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Infrared study of the oxidation of porous silicon: evidence of surface modes

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Received 28 February 2008, revised 20 October 2008, accepted 17 November 2008

Published online 5 February 2009

PACS 68.43.Pq, 78.30.Am, 78.30.Ly, 81.05.Rm, 81.65.Mq

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The evolution of FTIR spectra of PS during oxidation is studied in the range 450–1300 cm⁻¹. We show that the small scale of the PS structure leads to a significant scattering cross section for Fröhlich surface modes associated to stretching modes in siloxane bridges. The kinetics of the evolution of both bulk- and surface-related modes are studied using Prin-

cipal Component Analysis. As a result, two independent components are found, one of them related to TO modes associated to silicon oxide covering large structures and the other one associated to the oxidation of a distribution of prolate ellipsoids with nanoscopic size.

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1 Introduction The efficient luminescence of electrochemically etched porous silicon (PS) has been a matter of great interest since the Canham report [1] in 1990. Porous silicon is characterized by a large specific area, which confers it a significant chemical reactivity [2] and, consequently, a strong dependence of their chemical properties on the surrounding ambient. These characteristics, although attractive for sensing applications, lead to an unstable behaviour. Different oxidation methods [3, 4] have been proposed to stabilize the luminescence and other properties of PS, and a considerable effort has been made to study the oxidation processes. FTIR spectroscopy has been one of the main techniques used to study this process. The size scale and characteristics of the PS structure depend on the anodization conditions. Photoluminescence is usually present in PS having a nanostructure within the scale of few nanometers. The small size of this nanostructure can induce peculiar behaviours on the characteristics of the luminescence spectrum. In particular, quantum confinement effects enlarge the gap of PS with the consequent reduction in the density of thermally promoted carriers. This reduction precludes the oxidation process, which needs a charge exchange to proceed [5, 6]. Therefore, the small scale structures oxidize following a slower kinetics than the one corresponding to larger structures.

Another effect of the PS nanostructure is that the presence of very small porous and tortuous paths may produce a diffusion-limited process, so that the kinetics of the oxidation will be controlled by the slower between the chemical reaction and the diffusion process. As we will show, the characteristics of the FTIR spectra of PS are also modified by size effects, so that the kinetics of the oxidation of structures with different scales can be discriminated using this technique.

In previous studies about PS oxidation, features that evolve in the high energy side of the band related to Si-O-Si stretching modes have been assigned to a contribution of LO-TO modes related to SiO₄ tetrahedron vibrations [7, 8]. In order to couple LO modes in a uniform crystal it is necessary to obtain the IR spectra in the out of normal incidence configuration [9–11]. Otherwise, scattering must be present in a sub-structure in order to get field component in the propagation direction.

In this work we show that the appearance of LO-TO modes in the FTIR spectra of oxidized PS can be explained in terms of the coupling of uniform polarization surface modes (Fröhlich modes), having a high scattering cross section in the limit of the low size scale. The IR modes related to oxidation of both the bulk and the nanostructure of PS follow similar kinetics as that of high pressure sputtered

porous amorphous silicon [12]. In this approach the high energy side of the Si-O-Si stretching band, associated to Fröhlich modes, increases efficiently during the oxidation of nanoporous silicon due to a size effect phenomenon. We show that the surface modes appearing during PS oxidation seem to be related to the oxidation of ellipsoidal prolate structures.

2 Experimental PS samples were prepared by anodic etching of both p-type (7–17 Ωcm) and n-type (1–10 Ωcm) crystalline silicon substrates using a 1:2 HF(50%):EtOH mixture, and a current density of 20 mA/cm² for all the samples. The p-type sample was etched in darkness and the n-type one was etched under an illumination flux of 140 mW/cm² using white light from a dichroic lamp. FTIR transmission spectra of the fresh samples were taken at normal incidence. Afterwards, n- and p-type samples were oxidized in air by a series of isothermal annealing steps at 200 °C and at 100 °C, respectively. FTIR spectra also at normal incidence were taken at room temperature after each annealing step. The samples were maintained in darkness during the whole process to prevent photo-oxidation.

In order to estimate the Real Error (RE) function in the Factor Analysis [13] process, we took a set of seven successive spectra for the samples oxidized during more than 130 hours. In this situation no changes can be expected in the spectra other than due to noise. Therefore, the RE function corresponding to the first eigenvalue for these seven spectra can be compared with the RE function for a series of spectra taken after each annealing in order to obtain the number of independent factors.

3 Results and discussion A series of the resulting spectra for the n-type sample is shown in Fig. 1. It can be roughly observed the increase of oxygen-related features at around 450 cm⁻¹ (bending modes), 850 cm⁻¹ (oxidized hydride deformations), and 1000–1200 cm⁻¹ (stretching modes of Si-O-Si bridges). A band related to the wagging modes of Si-H bonds is observed at 630 cm⁻¹, and a peak corresponding to scissor modes of Si-H bonds in dihydrides can be observed at 910 cm⁻¹. As we demonstrated previously [3], during the first stages of photo-oxidation, oxygen atoms displace hydrogen atoms preferentially from dihydride sites. Although the breaking energy of Si-Si bonds is lower than that of Si-H ($E(\text{Si-H})$) ones, molecular H₂ formation is involved in the process, as usually occurs in effusion experiments [14, 15]. The actual amount of energy needed to overcome the energy barrier E_B should be:

$$E \geq E_B = 2E(\text{Si-H}) - E(\text{H-H})$$

where $E(\text{H-H})$ is the H₂ formation energy. Hence, instead breaking a Si-Si bond, oxygen will break Si-H bonds from two SiH₂ (which are weakly bounded than Si-H ones) displacing one hydrogen from each site, and forming a H₂ molecule.

The isosbestic point around 910 cm⁻¹, labelled IP in Fig. 1(a), is related to the presence of two different species kinetically correlated that participate in the evolution [3]. One of that species is related to vibrations of Si-H bonds, and its spectrum contains no oxygen-related IR modes. The other species contains modes related to bonded oxygen (all of them in the studied range), and also related with wagging modes of SiH and SiH₂. We can conclude that during the thermal annealing, oxygen incorporates in a similar

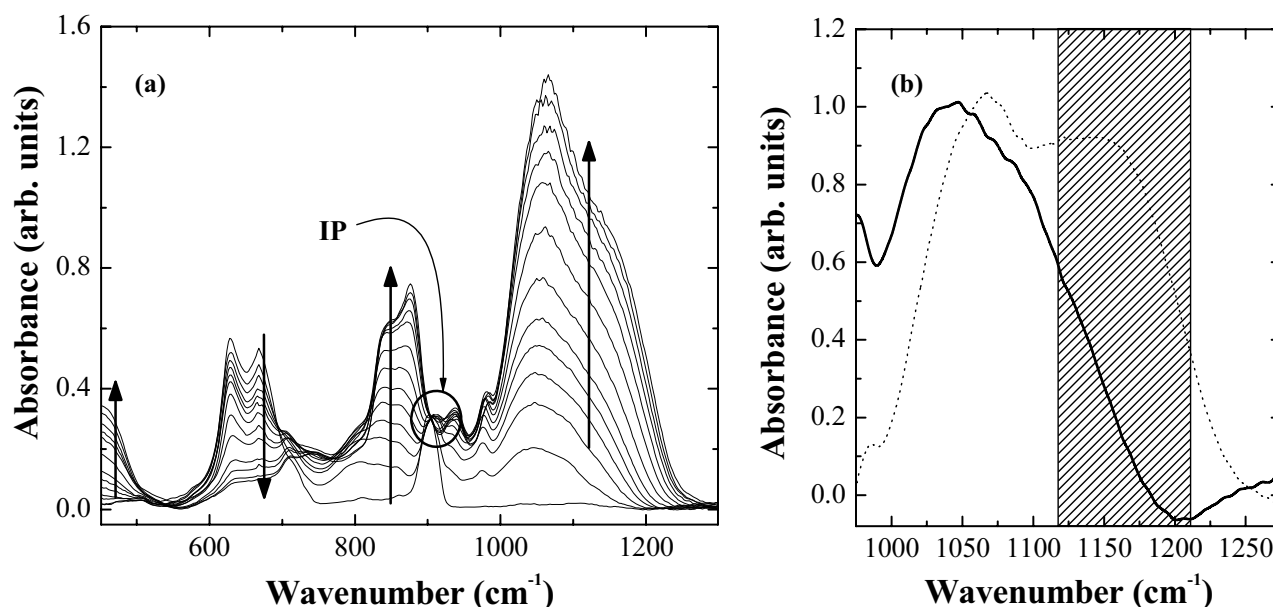


Figure 1 (a) Evolution of the FTIR spectra of an n-type PS sample during oxidation at 100 °C. Arrows show the sense of the evolution of each feature. (b) Full line: first component of the factor analysis. Dotted line: second component. The shaded area shows the region where Fröhlich modes may occur. Total oxidation time was 7731 min.

way to the case of the first stages of photo-oxidation, reported in Ref. [3]. Therefore, during thermal oxidation at 100 °C, oxygen incorporates to the silicon surface displacing hydrogen atoms from the PS surface preferentially from di-hydride sites, at least for annealing times as long as 110 hours.

The band from 960 to 1300 cm⁻¹ was processed by Factor Analysis [13]. Using the value of the RE function corresponding to the first eigenvalue in the Principal Component Analysis of the seven spectra taken without evolution, we obtained two significant factors for the whole set of spectra (shown in Fig. 1). This means that all these spectra can be reproduced by linear combinations of only two spectra. In a previous work we studied the kinetics of oxidation of sputtered porous amorphous silicon [12]. We found that surface modes related to the oxidation of small structures evolve during the oxidation process, both at room temperature and during samples annealing. The behaviour of PS is similar to that of amorphous porous silicon [12] as regards to the evolution of IR spectra during oxidation. We assumed a similar oxidation mechanism for both cases, i.e., a large scale structure which passivates after a quick oxidation process, and a small scale structure which oxidizes slowly. The difference in the oxidation rate is supposed to be related to the differences of carrier densities of structures having small or large sizes. For structures with characteristic sizes of a few nanometers there are quantum confinement effects that enlarge the gap, so that the thermal generation rate of electron-hole pairs in dark is lower than in the case of larger structures. Since the oxidation process of silicon requires charge exchange [5], the oxidation rate of small structures is lower than that of larger ones. We analyzed the behaviour of photoluminescence and the FTIR spectra evolution during illumination, concluding that this size effect is present in PS.

We assumed that during the first stages of the oxidation process the only significant contribution to the evolution of the spectra comes from the quick oxidation of large structures. With this hypothesis we obtained the spectra and weights of the two participating species, shown in Fig. 1(b) and Fig. 2, respectively. All the spectra in Fig. 1(a) can be reproduced by linear combinations of the two components spectra shown in Fig. 1(b), with the corresponding weights shown in Fig. 2.

As it can be seen from Fig. 2, the first stages of oxidation proceed with the quick evolution of the first component, which saturates after around 5-10 minutes. The second component evolves slowly, increasing monotonically. This behaviour of the two components supports our hypothesis: the kinetics shown by the first component agrees with that expected for large structures that oxidize during a short time, and after that passivate. The kinetics of the second component agrees with that expected for a nanostructure in which quantum confinement effects enlarge the gap, limiting the carrier density and thus the oxidation rate. The shapes of the spectra of the two components also support our hypothesis if size effects are taken into account.

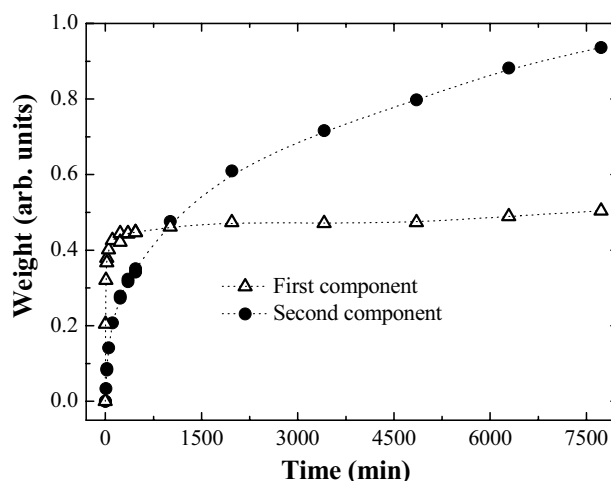


Figure 2 Weights evolution of the two components presented in Fig. 1(b) along with the oxidation at 100 °C of the n-type sample. The weights shown in this figure represent the contribution to the linear combination that reproduces each measured spectra.

The condition for excitation of the first order surface mode (Fröhlich modes) can be obtained from electrostatics. Consider in a first approximation that the nanostructure can be assimilated as an aggregate of little nanospheres of silicon, gradually covered by a mantle of oxide. For these spheres uniformly coated with a mantle of different composition, in the limit of vanishing size, it can be demonstrated that the condition for excitation of Fröhlich modes is [16]:

$$(\varepsilon_1 + 2\varepsilon_m)(\varepsilon_2 + 2\varepsilon_m) + f(2\varepsilon_2 - 2\varepsilon_m)(\varepsilon_1 - \varepsilon_2) = 0, \quad (1)$$

where ε_1 , ε_2 and ε_m are the dielectric functions of core, mantle and surrounding medium, respectively, and f is the fraction of the total particle volume occupied by the core. Using f values ranging from 0.1 to 0.9, the wavenumbers corresponding to Fröhlich modes were computed. The shaded area in Fig. 1(b) shows that these modes should have wavenumbers in the range from 1120 to 1215 cm⁻¹, where a feature in the second component can be seen as well. The contributions for lower wavenumbers of the same component can be attributed to shape effects, and also to the presence of TO modes due to the non-vanishing size of the structure. The general shape of the spectrum of the second component may be assimilated as corresponding to the oxidation of a distribution of prolate ellipsoids associated to small structures. In fact, if the core effect is neglected, and perfect spheres of SiO₂ are considered, the resonant condition of Fröhlich modes in the limit of small sizes should be at a wavenumber in which [16] $\varepsilon/\varepsilon_m = -2$. However, the resonant condition for prolate ellipsoids is split into three bands [16]. It has been previously shown [7] that the stretching band of Si-O-Si bridges in PS can be deconvoluted in four bands, one of them centred in 1080 cm⁻¹ – near the bulk TO mode – and other three bands centred at larger wavenumbers. Comparing Figs. 5A and B in Ref. [7] (and also Fig. 5(b) in Ref. [8])

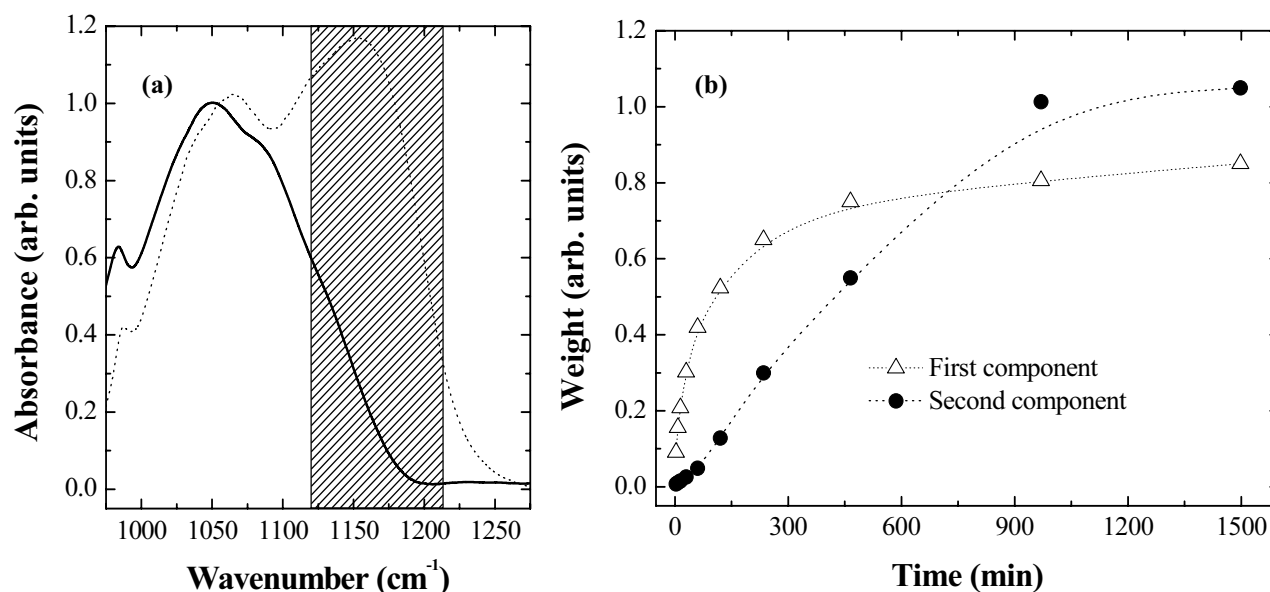


Figure 3 (a) Spectra of the two independent factors that can reproduce the evolution for the p-type sample. Full line: first component of the factor analysis; dotted line: second component. The shaded area shows the region where Fröhlich modes can occur. (b) Weights of the two components that allow to reproduce the whole evolution of the IR spectra during oxidation at 200 °C.

with Fig. 12.11 in Ref. [16], the assignment of the three high energy bands to Fröhlich modes of prolate ellipsoids seems to be evident. Therefore, the first component in Fig. 2 can be associated to the TO modes, coming from oxidized large structures which have negligible contribution of Fröhlich modes, and the second component can be assigned to the oxidation of a nanostructure composed by prolate shaped ellipsoids, showing Fröhlich modes, with a contribution near the TO bulk mode, which can be attributed to the non-ideal small size limit approximation.

The Factor Analysis of the FTIR spectra for the p-type sample also led to two factors. Assuming hypothesis similar to that employed for the n-type sample, we were able to obtain the spectra corresponding to the two participating species. These spectra are shown in Fig. 3(a). The shapes of the two independent spectra are similar to that of the n-type sample. The discrepancies can be attributed to differences in the size of the nanostructures. The evolution of weights for each species is shown in Fig. 3(b). The behaviour of the p-type sample is similar to that of the n-type, but the oxidation rate is slower. In fact, although the p-type sample was oxidized by isothermal annealing steps at around 200 °C, the evolution of the oxygen related features in the IR spectra is slower.

It is worth to note that the entire spectrum is shifted to lower wavenumbers compared with the spectra shown in Refs. [7] and [8], being the band corresponding to the TO mode at around 1050 cm^{-1} . This shift is present in both n- and p-type samples spectra. The samples were measured using different spectrometers, so that an instrumental artefact is unlikely to cause that shifts. We are working in order to clarify the origin of the shift.

4 Conclusions The evolution of normal incidence FTIR transmission spectra of n- and p-type PS samples during the oxidation in air shows the growth of TO modes associated to Si-O-Si bridges of relatively large structures, which saturates after a short time, and the growth of Fröhlich surface modes coupling both TO and LO modes. The competition between diffusive and chemical reaction processes leads to different rates in the evolution of different modes. For relatively large structures, the limiting process is diffusion, so that the TO modes associated with large structures increase rapidly in a first stage, and then saturate, just as occurs in bulk silicon surface. The chemical reaction process, which is mediated by charge transfer, is limited by the carrier density. Since quantum confinement effects enlarge the gap of the nanostructures, the carrier densities are reduced, and the limiting process for nanostructures is the chemical reaction. Therefore the surface modes, which are efficiently coupled for nanostructures, follow a slower kinetics. The shape-dependent Fröhlich modes evolving for PS seems to be associated to structures having prolate ellipsoids. The kinetics of the evolution, and the assignment of the TO and LO are correlated with a structural model.

Acknowledgements This work was supported with grants CAI+D 002-011 (2005) (UNL), PIP 5730 (CONICET), and PICT 05 32515 (SECyT).

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