fig. 2c) to clarify the photoluminescence evolution as a function of the observation point.

According to the SNOM image (Fig. 2b), the photoluminescence increases when getting closer to the edge of the structure and then decreases approaching the center. We can also notice a blue shift of the photoluminescence peaks (Fig. 2c).

To clarify the evolution of the photoluminescence, we have plotted the maximum intensity and the wavelength at maximum intensity as functions of the position (from the outside to the center of the structure) (Fig. 3).

As is evident from Fig. 2c, the photoluminescence peak shows a maximum and a blue shift (approximately 15 nm from edge to center). More precisely, two different phases can be differentiated, first the peak wavelength is blue shifted from 687 to 672 nm, then in the central zone of the structure (from –20 to 0 µm) the photoluminescence peak wavelength remains unchanged (at about 672 nm).

Knowing that the sample was initially non-luminescent, the oxidation is believed to have modified the Si nanocrystallites in a way sufficient to induce photoluminescence. More particularly, the oxidation had two effects. First, as SiO_2 occupies more space than Si atoms the volume of the entire cluster, the Si nanocrystallite covered by SiO_2, is increased. Second, due to the replacement of Si by SiO_2 the size of the Si nanocrystallite core is decreased. Thus, thanks to the oxidation and according to the quantum confinement model [4, 5], a non-luminescent Si nanocrystallite can be turned into a photoluminescent one. Moreover, as the size distribution of the nanocrystallites is a Gaussian, at the first stage of the oxidation, only few nanocrystallites would have reached the critical size to be photoluminescent. The average photoluminescence of the sample will be weak. As the oxidation occurs, more and more nanocrystallites would turn luminescent. But it is most likely that reaching strong oxidation of the sample, a few Si nanocrystallites vanish, leading finally to a decrease of photoluminescence. To summarise, as the oxidation takes place, first the photoluminescence will increase and then decrease. This effect can explain why no photoluminescence is visible at the center of the structure (Fig. 2b). On the other hand, the size decrease of the nanocrystallite will induce a blue shift of the luminescence (if there is any). On the photoluminescence evolution graph (Fig. 3), we observe both a blue shift of the photoluminescence, and a peaked shape for the photoluminescence intensity. The shift suggests that the oxidation had been deeper in the central zone, which is consistent with the evolution of the intensity.

To corroborate these hypothesis, we have retrieved the height profile (not shown here) of the structure from the AFM image (Fig. 2a). As the oxidation induces an increase of the oxidised nanocrystallites volume the height variation can be linked to this oxidation. The profile reveals a height shift between the edge and the center of the structure confirming that the oxidation was stronger at the center. Moreover, the beam analysis shows that the intensity of the focused beam was maximum at the center.

3.2.2 Interferometric pattern

By exposing a p-type 61% porosity and 8 µm thickness sample with two incident laser beams during 3 hours at 250 mW/cm^2, we achieve large scale soft photo structuring of PSi in water. As an example, AFM images of Fig. 4 show a 2 dimensional patterning consistent with the incident interferometric pattern.

The pattern is approximately 10 nm deep, and the period is 7.3 µm. The PSi sample was made of p+ type silicon, with a 1nm roughness after etching. The height variation is very smooth compared to the periodicity of the pattern, yet the diffraction from the grating was easily observable and is shown on Fig. 4. The most probable hypothesis is that the refractive index variation due to the different oxidation induces a phase grating leading to the diffraction observed (topographic diffraction is also expected but to a less extent).

Finally, we have made a photoluminescence image of the sample (Fig. 5a and b). The photoluminescent patterning is quite visible, the oxidation was thus enough to locally induce photoluminescence. It should be stressed that the sample was initially non luminescent.

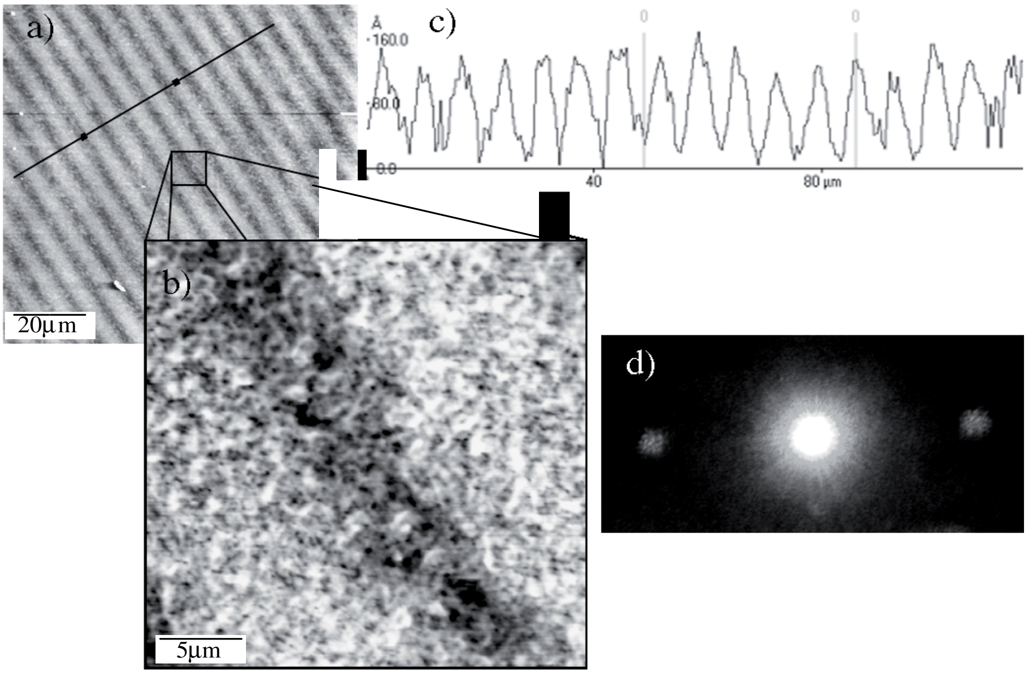

Fig. 4 AFM images (a) 100 × 100 µm^2 and (b) 10 × 10 µm^2, (c) height profile and (d) the diffraction of the photo generated 2D pattern.

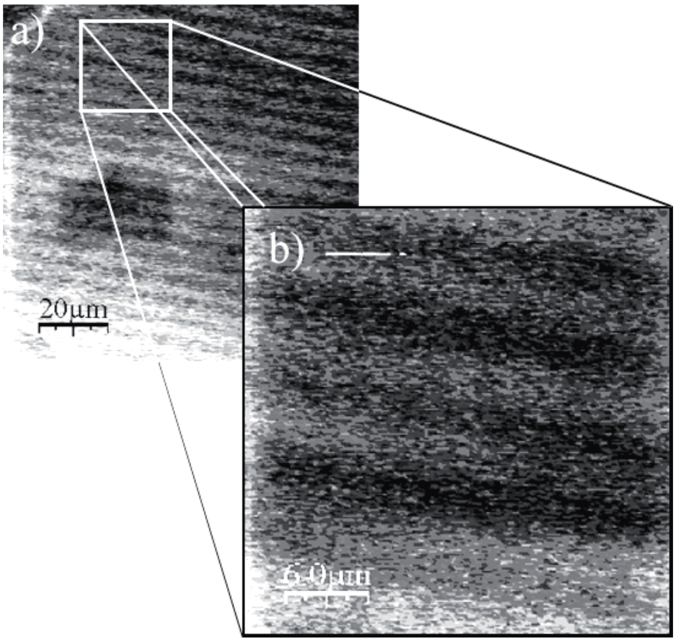

Fig. 5 (a) 120×120 µm^2 and (b) 10×10 µm^2 photoluminescence images of the sample after 3 hours exposition at 250 mW/cm^2 under an interferometric pattern.

4 Conclusions

In summary, it was shown that combining holography and soft photochemistry in water, porous silicon can be locally photo structured leading to noticeable emission, topography and refractive index modification. Moreover, tunability of the photoluminescence has been observed depending on the oxidation of the PSi sample. As a possible application, optical phase recording appears already promising. In addition, since one would expect the reaction to take place at the pore scale, these results also strongly suggest the possibility of pore size engineering.

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