

Ultraviolet Photoluminescence of Silanol Species in Mesoporous Silica

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The optical properties of sol–gel synthesized porous silica excited by synchrotron radiation in the 4–10 eV range of samples with different porosity at 8 K and room temperature are reported. The analysis of the ultraviolet photoluminescence indicate the contributions of two different emitting centers. The spectral and temporal characteristics of the two luminescence bands are reported: emission peaks at about 3.7 and 4.0 eV, excitation channels around 5.4–5.7 and 6.2–6.5 eV, and mean lifetimes of about 17 and 2 ns, respectively. The analysis of the optical properties in samples with different porosity allows us to propose a silanol-related model for the two centers.

I. Introduction

The growing interest in porous silica (PS) lays on its possible applications in the optoelectronic field: the observed ultraviolet (UV) emission at about 3.7 eV shares common optical features with UV photoluminescence (PL) of oxidized porous silicon, silicon nanostructures, and silicon oxide films.^{1–3} Beyond the technological development of silicon-based UV-emitting devices, the analysis of these optical properties as a function of the porous media could help to clarify the debated origin of the UV and visible luminescence in porous silicon.^{4–7}

Porous silica properties are related to the surface chemistry of the samples. The surface of sol–gel synthesized PS is generally terminated with OH groups bounded to a silicon atom, SiOH units called silanols.^{8,9} Depending on the hydrogen-bonding interaction, which means depending on the surface curvature,⁸ different forms of silanol units can be expected: isolated, geminals, and vicinals.^{8,9} The concentration of OH groups at the surface is about 4–5 OH/nm², and it is almost independent of the synthesis conditions of porous silica.⁸

As regards the PL properties, the effects of the chemical and physical structure of the PS surface call for emitting surface centers.¹⁰ Indeed, experimental and theoretical works have indicated OH and H related centers as possible candidates of the PL observed in PS and porous silicon.^{6,11–15} By exciting in the UV range, PS displays a composite PL^{10,16,17} whose contribution at about 3.7 eV has been ascribed to OH-related surface defects.^{16,17} However, the attribution of the reported spectroscopic data to a specific defect is still lacking. In a recent paper,¹⁸ we have investigated the time-resolved photoluminescence of mesoporous silica with pore diameter of 3.2 nm, and we have ascribed the reported PL characteristics to two different interacting surface silanols. The spectral characteristics were emission peaks at about 3.7 and 3.9 eV and decay time of about 20 and 2 ns, respectively. In this paper, we present a detailed optical characterization of these defects in PS samples with different porosity. The analysis of spectral and temporal properties of the UV PL band by means of synchrotron radiation

TABLE 1: Characteristics of the Porous Samples^a

| sample | Φ (nm) | SSA (m ² /g ¹) | ρ (g/cm ³) |
|--------|-------------|---------------------------------------|-----------------------------|
| S1 | 3.2 | 594 | 1.2 |
| S2 | 5.5 | 540 | 0.9 |
| S3 | 7.5 | 525 | 0.7 |
| S4 | 18.2 | 264 | 0.6 |

^a Φ = pore diameter (5% standard deviation); SSA = specific surface area; ρ = density.

over an extended excitation energy range allows us to resolve the contribution of two kinds of UV emitting defects with the following characteristics: emission peaks at about 3.7 and 4.0 eV, excitation channels at 5.5 and 6.5 eV, and mean lifetimes of about 17 and 2 ns, respectively. By combining the reported spectroscopic data with vibrational evidences,^{19,20} we propose to associate the observed optical features as follows: emission peak at 3.7 eV, excitation channels at 5.4 and 6.2 eV, and mean decay time of 17 ns to the strong interacting silanols (IS-1); emission peak at 4.0 eV, excitation channels at 5.7 and 6.5 eV, and mean decay time of 2 ns to weak interacting silanols (IS-2).

II. Experimental Methods

Measurements were performed on sol–gel synthesized porous silica monoliths produced by Geltech Inc. (U.S.). Investigated samples have pore diameters ranging from 3.2 to 18.2 nm (5% of standard deviation); details are reported in Table 1.²¹

Photoluminescence (PL) and excitation of PL (PLE) measurements were carried out at the SUPERLUMI experimental station on the I beamline of the HASYLAB synchrotron laboratories at Desy (Hamburg) by using the pulsed excitation light of the synchrotron radiation (SR). The PLE measurements were performed in the 4–10 eV energy range with 0.3 nm of bandwidth. Excitation spectra were corrected for the spectral efficiency of the excitation source by using a sodium salicylate standard. The PL signal was dispersed by a 0.5-m Czerny–Turner monochromator and was detected in the 1.5–5.0 eV energy range with a photomultiplier (Valvo XP2020Q). Emission bandwidth was 16 nm. PL and PLE spectra were recorded under multibunch operation and were detected with an integral time

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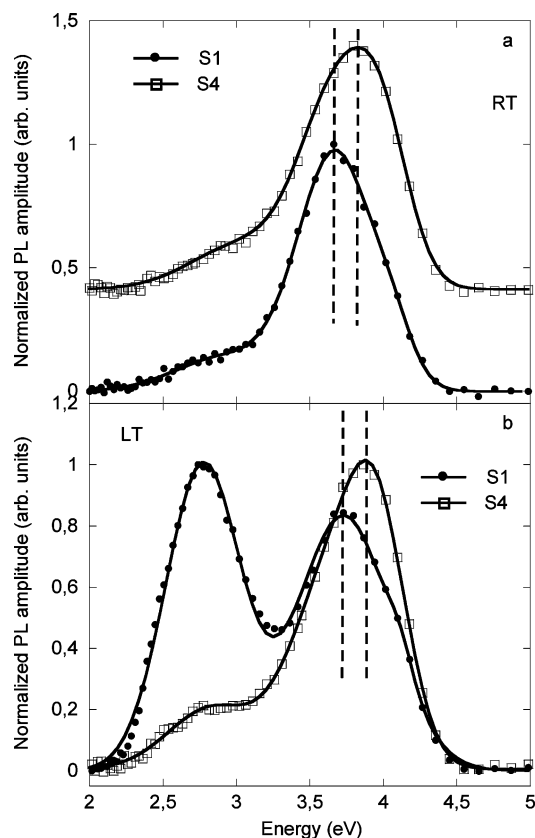


Figure 1. Normalized PL spectra of S1 and S4 samples excited at 5.64 eV at RT (a) and LT (b); lines are fitting curves (see text and Table 2 for details).

window of 192 ns correlated to the SR pulses. Time-resolved PLE spectra were acquired over time windows of 20 and 150 ns and delay time with respect to the exciting synchrotron radiation pulse of 1.5 and 40 ns, respectively. Decay time in the ns domain was gathered under single-bunch operation, using 1024 channels to scan the 192-ns interval time between adjacent pulses (pulse width of 0.2 ns²²). A continuous-flow liquid helium cryostat was used to set the temperature of the sample chamber at 8 K (LT).

III. Results

The PL spectra of S1 and S4 samples at room temperature (RT) and at LT excited at 5.64 eV are shown in Figure 1. Because of the similarities of S2 and S3 PL spectra to those of S1 and S4, respectively, the former spectra are not reported for the sake of clarity. The spectra have been arbitrarily rescaled to their maximum to better compare peak position and shape. Two main contributions can be detected in the visible and UV range: the peak position of the UV band blue shifts from S1 to S4 samples both at RT and at LT, from 3.6 eV to 3.8 eV at RT, and from 3.7 to 3.9 eV at LT. In addition, the PL spectrum of S1 sample at LT shows a shoulder in the high-energy range, at about 4.0 eV. The relative intensity ratio of the UV band with respect to the visible one changes at LT and depends on the samples; however, the analysis of the blue band is beyond the scope of this article. The blue shift of the peak position and the observed shoulder in the S1 sample at LT indicate the presence of two different emissions in the UV range. The spectra have been successfully fitted with three Gaussian bands (one to heuristically account for the contribution of the visible band) by means of a least-squares fit procedure (square correlation factor $R^2 \geq 0.99$). As reported in Table 2, the UV band is

TABLE 2: Spectral Characteristics (in eV) of the Gaussian Bands Used to Fit the PL Spectra of Figure 1^a

| sample | | g1 (E_0 - fwhm) | g2 (E_0 - fwhm) | g3 (E_0 - fwhm) | A(g2)/A(g3) |
|--------|----|-----------------------|-----------------------|-----------------------|-------------|
| S1 | RT | 2.94–0.82 | 3.67–0.58 | 4.07–0.32 | 12.0 |
| | LT | 2.77–0.60 | 3.73–0.74 | 4.11–0.20 | 38.5 |
| S2 | RT | 2.81–0.63 | 3.69–0.65 | 4.17–0.52 | 9.7 |
| | LT | 2.75–0.59 | 3.71–0.72 | 4.07–0.28 | 40.7 |
| S3 | RT | 3.15–1.34 | 3.74–0.60 | 4.02–0.41 | 3.6 |
| | LT | 2.79–0.65 | 3.69–0.68 | 3.99–0.44 | 2.4 |
| S4 | RT | 3.05–0.84 | 3.69–0.60 | 4.00–0.43 | 2.4 |
| | LT | 2.83–0.69 | 3.66–0.67 | 3.97–0.47 | 1.50 |

^a Peak position (E_0 , maximum standard deviation 5%), full width at half maximum (fwhm, maximum standard deviation 15%), integrated area ratio, A(g2)/A(g3).

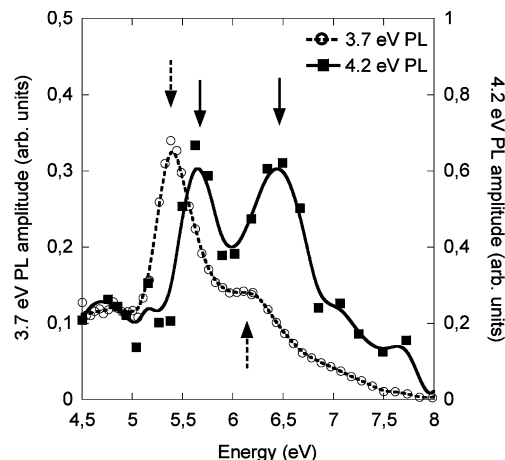


Figure 2. PLE spectra of 3.7 and 4.2 eV emissions in S1 samples (lines are guides for the eyes).

composed by two emissions at about 3.7 and 4.0 eV in all the samples but with relative weight depending on the sample: the contribution of the 4.0 eV emission band increases with respect to the one of the 3.7 eV in samples with larger pore diameter (S3 and S4).

In Figure 2, the PLE spectra recorded at RT for the emission energies of 3.7 and 4.2 eV are reported. The spectra show two main channels for both the emissions, peaked at 5.4 and 6.2 eV for the 3.7 eV PL and at 5.7 and 6.5 eV for the 4.2 eV PL, with different relative intensities. Other excitation channels can be individuated at 4.8 and above 7.0 eV.

The picture of two UV emitting centers is supported by the decay time measurements reported for the 3.7 eV emission energy excited at 5.64 eV at RT (Figure 3a) and at LT (Figure 3b). The whole set of samples shows a nonsingle exponential decay. Indeed, the recorded data can be successfully fitted with two exponential decays with mean lifetime of about 2 and 17 ns (details are reported in Table 3, square correlation factor $R^2 \geq 0.97$).

To complete the observed scenario, the PLE spectra at two different time delays (1.5 and 40 ns) with respect to the SR pulse and with different time windows (20 and 150 ns) have been recorded. In Figure 4, the PLE spectra of the 3.7 eV PL band at RT are reported: among the three excitation channels at 4.8, 5.4, and 6.2 eV observed with the shortest time windows, the 5.4 eV one is the only observed one also with the longest time windows. As regards the PLE spectra of the 4.2 eV band, no PL signal was detected with the second time window. Thus, we can deduce that the emission at about 4.0 eV is characterized by the shortest decay time (2 ns), while the emission at 3.7 eV is characterized by the longest decay time (17 ns).

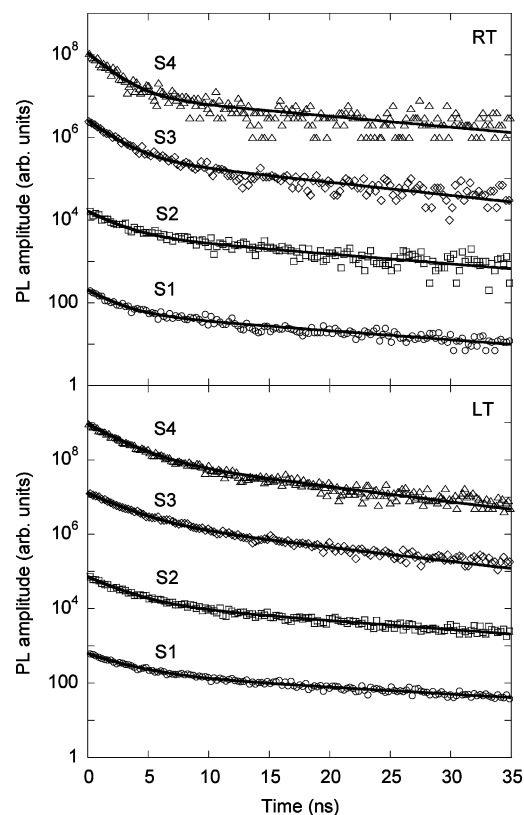


Figure 3. Decay time spectra of 3.7 eV emission excited at 5.64 eV at RT (a) and LT (b); lines are fitting curves (see text and Table 3 for details).

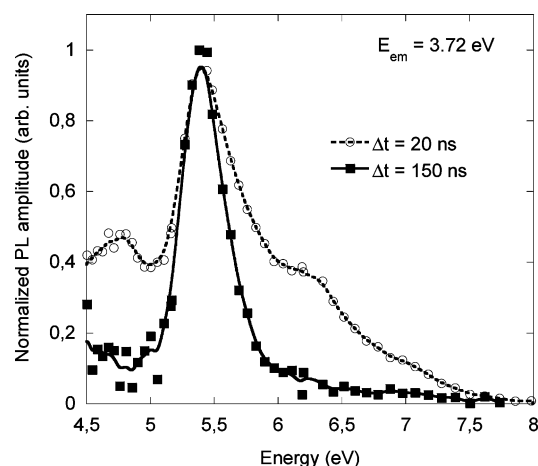


Figure 4. PLE spectra of 3.7 eV PL band at different delays from the excitation pulse and with different temporal windows (lines are guides for the eyes).

By collecting all the results here reported, we can conclude that two different distributions of emitting centers can be excited in the UV range in mesoporous silica: the first one is characterized by an emission centered at 3.7 eV, excitation channels at 5.4 and 6.2 eV, and lifetime of about 17 ns; and the second one is characterized by an emission peaked at 4.0 eV, excitation channels at 5.7 and 6.5 eV, and lifetime of about 2.0 ns.

IV. Discussion

As reported in a recent paper,¹⁹ the Raman spectra of porous silica with different pore diameters in the 3200–3900 cm^{-1} range can be resolved in the contribution of three different kinds

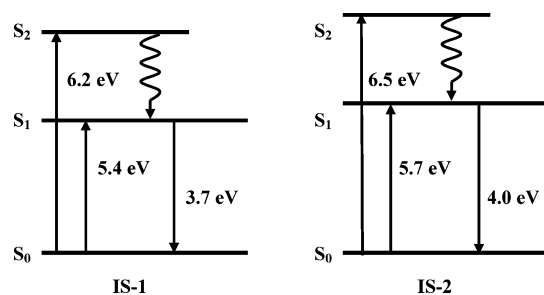


Figure 5. Schematic picture of electronic levels of interacting silanols; vertical arrows represent radiative transitions, and curled arrows indicate nonradiative transitions.

TABLE 3: Time Decays of 3.7 eV PL Band Excited at 5.64 eV as Deduced from Best-Fit Procedure

| sample | RT | | LT | |
|--------|---------------|------------|---------------|------------|
| | τ_1 | τ_2 | τ_1 | τ_2 |
| S1 | 2.1 ± 0.1 | 20 ± 1 | 3.0 ± 0.1 | 24 ± 1 |
| S2 | 2.2 ± 0.1 | 18 ± 1 | 2.7 ± 0.1 | 18 ± 1 |
| S3 | 1.9 ± 0.1 | 14 ± 1 | 2.5 ± 0.1 | 12 ± 1 |
| S4 | 1.7 ± 0.1 | 16 ± 1 | 2.3 ± 0.1 | 11 ± 1 |

of surface silanol centers (Si–OH): isolated silanols, with vibration mode peaked at 3750 cm^{-1} , and two species of interacting silanols via hydrogen bonding, the strong ones with Raman peak at about 3525 cm^{-1} and the weak ones with vibration peak around 3660 cm^{-1} .^{8,23} The contribution of strong and weak interacting silanols depends on the porosity of the samples: the weight of weak interacting silanols with respect to strong ones is larger in samples with larger pore diameter. As expected, the larger the curvature of the pore, the larger the hydrogen-bonding interaction between neighboring silanols.¹⁹ In addition, because of its dependence on the hydration conditions of the samples, the UV PL excited at 5.6 eV has been ascribed to interacting silanol species.^{16,17} Indeed, absorption bands in the UV range have been observed in high surface silica and have been related to paramagnetic Si–OH and Si–H defects.²⁴ In a recent paper,¹⁸ we reported the UV PL properties of mesoporous silica with pore diameter of 3.2 nm and proposed the attribution of the observed spectroscopic characteristics to two kinds of interacting silanols (IS-1 and IS-2). The data here reported allow us to proceed further in the proposed interpretation. The contributions of the two PL bands depend on the sample porosity (Table 2): the relative intensity of the PL band at 4.0 eV with respect to the 3.7 eV one is larger in samples with larger pore diameter. Moreover, the reported time decays call for emitting centers with different contributions of non-radiative de-excitation pathways. According to the following equation: $\tau = (k_r + k_{nr})^{-1}$, k_r and k_{nr} being the radiative and nonradiative decay rate constants, a longer time decay (τ) is expected if the emitting center is characterized by a stronger interaction with the surrounding environments. In addition, the ns domain of the lifetimes calls for singlet–singlet transitions.

On the basis of the previous discussion, the two emitting centers investigated in this paper could be identified as strong and weak interacting silanols, and we propose to assign the PL band at 4.0 eV to the weak interacting silanols (IS-2) and the PL at 3.7 eV to the strong interacting silanols (IS-1). The detected spectroscopic properties can be summarized with the electronic level scheme depicted in Figure 5 where the emission and excitation channels are reported.

A final comment pertains the modifications of time decays and relative contributions of the two PL bands at low temperature (Tables 2 and 3). Changing from RT to LT, the contribu-

tion of the 3.7 eV band increases in S1 and S2 samples with respect to the contribution of the 4.0 eV band while in S3 and S4 samples it decreases. It calls for a different surrounding of the defects in samples with different porosity: the local disorder around the defects could affect the PL quantum yield at LT. Indeed, different vibrational contributions might also explain the decrease of the longest time decay in S3 and S4 samples.

V. Conclusions

We have investigated the UV PL detected in porous silica with different porosity and individuated the contributions of two different centers. The spectral characteristics of the two centers are the following: emission peak at 3.7, excitation channels at 5.4 and 6.2 eV, and mean lifetime of about 17 ns; and emission peak at 4.0 eV, excitation channels at 5.7 and 6.5 eV, and mean time decay of 2 ns. We propose to associate the observed photoluminescence properties to strong and weak interacting surface silanols.

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