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Oxidized porous silicon as a non-interfering support for luminescent dyes

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Abstract: The objective of this work is to elucidate the possibility to passivate the surface states of porous Si (PSi) by thermal oxidation to be used as a passive host matrix. It is known that a large contribution to the Photoluminescence (PL) of PSi comes from defects at the surface. This PL could overlap the PL of guest materials making it difficult to identify the details of the PL spectrum of the guest. We report on an experimental study about the effect of thermal oxidation at low temperature on the PL of PSi and on the functionalization of oxidized PSi with fluorescein. The background PL is minimized allowing a better detection of fluorescein molecules adsorbed on oxidized PSi.

Keywords: Porous silicon, support for dyes, photoluminescence, silanization, fluorescein

1 Introduction

The discovery of the intense luminescence of porous silicon together with the great technological development of bulk crystalline Si are the reasons for the intense research devoted to PSi. Besides the quantum confinement model proposed by Canham [1], it is known that a large contribution to the Photoluminescence of PSi comes from its surface defects [2]. This PL could overlap the PL of guest materials, making difficult to identify the details of the PL spectrum of the guest. It is also known that freshly produced PSi has an H-terminated surface, while aged PSi or thermally oxidized PSi has O-terminated surfaces. Oxidation processes in a wide range of temperatures and times have been used in the literature to stabilize or passivate non-radiative PSi surface defects [2]. Oxidation could also passivate radiative defects; in fact, it has been reported that the oxidation (aging in air) of PSi is the primary cause of its luminescence degradation [3, 4]. Oxidation is also commonly required as a step prior to chemical functionalization of PSi surfaces, for different purpose, e.g. to enhance the infiltration of dyes [5]. In this experiment due to the high quantum yield (0.95) [6] of fluorescein it is being used as a photoluminescent probe.

According to the literature [7], a common route to functionalize a PSi surface with fluorescein consists of 3 steps: 1) PSi surface passivation by a thermal oxidation process 2) silanization of the oxidized PSi surface and 3) functionalization. Fig. 1 shows a standard coupling reaction using 3-mercaptopropyltrimethoxysilane (MPTS) as a linker to functionalize a PSi surface [7]. In this process the MPTS places easily conjugated silane groups ($Si\text{-}R_4$) on the surface.

In this work the oxidation process is used for two purposes: to eliminate the broad luminescence band of PSi to use it as a non interferent support of luminescent matter (fluorescein), and to allow functionalization with O-linking species (MPTS) to improve infiltration with that emitting matter.

2 Experimental details

The thickness of samples was measured with a surface profile meter Bruker-Veeco model DEKTAK 150. PL spectra were recorded at room temperature with a spectrofluorometer Horiba Jobin Yvon, model Fluoro Max 3, using a 35° optical geometry. The samples were excited with light with λ = 300 nm, using an additional band pass filter (λ = 400 nm), keeping slits at 3 nm aperture. The FTIR spectra were measured with an FTIR spectrometer, Spectrum One Perkin Elmer, in ATR configuration.

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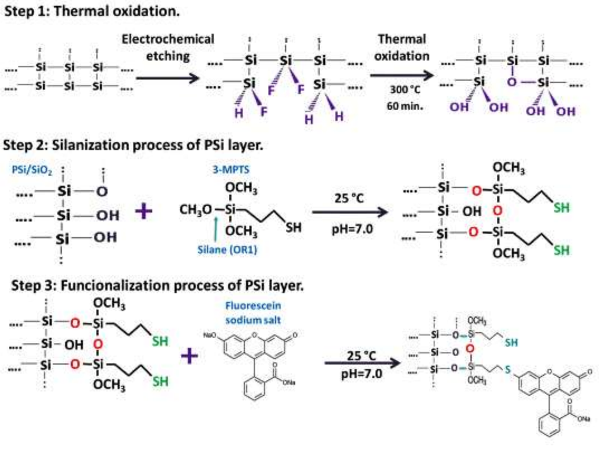

Figure 1: Reaction scheme for the functionalization of a PSi surface with fluorescein via silanol-based coupling. After Sailor [7].

PSi layers were prepared on polished (100) silicon p-type wafers with resistivity of 0.01-0.02 Ω·cm by electrochemical etching. The etchant contained: Ethanol (J. T. Baker, 99.9%), Hydrofluoric acid (Aldrich, 48%) and Glycerol (Sigma, 99% purity) in volume proportions: 60:30:10 and 20 mA/cm^2 current density.

The porosity and thickness of PSi layers were determined by gravimetric measurements [8]. By considering PSi as a mixture of air and Si, the refraction index of the effective media, n_{PSi}^{EMA}, was calculated using Bruggeman's effective medium approximation [9, 10]. The porosity of the PSi layers has been estimated to be of 61 %, producing an average refraction index of 1.81. The thickness of the layers is 0.78 µm.

3 Results and discussion

To discriminate between the luminescence of the different materials used in the present study, PL spectra of as-prepared PSi, and then after being infiltrated with MPTS, and successively after infiltration with fluorescein were recorded (see Fig. 2). MPTS was infiltrated in PSi by introducing PSi in a beaker containing 2.5 v/v MPTS (95%) and 2- propanol solution for 15 min (sample labeled PSi/MPTS). This sample was then infiltrated with fluorescein by immersing it into 1.2 mM fluorescein sodium salt (FM) diluted in a buffer Phosphate solution, pH = 7, for 120 min (sample labeled PSi/MPTS/FM(1.2mM)).

As can be observed in Fig. 2, the PSi layer presents a wide PL band center at 696 nm, typical for mesoporous PSi with different kinds of surface defects.

The PL spectrum of the PSi/MPTS sample shows a similar behavior, just with lower intensity and blue-shifted. This band may be also originated in PSi, but its intensity could be quenched by a screening effect of MPTS, acting differently at different wavelengths, not to mention the interaction of MPTS with the different kinds of radiative defects of PSi. Sample PSi/MPTS/FM (1.2 mM) presents a band peaked at 521 nm, which is assigned to fluorescein [11], indicating that fluorescein was successfully infiltrated in PSi. However, the spectrum has a shoulder in the 700 nm region, thus PSi contributes to the PL. This result supports the idea of eliminating this interfering luminescence, especially if the amount of infiltrated fluorescein would be minimal (as happens when just the PSi surface is functionalized). Thermal oxidation is used in this work for this purpose, needing an optimization process.

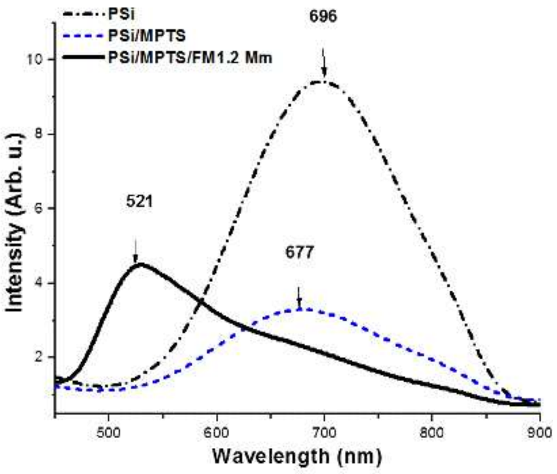

Figure 2: PL spectra recorded from an as etched PSi layer, after silanization with MPTS and after a successive infiltration of a 1.2 mM of fluorescein solution.

3.1 Producing a dual function Oxide

As indicated previously, in the present work, the oxidation of PSi is proposed to produce Si oxide with double function: a) eliminate the background PL of PSi, so that it does not interfere with the PL of the supported material; and b) to provide an oxygen-terminated surface, to enhance functionalization through O-linking molecules.

To find out the optimal conditions for the thermal oxidation process, prepared PSi layers were divided in 2 sets. One sample of set 1 was left as an as etched PSi reference and the others were thermally oxidized under 10 ml/min oxygen gas flux at 300 °C for 5, 30 and 60 min. The PL spectra are shown in Fig. 3. They have been smoothed and normalized to the same vertical logarithm scale in order to emphasize the main spectral features. The as etched PSi layer presents a wide PL emission spectrum in the wavelength range between 550 and 900 nm. This band belongs to the S-band of PSi, the "S" means slow decay of Photoluminescence typically in the microsecond range, its external quantum efficiency is up to 23% at 300 K its value depends on porosity and surface passivation [11, 12]. The main emission component is located at 752 nm (1.65 eV) and Gaussian fittings resolve a minor component at 850 nm (1.45 eV). The oxidized PSi layers have very similar shapes tending to resemble the shape of the as grown layer but with a maximum 27 nm blue shifted. It is seen that, as the oxidation process time is increased from 5, 15, 30, to 60 min, the PL intensity of PSi is decreased. Oxidizing for 60 min reduces the PL intensity by more than 2 orders of magnitude. Intensity quench is probably due to the fact that during thermal oxidation Si-H bonds are replaced by Si-O bonds, which are more stable, generating non radiative transitions [14].

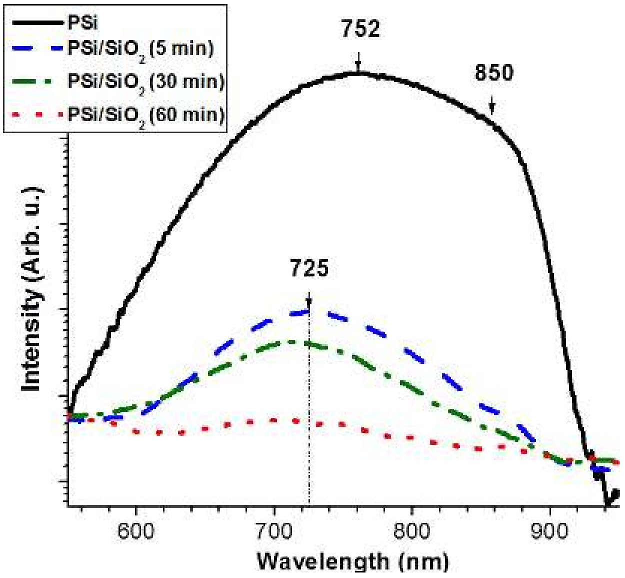

Figure 3: PL spectra of PSi layers with thermal oxidation process at 300 °C for 5, 30 and 60 min excited under the same conditions. The PL spectrum of an as etched PSi layer is included for comparison (note the vertical logarithmic scale).

3.2 PL of infiltrated oxidized samples

Based on these spectra, a thermal oxidation for 60 min was performed on a PSi layer so as to remove the PL emission of PSi, this sample was labeled (PSi/SiO_2). Then, the PSi/SiO_2 layer underwent a silanization process, the sample is labeled PSi/SiO_2/MPTS and finally, the infiltration of the PSi/SiO_2/MPTS sample with FM molecules, as described above, was performed by soaking the sample into a solution of 1.2 mM of FM diluted in a buffer Phosphate, pH=7 for 15 min (sample label: PSi/SiO_2/MPTS/FM(1.2mM)). Thus, in this case the MPTS has been used to attach fluorescein molecules to the surface of an oxidized PSi.

Fig. 4 shows PL spectra recorded from: the reference PSi layer, and after it has been: thermally oxidized, with MPTS silanized, and infiltrated with 1.2 mM FM in solution. It appears a typical PL wide band of PSi in the wavelength range from 600-850 nm. The PL contribution of the PSi/SiO_2, PSi/SiO_2/MPTS and that of the PSi/SiO_2/MPTS/FM (1.2mM) samples is almost negligible in this range. Additionally, it appears the emission band well defined with maximum at 521 nm of fluorescein, which according to Jalkanen et al. it appears at (520 ± 5) nm [13]. These results mean that the oxidation process quenched the PL of PSi, the MPTS is adhered to the O-terminated surface and the fluorescein is also well adhered to the surface of the PSi host matrix by means of the MPTS linker.

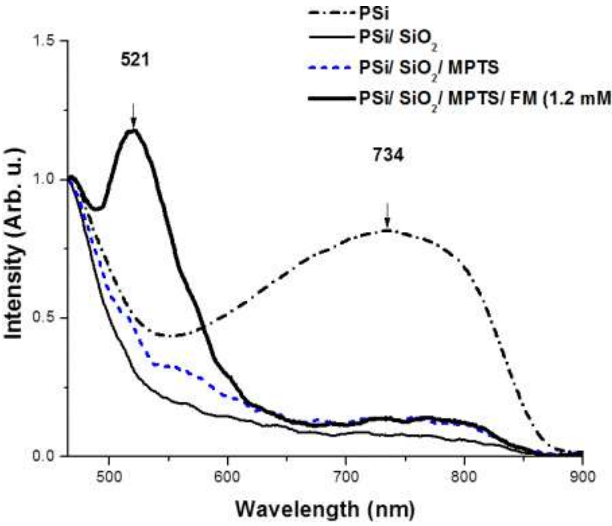

Figure 4: PL spectra of a PSi layer infiltrated with 1.2 mM fluorescein solution recorded at each processing step: thermal oxidation, MPTS silanization and infiltration of 1.2 mM fluorescein in solution.

According to Figs. 2 and 4, the FM molecules have been adhered either to an as etched PSi surface or to an oxidized PSi surface by means of the MPTS linker.

3.3 FTIR and PL of functionalized oxidized samples

Furthermore, we made additional simple experiments in order to confirm that PSi layers really did get functionalized with fluorescein molecules. First a transmission FTIR spectrum was measured from a Si substrate in the range 400-4000 cm^{-1}, the spectrum is wide, smooth and curved, (not shown). Second, a spectrum was recorded from some fluorescein in powder put on a Si chip. This spectrum is very similar to the one of Si substrate but with a ripple lying in the range 2200-2400 cm^{-1} that, with no doubt corresponds to fluorescein, see Fig. 5. In the inset the region of interest is shown and the peak of the largest band is at 2322 cm^{-1}.

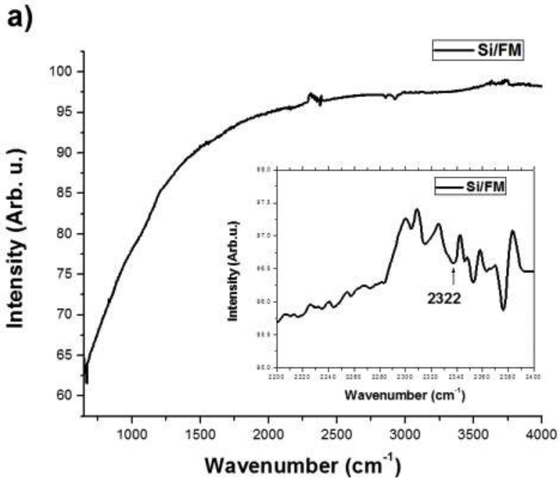

Figure 5: (a) A transmission FTIR wide spectrum measured from some fluorescein powder deposited on a Si chip. In the inset, the spectrum in the range 2200-2400 cm^{-1} is shown.

Afterwards, transmission FTIR spectra were measured from: a PSi/SiO_2 layer, a PSi/SiO_2/MPTS layer-rinsed with propanol to remove unbound MPTS; and from the sample infiltrated with 1.2 mM of FM solution, dried and afterwards rinsed it with a buffer solution to remove the unbound fluorescein dye. These spectra after some data processing that consisted on normalizing each spectrum with respect to its amplitude at 2400 cm^{-1}, are shown in Fig. 5. The band with peak at 2322 cm^{-1} has the largest intensity. From these spectra it can be seen clearly that the set of transmission bands really correspond to the bounded fluorescein dye. Consequently, the oxidized PSi surface is indeed functionalized with fluorescein by the immersion method.

At this point we speculated if really a functionalization of an as etched PSi surface with fluorescein molecules took place. To find it out, a new PSi sample surface underwent the following sequence of processes: A drop of MPTS solution was put on the sample surface, it was dried at 60 °C then, the sample was rinsed with propanol to remove unbound material and dried. Later on, a drop of the FM solution 1.2 mM was deposited on the sample surface, it was dried, rinsed with a buffer phosphate solution, pH=7 to remove unbound fluorescein and dried again. The PL spectra measured at the different processing steps are shown in Fig. 6. The main result in this figure is the presence of the PL band of fluorescein at 524 nm which means that the PSi surface is indeed functionalized with fluorescein.

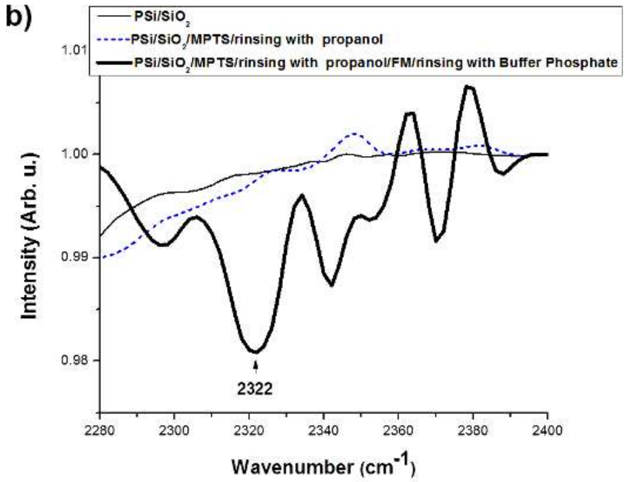

Figure 5: (b) Transmission FTIR spectra of: a PSi/SiO_2 layer, of a PSi/SiO_2/MPTS layer-rinsed with propanol to remove residual MPTS then infiltrated with 1.2 mM of FM solution, dried, and afterwards rinsed with a buffer solution to remove unbound FM from surface.

Furthermore, the sequence of processes described above, was carried out on a new PSi/SiO_2 layer. Afterwards, PL spectra were recorded at the different processing steps of this sample and the corresponding spectra are shown in Fig. 7. Once again, the PL band of fluorescein appears on the spectrum with maximum at 524 nm. The observation of the fluorescein band in Fig. 2 and 4 could be considered proof of the functionalization of PSi surfaces with fluorescein.

Based on PL spectra shown in Figs. 6 and 7 we infer that both non passivated and passivated PSi surfaces get functionalized with fluorescein molecules.

Nevertheless, the efficiency in functionalizing a non-passivated PSi surface and a passivated PSi surface with fluorescein via an MPTS linker can be observed clearly in

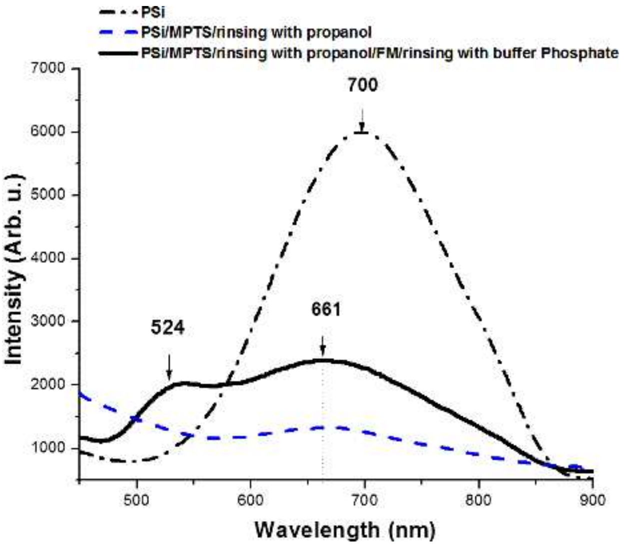

Figure 6: PL spectra measured from an as etched PSi layer and after its different processing steps.

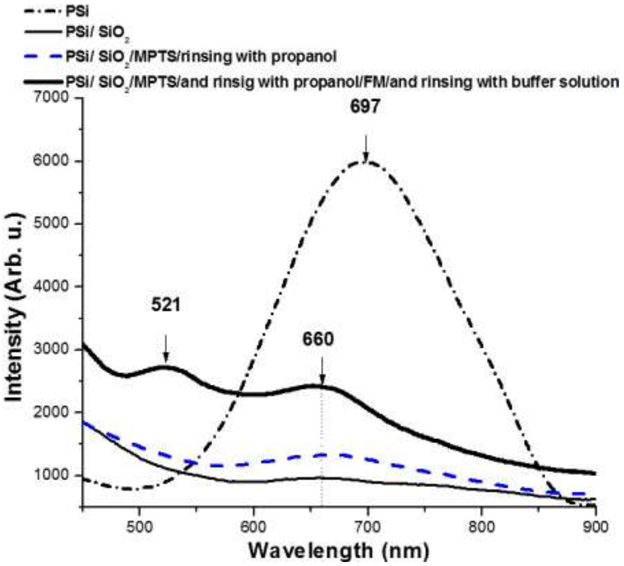

Figure 7: PL spectra measured from an oxidized PSi layer and from the layer at different processing steps.

Fig. 8 where the ratio of the PL intensity at 524 nm of the PSi/MPTS/rinsing with propanol/FM/rinsing with buffer solution spectrum and the PL intensity of the PSi spectrum at the intersection point of this curve with that of the as etched PSi layer, see Fig. 6, and similarly the ratio of the PL intensity at 521 nm of the PSi/SiO_2/ MPTS/rinsing with propanol/FM/rinsing with buffer solution and the PL intensity of the PSi/SiO_2 spectrum at the intersection point, see Fig. 7, are plotted. Based on the data of this figure we conclude that the functionalization with the fluorescein dye is more efficient on a passivated PSi surface.

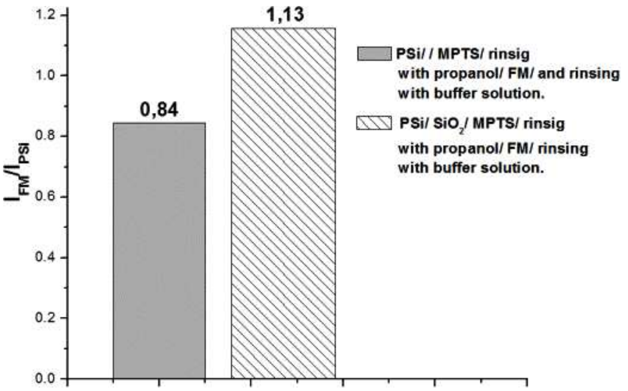

Figure 8: Plot of the ratios of PL intensity of the fluorescein band at 524 nm to the intensity of this spectrum at the crossing point with the PSi spectrum Fig. 6, and a similar ratio of data from Fig. 7.

4 Conclusion

By monitoring PL spectra of an as etched PSi surface and passivated PSi surfaces by means of thermal oxidation processes, we have found the optimal oxide growing conditions to passivate surface dangling bonds that generate the photoluminescence emission, that is, the PL of PSi has been quenched to a negligible intensity. The analysis of FTIR spectra measured from: fluorescein powder alone, fluorescein deposited on Si substrate, on a non-passivated and on a passivated PSi surface and after its removal from these substrates has proven that the functionalization takes place on both non- passivated and passivated PSi surfaces by the immersion method. Furthermore, by carrying out the reaction scheme for a surface functionalization with the fluorescein dye on both a non-passivated PSi surface and a passivated PSi surface, and by monitoring PL surface changes we are able to conclude that the functionalization of a passivated PSi surface is 1.34 fold more efficient than the one of a non-passivated PSi surface.

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