

Infrared studies combined with hydrogen effusion experiments on nanostructured porous silicon

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Abstract

Nanostructured porous silicon samples prepared by electrochemical anodization of p-type crystalline silicon were exposed to blue light irradiation ($\lambda = 400$ nm) in air atmosphere. We observed that both photoluminescence and IR spectra evolve during irradiation. We have monitored the evolution of the IR spectra and we have performed effusion experiments to study the photo-oxidation kinetics. Bands located at around 1100 and 900 cm^{-1} attributed to Si–O related modes are observed to grow with the illumination time, whereas a mode at 910 cm^{-1} assigned to SiH_2 scissoring vibration decreases. The existence of an isosbestic point and the results from factor analysis reveal the presence of only two species evolving in a correlated way. The hydrogen effusion experiments corroborate that the photo-oxidation takes place in a preferential manner, at the expense of hydrogen bonded as dihydride.

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1. Introduction

The search of a stable bonding configuration for the porous silicon (PS) surface has stimulated the research on different stabilization processes [1]. Thermal oxidation has been one of the most explored methods used to stabilize the PS surface, but as a consequence of this action some characteristics of the material are also altered [2]. A violet or red shift in the photoluminescence (PL) peak has been observed depending upon the sample preparation conditions and the oxidation method used [3,4]. Different models have been proposed to explain this behavior, but the discussion is still open [5]. It is also known that light exposure dramatically accelerates the oxidation process in PS [3]. A detailed study of the photo-oxidation mechanisms is needed in order to understand its correlation with other photo-induced processes.

Due to the large area of PS, oxidation may be easily tracked with IR spectroscopy through the Si–O bands.

On the other hand, hydrogen effusion (HE) has been widely used in hydrogenated amorphous and polycrystalline silicon as a powerful tool to explore structural properties in these materials. Despite its potentiality, hydrogen effusion has rarely been taken into consideration for the analysis of the PS structure [6]. In this work we combine HE studies with IR and PL spectroscopies with the aim of clarifying the kinetics of oxidation of PS under illumination.

2. Experimental details

The porous silicon layers employed in this work were prepared by electrochemical anodization. Lightly p-type boron doped (100) silicon wafers with resistivities of 7–17 Ω cm were used. An aluminum contact was evaporated on the backside of the wafers. The anodization was done using a constant current density of 20 mA/cm^2 for 40 min under ambient conditions of temperature and illumination. The electrolyte was a solution of HF (48%): $\text{C}_2\text{H}_5\text{OH}$ in a proportion 1:2 by volume. The anodization cell was made of Teflon, with a platinum wire as a cathode contact. The PS surface was rinsed with ethyl alcohol and dried under N_2 flow, after which

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it looked brownish. As soon as the etching process finished, the samples were kept in darkness, except when exposed to controlled amounts of radiation to study photo-induced effects.

Hydrogen effusion was measured in a vacuum chamber pumped with a turbomolecular pump. Ultimate pressure was in the order of 10^{-7} Torr. Part of the chamber consists of a quartz tube that can be introduced in a tubular oven. The samples were placed inside the tube and, after pressure stabilization, the temperature was raised at a constant rate of $7\text{ }^{\circ}\text{C}/\text{min}$. A residual gas analyzer was used to track atomic hydrogen and molecular hydrogen peaks as the temperature increased.

Photoluminescence spectra were measured using a fluorimeter, setting the excitation at 400 nm and adding an interference filter in order to minimize scattered stray light coming from the excitation monochromator. The intensity of the excitation beam was $4\text{ mW}/\text{cm}^2$. A sample holder was designed in order to maintain the sample surface at an angle of 70° with respect to the excitation beam. The IR spectra during the photo-induced evolution were obtained with a conventional FTIR spectrometer.

Oxidation of the samples was performed in air under light irradiation. The intensity of the irradiation beam was $0.7\text{ mW}/\text{cm}^2$, with the light impinging perpendicularly. The light was supplied by a conventional halogen lamp, filtered by a 400 nm interference filter, in order to reproduce the conditions of the PL experiment.

Immediately after preparation each sample was split into two pieces. One of them was introduced in the HE measurement chamber, pumped and kept in darkness until the effusion experiment get to the end. The second piece was measured in the IR and in the PL spectrometers. Then, this portion of the sample was exposed to the 400 nm light source during different time intervals up to 6.5 h. After each photo-oxidation step the IR and PL spectra were recorded again. Finally, the photo-oxidized sample was also measured in the effusion chamber.

3. Results and discussion

The PL spectra of the as-prepared and the photo-oxidized samples are shown Fig. 1. As it can be seen, after 6.5 h of light exposure there is an increase in the luminescence yield, and the PL peak shifts from 1.9 to 2.15 eV. This behavior has been discussed in the literature [5], and a work explaining it in terms of a quantum confinement model is in preparation [7].

The evolution of the IR absorption spectra for the illuminated sample is shown in Fig. 2 (the exposure time corresponding to each spectra is shown in the figure). We present only the range from 400 to 1400 cm^{-1} , where prominent structures are observed to grow as oxidation goes on. We have also observed small peaks growing at

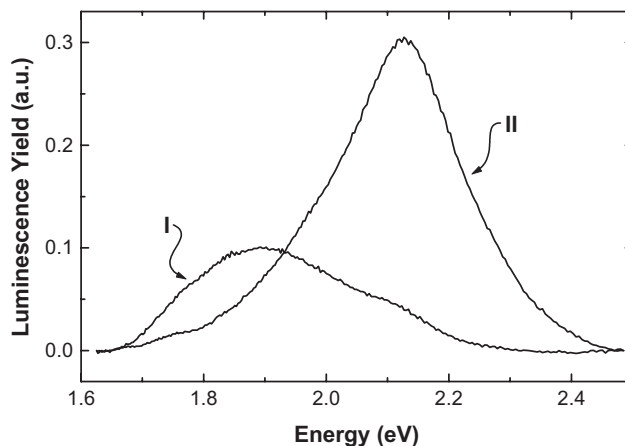


Fig. 1. Photoluminescence of the sample in the as-prepared condition (I) and after 6.5 h of light exposure (II).

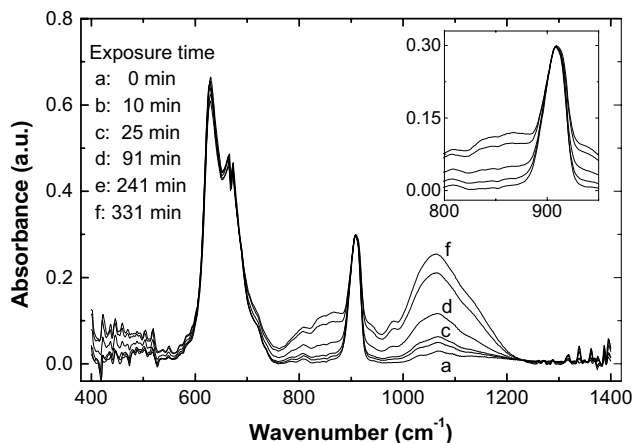


Fig. 2. Evolution of IR spectra as a function of illumination time for a sample exposed to light irradiation ($\lambda = 400\text{ nm}$). Details of the evolution of the 910 cm^{-1} peak are shown in the inset.

2150 and 2190 cm^{-1} , which can be identified with the stretching of Si–H groups backbonded to oxygen atoms. No other significant structures are detected to grow outside these regions during oxidation. It is worth to note that the oxygen related features of the IR spectra also evolve in darkness, but with a much lower rate.

The peak assignment for the as prepared sample is the commonly found in the literature: the 640 cm^{-1} broad band corresponding to the Si–H wagging mode, and the sharp band located at 910 cm^{-1} corresponding to the SiH₂ scissoring mode. The S–H stretching band can be observed around 2100 cm^{-1} , as usual in porous silicon. The structures detected to evolve due to the oxidation process in Fig. 2 may be assigned to the following modes: the band located at 1070 cm^{-1} corresponds to the Si–O–Si stretching mode, and the band growing at $\sim 450\text{ cm}^{-1}$ corresponds to the bending mode of Si–O–Si bridges. The broad band growing at $\sim 850\text{ cm}^{-1}$ has no clear assignment [8,9], although it is known

to be related to Si–O bonds, eventually associated with a H neighbor.

A qualitative analysis of the set of spectra shown in Fig. 2 reveals a remarkable behavior. Besides the growing of the previously mentioned bands associated to the Si–O bonds it can be observed that the absorption coefficient at 910 cm^{-1} (SiH₂ scissoring mode [8]) remains unchanged during the evolution, despite the fact that the background is changing (see details in the inset of Fig. 2). A point in a set of spectra with this particular behavior is usually called an isosbestic point. The presence of this kind of points strongly suggests that only two components kinetically correlated are present, with the same molar absorptivity at the wavelength of the isosbestic point. This kind of points are commonly met when absorption spectra are taken on a solution where a chemical reaction is in progress (in which case the two absorbing components concerned are a reactant and a product), or on a solution in which the two absorbing components are in equilibrium and their relative proportions are controlled by the concentration of some other component. It means that, in our case, one of the components (related to the Si–O bonds) is growing at the expense of the other (related to the SiH₂ bonds). Simultaneously, it can be observed that the intensity of the Si–H wagging mode is slightly modified as the photo-oxidation proceeds.

To study the behavior of the IR spectra for different stages of the oxidation process, we applied principal factor analysis (PFA) [10] to the whole set of spectra, from 400 to 1400 cm^{-1} . We first performed abstract factor analysis, determining the existence of only two factors with the aid of the usual criteria [10]. In order to get physically significant spectra we performed target transformation [10], obtaining the two independent components shown in Fig. 3. The concentration of each one of these components are plotted as a function of the illumination time in Fig. 4. Each one of the measured spectra can be reconstructed as a linear combination of

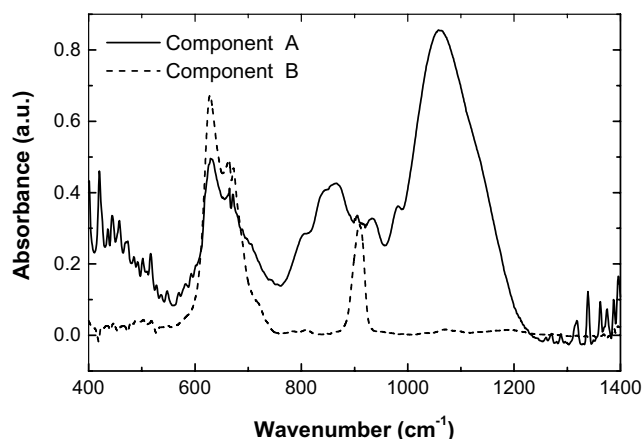


Fig. 3. Independent components resulting from the factor analysis.

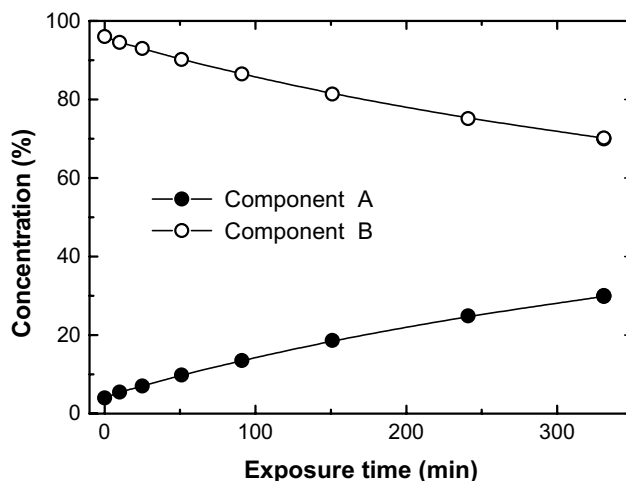


Fig. 4. Evolution of the concentrations resulting from factor analysis for each of the components shown in Fig. 3.

the components of Fig. 3 weighted by the concentrations given in Fig. 4 for the corresponding time. As expected, the absorption for the two components is the same at the wavelength of the isosbestic point (910 cm^{-1}). It is worth to note from Fig. 3 that component A has all the features related to Si–O modes but it has no contribution from SiH₂ modes, while component B includes SiH₂ modes but it has no contribution from Si–O modes. The 640 cm^{-1} band, which is present in both components, is known to be related to vibrations belonging to Si–H bonds, either from mono or di-hydride configurations. However, the absence of the 910 cm^{-1} peak in component A indicates that, in this component, the 640 cm^{-1} band is related to monohydrides only. No significant features related to Si–O vibrations are expected around 640 cm^{-1} . Therefore, the Si–O modes are exclusively associated to the component that increases upon photo-oxidation, whereas the SiH₂ band is exclusively associated to the decreasing component. These results, as well as the existence of an isosbestic point, indicate that the oxygen incorporation is kinetically correlated to the dihydride removal, i.e., each time that a given amount of oxygen is incorporated to the sample, a precise amount of bonds belonging to SiH₂ structures is removed. This argument does not exclude the possibility that oxygen incorporation could remove hydrogen bonded as monohydride, provided that the rate of this process is also proportional to the rate of oxygen incorporation. However, the rate of hydrogen removal as mono or di-hydride should not be necessarily the same. As it can be seen in Fig. 2, the band at 640 cm^{-1} , related to both mono and di-hydride bonds, decreases at a relative rate much lower than the band related only to di-hydrides (910 cm^{-1}). Therefore, the total concentration of Si–H oscillators decreases more slowly than the concentration of SiH₂-related oscillators. Consequently, if oxygen

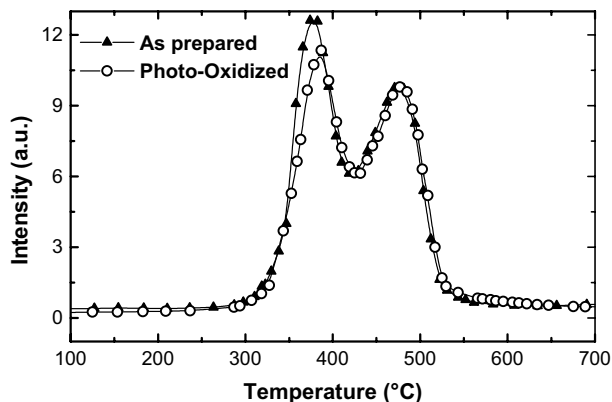


Fig. 5. Normalized HE spectra corresponding to the as-prepared and the 6.5 h photo-oxidized sample.

displaces hydrogen as monohydride, the process is less efficient than the displacement of hydrogen as dihydride.

The preferential incorporation of oxygen can be verified performing a hydrogen effusion experiment. Fig. 5 shows the result of such experiment, where we have plotted the normalized HE spectra for the as prepared and the photo-oxidized samples. Two peaks can be clearly distinguished in this figure, one centered at around 370 °C and the other centered at 490 °C. The normalization was made in order to match the 490 °C peak. Based on the comparison to earlier work by Gupta et al. [11], these peaks can be assigned to the effusion of H bonded as dihydride and mono-hydride, respectively. Comparing the spectra of the as prepared and the photo-oxidized samples it is possible to observe that the di-hydride peak has been reduced with respect to the mono-hydride one. This result supports that oxygen incorporation takes place preferentially at SiH₂ related sites.

4. Conclusions

FTIR, PL and HE spectroscopies were performed in order to follow the photo-induced oxidation of porous

silicon. The series of IR spectra shows an isosbestic point, and factor analysis corroborates the presence of two different components kinetically correlated. These results, combined with the HE behavior, allow us to conclude that during photo-oxidation oxygen is incorporated preferentially at the expense of hydrogen bonded as dihydride.

Acknowledgements

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