

Evidence of x-ray absorption-edge shift as a function of luminescence wavelength in porous silicon

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X-ray absorption fine structure (XAFS) at the Si K edge in porous silicon has been measured by monitoring the photoluminescence yield (PLY) in different parts of the luminescence band: at increasing luminescence energy, a continuous positive shift of the x-ray absorption edge has been observed. The peculiar selectivity of the partial PLY-XAFS technique to the luminescent sites allows us to perform a size selection of the different nanostructures distributed in a single porous-silicon sample. The recombination of carriers localized in quantum confined nanocrystals is confirmed to be the main cause of the optical emission.

In recent years, a great amount of scientific effort has been made to understand the mechanism of visible light emission in porous silicon.^{1,2} Photoluminescence in porous silicon is due to the reduced dimensions of the nanostructures (wires or dots) obtained by a partial electrochemical dissolution of bulk crystalline silicon. Shape and dimensions of the porous structures are determined by the physical properties of the starting Si wafer and by the electrochemical process parameters (HF content, current density, etching time, light exposure time).³ By varying one of these quantities, it is possible to change the porosity and the nanostructure dimensions, obtaining a shift of the emitted light wavelength, typically from the infrared to the green-blue region.

At present, a strong agreement has been reached on the ability of the quantum confinement (QC) model to explain the light emission properties of porous silicon.^{4,5} This model predicts an enlargement of the band gap when the porous structures are reduced to nanometer sizes: owing to the momentum uncertainty, radiative recombination of carriers localized in the quantum-confined nanocrystals is highly favored with respect to bulk Si. According to the QC model, the emission energy should correspond to the width of the energy gap E_{gap} , in case of a band-to-band transition. The observed broadening of the luminescence band is attributed to the presence of a distribution of nanostructure sizes, which corresponds to a distribution of E_{gap} values inside the porous layer.

Up to now, the effects of QC in porous silicon have been tested only by comparing different samples, without considering the size distribution of luminescent sites inside each single specimen.^{6,7} In this paper we exploit the peculiar site sensitivity of x-ray absorption fine structure (XAFS) measured in photoluminescence yield (PLY) mode,⁸ making a selection of nanostructure sizes within each single sample. The work is based on the simultaneous measurement of several x-ray absorption near edge structure (XANES) spectra in PLY mode, each spectrum corresponding to a different emission energy range within the same optical band. This technique will be referred to as "partial PLY-XANES." Actu-

ally, following the hypothesis that each nanoparticle of the porous-silicon layer yields a sharp luminescence spectrum (whose emission energy is defined by its size), we may expect to obtain different partial PLY-XANES spectra by sampling different energy ranges of the broad optical luminescence band.

An essential role in supporting the QC model has already been played by XAFS, by considering both XANES and extended x-ray absorption fine structure (EXAFS). XAFS has been implemented in three different detection modes at the K edge of Si: transmission,⁹ total electron yield (TEY),¹⁰⁻¹² and PLY,^{8,13} also called XEOL (x-ray excited optical luminescence).¹⁴ These detection modes are characterized by different sensitivities. Transmission probes all the Si atoms on the surface and in the bulk of the sample. TEY, measuring secondary electrons, is sensitive to all Si atoms of the porous layer; PLY measures the intensity of visible radiation emerging from luminescent Si sites. TEY-EXAFS experiments have shown^{10,12} that porous-silicon samples with luminescence bands centered at higher energies have in general smaller site dimensions. In previous papers,^{8,15} the present authors have experimentally shown that PLY, contrary to TEY, monitors the local structure only of the Si atoms in the luminescent sites. This site sensitivity appears to be specific for quantum-confined systems and cannot be considered a general property of all light emitting systems.^{16,17} This peculiarity has been attributed to the presence of a very efficient radiative recombination channel in the vicinity of a subset of the absorbing Si atoms. For porous silicon, the localization of carriers has been proved by different experiments:¹⁸ it is proposed to occur via local size modulation of wire structures^{1,19} or surface-confined states.²⁰

The porous Si samples analyzed in this work were prepared using a standard procedure,²¹ starting from p -type boron-doped (100) Si wafers, with resistivity 20 Ω cm. In the following, two types of samples, denoted as *red* and *green*, will be considered. The *red* sample was obtained in an ethyl alcohol solution of HF (15%) by applying a current density of 40 mA/cm² for 7.5 min; the *green* one by a current den-

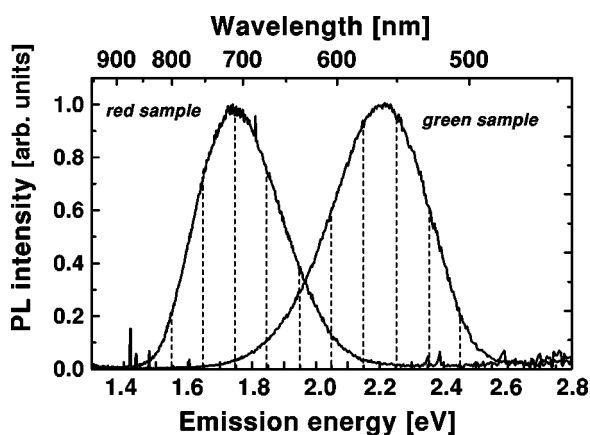


FIG. 1. Normalized XEOL spectra of two porous-silicon samples obtained from a 20 Ω cm crystal silicon wafer. The luminescence intensity has been integrated over intervals of 0.1 eV width (vertical dashed lines) to obtain partial PLY-XAFS spectra.

sity of 100 mA/cm² for 6 min and a post-etching treatment (5 min under a 500 W halogen lamp). After the etching procedure, the samples were rinsed (the *red* one first in methanol, then in pentane; the *green* one in deionized water) and transferred, still wet, inside the experimental chamber on the x-ray beamline, which was immediately evacuated to avoid exposure to the air. Both samples presented homogeneous porous layers, with thickness 8 and 11 μ m, respectively. Their luminescence bands were centered at about 730 and 570 nm, respectively. The normalized x-ray excited emission spectra of *red* and *green* samples are shown in Fig. 1: they exhibit a FWHM of about 0.3 eV and are about 1 eV wide at the bottom. The shape difference shown by the two luminescence bands is due to the different preparation parameters and post-etching treatment. The bands shown in Fig. 1 were obtained at the excitation energy of 1850 eV, just beyond the Si absorption *K* edge (1839 eV). When exciting at different energies, below and above the edge, no large changes of the shape and position of the bands were observed. Slight variations of the relative intensities were, however, produced by varying the x-ray energy near the absorption edge, and are considered in the following analysis.

XAFS measurements were carried out with synchrotron radiation at the Super ACO storage ring of the LURE Laboratories in Orsay (France), using the SA 32 beamline. Electron energy and average current were 800 MeV and 400 mA, respectively. The x-ray energy resolution was estimated 0.7 eV at 2000 eV. A system of lenses and optical fibers collected the light emitted from the sample focusing it on a dispersive spectrometer (CP200 Jobin-Yvon). An optimized back-illuminated CCD (1100PB Princeton Instrument), cooled with liquid nitrogen, was used as a detector to collect in a few seconds the whole luminescence band at each x-ray energy. After the x-ray energy scan, each band was corrected for the spectral function of the XEOL apparatus, and subdivided in stripes of 0.1 eV width (Fig. 1). Considering both the samples, a total interval of luminescence energy ranging from 1.6 eV up to 2.4 eV was explored. Unsmoothed partial PLY-XANES spectra, obtained by integrating the luminescence intensity from each stripe, are shown in Fig. 2 for the *red* sample. These spectra do not reveal any presence of oxygen-related absorption structures, such as Si-O-H or

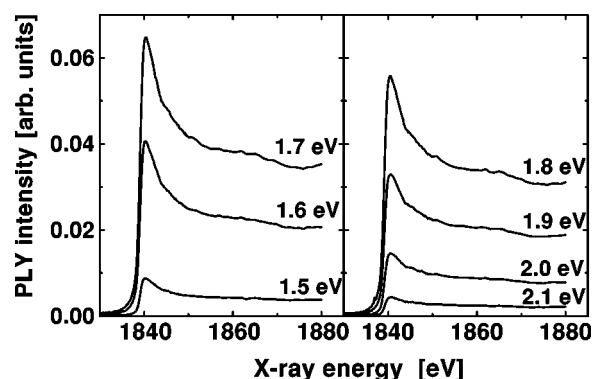


FIG. 2. Experimental partial PLY-XANES spectra of the *red* porous-silicon sample obtained by integrating the luminescence band shown in Fig. 1 over energy intervals of 0.1 eV width.

O-Si-O bonds, at the expected energies of 1844 and 1847 eV, respectively.¹³ By normalizing the spectra at their maximum value, a neat shift of the x-ray absorption edge position can be easily observed when the photoluminescence energy increases, as shown in Fig. 3 for some selected spectra. Since each set of PLY spectra was obtained from the same x-ray energy scan, relative shifts of the absorption edge smaller than the beamline energy resolution could be reliably appreciated. For each sample, the relative shifts of the partial PLY-XANES spectra have been evaluated with respect to the most intense spectrum (corresponding to the maximum of the XEOL band at 1.7 eV and 2.2 eV for *red* and *green* samples, respectively), after a normalization to the absorption maximum at about 1841 eV. The average relative energy shifts are reported in Fig. 4. They were evaluated in two ways: (a) the energy differences were measured in various points of the absorption edge around the inflection point and averaged; (b) the difference between spectra was minimized by shifting each spectrum in a best-fitting procedure. The error bars in Fig. 4 indicate the maximum spread of values obtained by the different data-analysis procedures. It is easy to recognize a common linear increase of the x-ray absorption-edge energy monitored by partial PLY as a function of optical emission energy.

Relative up-shifts of the x-ray absorption edge of porous silicon with respect to *c*-Si were measured by different authors both at *L* and *K* edges using TEY.^{6,22} These experimen-

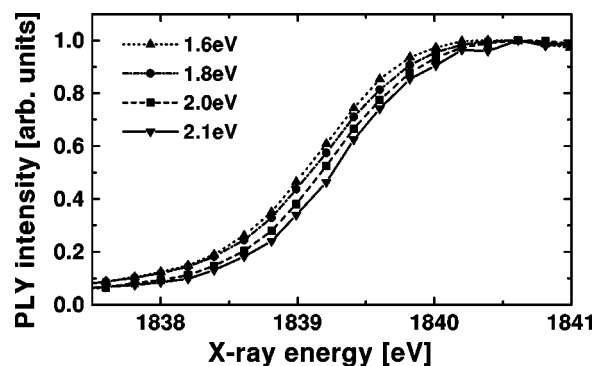


FIG. 3. Partial PLY-XANES spectra of the *red* porous-silicon sample normalized at the maximum: a neat positive shift of the edge position with increasing the photoluminescence energy is observed.

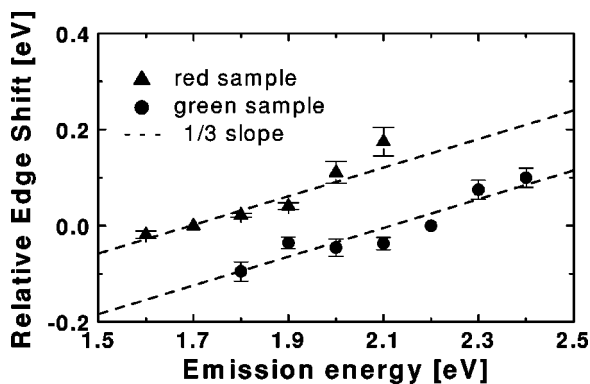


FIG. 4. The relative shifts of all the edges for *red* and *green* samples are plotted versus the photoluminescence energy. A straight line of 1/3 slope is superimposed to the data.

tal results were interpreted as strong evidence of QC effects, because the edge energy corresponds to a direct transition from inner core levels (considered insensitive to the local structure) to the unoccupied electronic states in the bottom of the conduction band (CB). On such a basis, we can interpret the relative shifts of the partial PLY-XANES edges as due to the energy raise of the bottom of the CB in different luminescence sites characterized by increasing light emission energy and decreasing size.

Figure 4 shows that the correlation between the photoluminescence energy and the x-ray absorption-edge position is linear. The present result can be compared with that found in an experimental work on the electronic properties of Si nanocrystals by van Buuren *et al.*²³ These authors, measuring different samples with selected sizes, correlated the observed shifts in both CB and valence band (VB) with the average dimensions of the nanocrystals, showing clear evidence of quantum size effects. From the Data in Ref. 23 one can deduce that the CB bottom is linearly correlated to the band gap, with 1/3 slope. We have reported this behavior in Fig. 4 (dashed lines): the agreement between the present partial PLY-XANES results and those of Ref. 23 is quite good, confirming that QC in nonoxidized porous silicon and in Si nanodots produces a similar effect on the electronic states, in particular on the enlargement of E_{gap} . Very recently, the same 2:1 ratio between VB and CB shifts has been measured by photoemission and XANES spectroscopies for a porous-silicon sample whose dimensions were reduced by successive wet-etching procedures.²⁴

The main advantage of the present experiment consists in the possibility to study the effects of QC on a continuous size distribution within the same sample, rather than on a few distinct samples, each one characterized by a different average size. Besides, since a PLY-XANES experiment is done on a single sample with a homogeneous surface, we get rid of the influence of different surface-coverage effects and of the experimental uncertainties due to successive, independent measurements of different samples.

The experimental differences between partial PLY-XANES confirm once more⁸ the site selectivity of this technique: in fact, for porous silicon by PLY-XAFS it is possible to study the local structure only of the emitting nanostructures, and in particular to distinguish those characterized by different dimensions. In principle, the partial PLY-XAFS can

also monitor changes of the local environments or chemical coverages of the nanostructures and their influence on the photoluminescence. The study of the XANES region (0-40 eV) as a function of photoluminescence energy can provide information on the variations of the CB electron density in luminescent sites with different sizes. Improving the statistics (i.e., using high-intensity synchrotron sources), the technique could also be exploited to study the EXAFS oscillations, in order to determine a quantitative correlation between the CB shift and the average dimensions of luminescent sites.

A quantitative evaluation of the nanostructure's size is out of the possibilities of the present work, because we have only measured relative shifts of the CB as a function of light emission energy. It is well known that the absolute value of the emission energy is influenced not only by the dimensions of porous nanostructures, but also by their chemical coverage:²⁵ a different chemical passivation induces a shift of the energy position of the photoluminescence band. However, the present results strongly support the importance of QC in the photoluminescence properties of porous silicon, because of the homogeneous surface properties inside the measured area of each sample. An interesting comparison can be done with the results presented in Ref. 25: our experience confirms that samples with yellow-green photoluminescence (in the native solution) show a redshift as soon as they are dried (in air, but also in vacuum). However, the relative up-shift of the CB energy shown in Fig. 4 does not present evidence of saturation: this result confirms that the surface of emitting nanostructures in both *red* and *green* samples is without any detectable oxygen coverage. As a matter of fact, as Allan and co-workers have shown,²⁵ the presence of oxygen would produce a much lower CB shift or even no shift. We note that their model for a free exciton recombination in Si clusters totally passivated by hydrogen foresees a ratio lower than 2:1 for the VB and CB shifts, indicating a more complicated situation for real samples than for model environments.

In conclusion, in this paper we have presented a technique, the partial PLY-XAFS, which allows us to correlate the x-ray absorption-edge position to the emission energy of luminescent nanocrystals, i.e., in an indirect way, the shift of the bottom of the CB to the nanoparticles sizes. Thanks to this technique, it is possible to follow the enlargement of the energy gap, due to the presence of different nanoparticle sizes in the same sample of porous silicon, without resorting to a comparison with different calibrated samples. The quantitative analysis of the positive x-ray edge shift at increasing photoemission energy in nonoxidized porous-silicon samples shows that the luminescence mechanism agrees with the quantum confinement theory.

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