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## Ultraviolet photoluminescence of porous silica

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Excitation pattern and decay kinetics of ultraviolet photoluminescence of porous silica are investigated between 4.5 and 10 eV by means of synchrotron radiation. Spectra are dominated by a 3.7 eV emission similar to the recently observed ultraviolet emission of oxidized porous Si and Si nanostructures. Emission intensity is found to be controlled by the material specific surface. Other emissions are observed at 2.9, 3.8, and 4.2 eV. All emissions show lifetimes of a few nanoseconds. Spectral and kinetic features are sensibly different than in glassy SiO<sub>2</sub>, suggesting a revision of previous assignments of ultraviolet emissions in oxidized porous Si and Si nanostructures. © 2000 American Institute of Physics. [S0003-6951(00)01122-0]

A great deal of work was done in the last 2 decades to identify the structure of the defects responsible for the ultraviolet (UV) photoluminescence (PL) in SiO<sub>2</sub>-based glassy materials.<sup>1</sup> This was mainly motivated by technological implications of PL defects in the physical properties of SiO<sub>2</sub>-based devices for fiber optics.<sup>2</sup> Nevertheless, further interest is recently growing in this field owing to the possible relation between PL sites in bulk oxide and PL sites at the surface of oxidized porous Si (OPS) and Si nanostructures (SNS), promising materials for optoelectronics.<sup>3,4</sup> Traditionally, in this area, PL studies are carried out in the visible and infrared spectral regions. Only recently, a strong UV emission at about 3.5–3.7 eV in OPS and SNS has been reported, suggesting possible applications of silicon-based UV emitting materials in the evolution of devices for optical data storage.<sup>5</sup> But the origin of this UV emission is not yet clear. Different attributions to oxygen-deficient-centers (ODCs)<sup>5,6</sup> or to small Si clusters in oxide were proposed.<sup>7,8</sup> However, a reliable analysis of these attributions has been prevented until now by the lack of extended excitation data and time resolved measurements.

In this letter we present the analysis of the UV PL of porous silica in a wide range of excitation energies, supported by optical absorption, Raman scattering, surface area and electron paramagnetic resonance (EPR) data. Different kinds of PL activity were discriminated. In particular, we detected the strong UV emission previously observed in OPS and SNS and we succeeded in controlling its intensity by modifying the material specific area. PL map and time resolved data also allowed us to reassess previous assignments to the ODC structure of glassy SiO<sub>2</sub>.

SiO<sub>2</sub> samples were produced by sol-gel hydrolysis and condensation of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> in H<sub>2</sub>O-ethanol solution. Reagent amounts were 5 ml Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, 14 ml ethanol, and 3 ml H<sub>2</sub>O. The sol so prepared was kept at 40 °C until com-

plete gelation. Final drying of the gel was obtained in 2 weeks at 40 °C. The xerogel was then heated in oxygen (50 ml/min) at a rate of 6 °C/h up to 450 °C, and kept 20 h at this temperature. Samples with different porosity were obtained by stopping the treatments at 450 °C, or further heating at 550, 650, 750 and 1050 °C in vacuum. Surface area was measured by the Bnanauer-Emmett-Taylor method: changes from 700 m<sup>2</sup>/g in the xerogel to less than 1 m<sup>2</sup>/g after treatment at 750 °C were found. Structural changes were also monitored by means of Raman scattering: shifts of the  $\omega_1$  and  $\omega_4$  modes<sup>9</sup> at 440 and 1190 cm<sup>-1</sup> suggested an increase of the mean Si-O-Si angle of about 3° from the xerogel to the glassy sample.

PL measurements were carried out at the SUPERLUMI experimental station at the HASYLAB synchrotron laboratories of DESY (Hamburg). The excitation spectral bandwidth was 0.3 nm. PL signals were detected by a charge-coupled-device camera with 3 nm of bandwidth. Three-dimensional spectra were obtained by collecting PL emission at different excitation energies. Time resolved data in the ns domain were obtained with a time window of 300 and 0.8 ns of excitation pulse duration. Optical absorption was measured by a spectrophotometer CARY2300 VARIAN.

The PL-PL excitation (PLE) pattern (Fig. 1) is dominated by the emission peaked at 3.7 eV with a narrow excitation band at 5.5 eV. Other PL components are observed at 2.9 eV (excited at about 5 and 6 eV), at 3.8 eV (with broad excitation structures from 6 to 7 eV, partially superimposed to the excitation of the main 3.7 eV PL) and at 4.2 eV (excited at 6.5 eV). Time resolved data show similar PL lifetimes: about 3–4 ns for the 3.7, 2.9, and 3.8 eV bands, and 8 ns for the 4.2 eV emission, quite independent of the excitation energy. Figure 2(a) shows PL spectra excited at some representative energies for one of the investigated samples. Excitation spectra at selected emission energies are reported in Fig. 2(b). Components at about 5, 5.5, and 6 eV are also present in the UV absorption spectrum [Fig. 3(a)] with intensities lower in samples sintered at higher temperature. No

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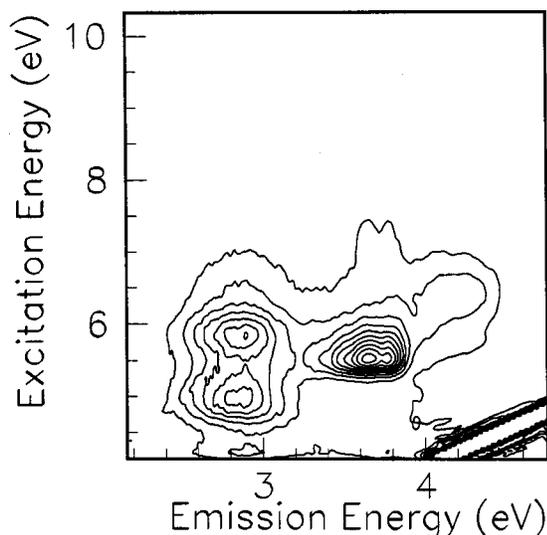


FIG. 1. Contour plot of the PL spectra vs excitation energy of a sample of porous  $\text{SiO}_2$  treated at  $450^\circ\text{C}$ . (The feature at high emission energy, linearly drifting from 4.2 to 4.8 eV, is due to reflected excitation light.)

absorption bands are detected below 6.5 eV in samples treated at  $T \geq 750^\circ\text{C}$ . Similarly, all PL emissions decrease by proceeding with the sintering process at increasing temperatures [Fig. 3(b)]. The 2.9 and 3.8 eV emissions, as well as the 4.2 eV PL component, disappear after heating at  $650^\circ\text{C}$ . Instead, the decrease of intensity of the 3.7 eV emission is less pronounced and shows a good correlation with the decrease of specific surface [inset of Fig. 3(b)]. No significant difference of peak position, bandwidth or lifetime is instead observed as a result of the changes of linkage geometry evidenced in Raman spectra.

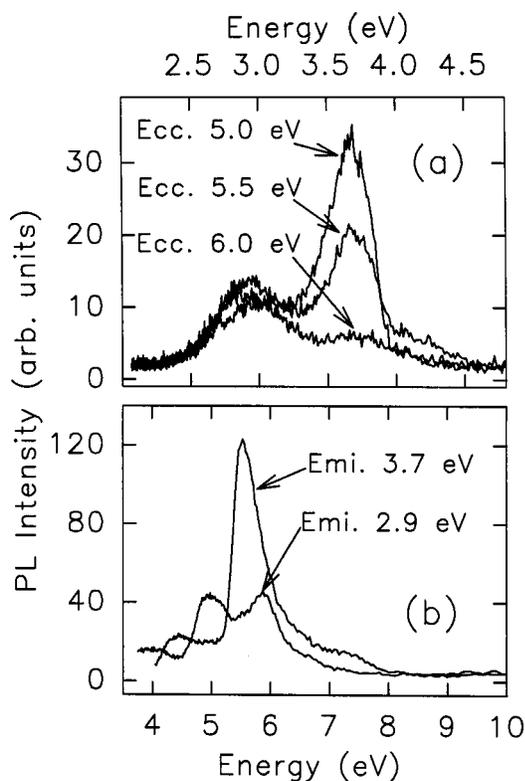


FIG. 2. (a) PL spectra excited at 5, 5.5, and 6 eV in porous  $\text{SiO}_2$  samples (treated at  $450^\circ\text{C}$ ); (b) excitation spectra of PL at 2.9 and 3.7 eV in the same sample.

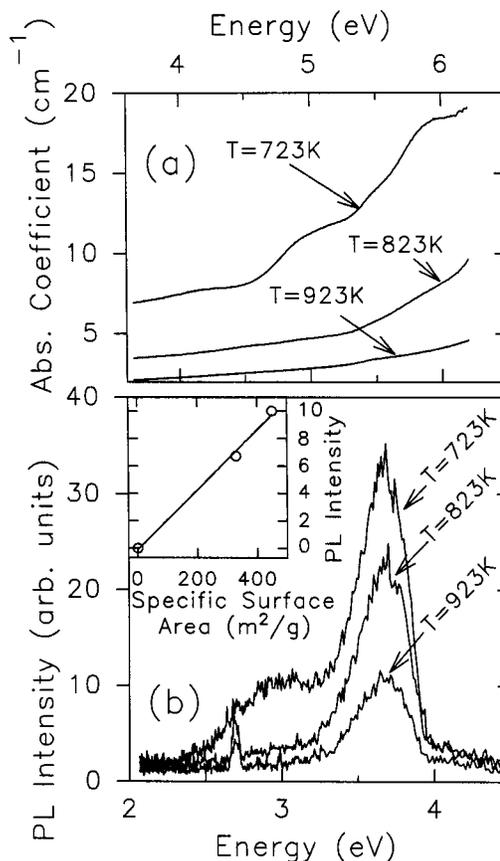


FIG. 3. (a) Optical absorption spectra in samples treated at  $450^\circ\text{C}$ ,  $550^\circ\text{C}$ , and  $650^\circ\text{C}$ . (b) PL spectra of the same samples excited at 5.5 eV. (Inset) 3.7 eV PL intensity vs specific surface area of the samples.

From our results different kinds of PL activity may be discriminated and ascribed to distinct emitting sites: (a) the 3.7 eV PL [a-PL] excited at 5.5 eV with 4 ns of lifetime, observed in the sample treated at  $T \leq 650^\circ\text{C}$ ; (b) the less stable emissions at 2.9 and 3.8 eV [b-PL], the former excited at 5 and 6 eV, the latter between 6 and 7 eV, both with about 4 ns of lifetime; (c) the emission at 4.2 eV [c-PL] with 8 ns of lifetime and a single excitation channel at 6.5 eV.

None of these PL activity matches known emissions of bulk silica. Indeed, PL in bulk silica usually arises from doping or radiation damage,<sup>1,10</sup> whereas pure stoichiometric silica does not show any PL. In our samples impurity content is negligible and no UV PL is indeed observed after complete sintering. So, intrinsic defects with “exotic” geometry (not typical of glassy silica) are responsible for this PL. Their possible features will now be discussed.

The 3.7 eV band is quite similar to the emission observed at 3.3–3.7 eV in OPS by exciting in the range 4.0–5.5 eV.<sup>6</sup> Different attributions were proposed: (i) small silicon clusters,<sup>8</sup> consisting of Si sites surrounded by four adjacent silicon atoms sharing one electron ( $E'_\delta$  center)<sup>4</sup> or two electrons (after radiative annihilation of  $E'_\delta$ );<sup>7</sup> (ii) ODCs similar to bulk defects of  $\text{SiO}_2$ <sup>5,6</sup> (as O–Si–O sites) in the oxide at the interface of Si nanoclusters. However, the relatively fast PL decay kinetics (few ns)—never measured before the present work—differentiates a-PL from emissions due to ODC in glassy silica, which always show a long-lived (10–

1000  $\mu\text{s}$ ) component ( $\beta$ -like PL).<sup>1</sup> Alternative models should thus be looked for.

The dependence of PL intensity on the specific surface indicates that a-PL is related to surface emitting centers of the oxide. Moreover, the spectral position of a-PL is unaffected by changes of Si–O–Si linkage geometry as revealed by Raman spectroscopy. Therefore, a-PL may be assigned to emitting centers localized at the surface of the oxide and with nonbonding apical-like geometry. The closeness of the 5.5 eV excitation band with the well known  $E'_\gamma$  and  $E'_\beta$  absorption bands at 5.8 and 5.4 eV, respectively,<sup>1,11</sup> might suggest the attribution to a surface apical  $E'$ -like center. Apical  $E'$  centers are threefold coordinated silicon sites with an unpaired electron in a  $sp^3$  Si orbital, as definitely demonstrated by EPR studies.<sup>11</sup> Although  $E'$  centers are characterized by a well assessed experimental lack of any PL emission in bulk silica,<sup>1,11</sup> recent theoretical calculations<sup>12</sup> suggest surface variants of the  $E'$  center might decay through radiative transitions. We controlled this possibility by looking for the EPR fingerprint of the  $E'$ -like center. No signal was observed above the detection limit, although the area below the 5.5 eV optical absorption band indicates that the concentration of the responsible defects is relatively high (taking the oscillator strength value of the  $E'$  center to be about 0.1.<sup>11</sup>) Therefore, assignments to  $E'$ -like structures are to be ruled out, as well as attributions to ODC of bulk silica, as suggested by the peculiarities of the excitation pattern and PL lifetimes described above.

Much more than a-PL, the spectral features of b-PL (by supposing for simplicity a single origin of the 2.9 and 3.8 eV PL bands) might slightly resemble the well known  $\alpha$ - $\beta$  PL pattern of ODC in glassy SiO<sub>2</sub>, where emissions are observed at 3.1 and 4.2 eV, the former excited at 3.7 and 5 eV while the latter is at 5 eV (neglecting high energy excitation channels).<sup>1,13–15</sup> The shift of PLE energies (from 3.7 and 5 eV to 5 and 6 eV coming from glassy to porous silica) might be consistent with theoretical calculations<sup>16</sup> which showed that ODC transition energies should decrease by increasing the mean Si–O–Si angle in the network. But the lifetimes of 2.9 and 3.8 eV PL are in the ns domain, whereas  $\beta$  3.1 PL in glassy SiO<sub>2</sub> has a long lifetime (about 100  $\mu\text{s}$ ).<sup>1</sup> This large difference is indeed difficult to justify within this analogy since changes of linkage geometry, such as those suggested by Raman spectra, may hardly increase the transition prob-

ability by a factor of  $10^4$ – $10^5$ . Different attributions should be considered.

With regard to c-PL, this emission does not possess a counterpart in glassy silica. Data regarding b-PL and c-PL in porous silica were never reported, probably because of its high excitation energy. Our results suggest assigning these activities to diamagnetic centers.

In summary, the detailed map of the UV PL of porous silica has been reported, showing the presence of the UV PL observed in OPS and SNS and clarifying excitation and decay features previously unreported. It was also found that the UV PL intensity can be controlled by changing the material surface area. Assignments to specific defects have been discussed, suggesting the attribution of a-PL to apical-like surface centers, distinct from  $E'$  sites. A revision of previous conjectures on the origin of UV PL of porous silica should be considered.

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