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OH-dependence of ultraviolet emission in porous silica

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Abstract

Photoluminescence and Raman measurements have been performed on sol–gel synthesized porous silica monoliths. Porous silica and polyethilenglycole/silica hybrids thermally treated at different temperatures have been analyzed. By exciting at 5.6 eV a structured photoluminescence emission centered at 3.7 eV is found in the whole set of samples. Hydration treatment of the pore surfaces increases the H-bonding interaction between silanols, inhibits the isolated silanols vibrations and changes the photoluminescence spectrum increasing the emission peaked at 3.7 eV.

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1. Introduction

The topic of porous materials has further increased the technological interest in silica [1]. Besides its environmental applications (adsorbent material, membranes, catalysis host) [2] the dielectric properties of porous silica films make the material a candidate for intermetal insulation in integrated circuit technology [3]. In the magnetic recording area sol–gel silicates are suitable host for iron nanocompounds [4] and for dye molecules in the optical field [5]. Recently the optical properties of the host silica itself have attracted attention because of their possible correlation with oxidized porous silicon [6] and silicon nanometer sized structures [7]. The ultraviolet (UV) photoluminescence (PL) reported for those materials recalls the UV emission observed in sol–gel prepared porous silica [8,9]. The attribution of this luminescence is still debated and includes different kinds of adsorbed water in Si–OH complexes [6,8,10,11] (including isolated and adjacent silanols) and water–carbonyl groups [10], apical-like Si surface centers and surface oxygen deficient centers [9]. Yao et al. [8] analyze the surface reactivity to OH and interpret the UV emission in terms of non-bridging oxygen hole centers. To determine the origin of the observed PL emission we performed a detailed analysis of differently synthesized porous silica samples. We present a comparative analysis of PL spectra of porous silica and polyethilenglycole (PEG) hybrids, supported

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by Raman scattering measurements. By showing the similarities of the emissions in the whole set of samples and the hydration effects on porous silica, we suggest that the PL activity in the 2.5–4.5 eV range is related to silanols and OH species adsorbed at the surface.

2. Experimental procedure

PL measurements were carried out at room temperature. A MgF_2-sealed Deuterium lamp (Hamamatsu mod. L1835) supplied the excitation light which was dispersed by 0.3 m scanning monochromator (McPherson mod. 218) under computer control; the final excitation spectral bandwidth was 5.0 nm. The PL signal was dispersed by a spectrograph (ARC-SpectraPro 275) and detected by a gatable intensified array (EG&G 1420). The spectral bandpass was 0.6 nm. The reported spectra are recorded applying a short wavelength cutoff filter (WG280) and corrected for the optical transfer function of the system.

Raman measurements were performed with a micro-Raman spectrometer (Dilor XY80). An argon ion laser operating at 514.5 nm (Coherent Innova90C-4) supplied the excitation. The signal, dispersed by a 600 grooves/mm grating, was detected by a 1024×256 LN_2 cooled charge coupled detector (CCD). The spectral resolution was ≈ 2.0 cm^{-1}.

PL and Raman measurements have been performed on a set of differently synthesized porous silica samples. Porous silica samples (produced by Geltech Inc.) via sol–gel route are provided in disks (diameter 6 mm, height 2 mm) with the pore diameter distribution peaked at around 3.2 nm, a pore volume of 0.488 $cm^3\,g^{-1}$ with a specific surface area of 594 $m^2\,g^{-1}$, (here after named samples A). Porous silica sol–gel synthesized samples thermally treated at 500 and 600 °C for 4 h (here after samples B and C, respectively) have a mean pore diameter about 3 nm and a specific surface of about 600 $m^2\,g^{-1}$ [12]. Porous PEG SiO_2 hybrid materials (here after samples D) have been prepared via sol–gel route by adding Polyethilenglycol-200 (PEG with an average molecular weight of 200) to the sol in a 35/65 weight ratio. The obtained xerogels have PEG embedded in the porous matrix [12]. Samples A have been studied both in their as-grown state and after having undergone a water treatment which is achieved by storing the sample in distilled water for about 12 h followed by evaporation in vacuum (10^{-2} Torr) of the inner pore water. The treated samples are fully hydrated and can contain clusters of free molecular water nested in puddles on the pore surface [13,14].

3. Results

The PL spectrum excited at 5.6 eV of samples A in their as-grown state is shown in Fig. 1. The excitation energy was selected in the 4.6–5.9 eV range as the most efficient in providing the PL activity. We observe a structured PL in the 2.5–4.5 eV range whose main features are a peak at 3.7 eV and a less intense component at about 4.1 eV. No variation of the PL shape and intensity is found with air exposure nor during excitation irradiation.

By exciting at 5.6 eV, similar spectra are found when studying the other sets of samples B, C and D as shown in Fig. 2. For a better comparison,

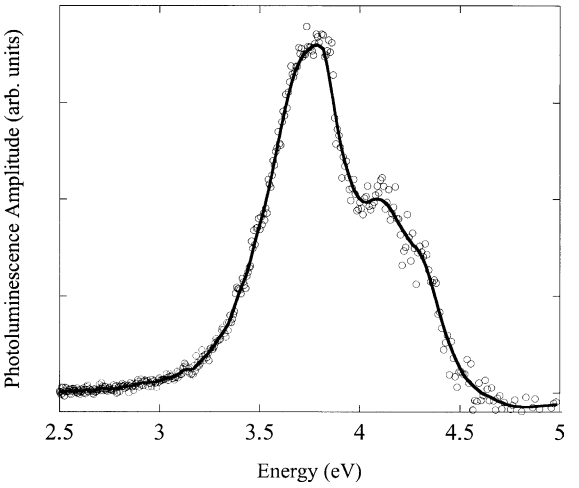

Fig. 1. Room temperature PL spectrum of porous silica (samples A) excited at 5.6 eV. Circles are experimental data, line is a guide for the eye.

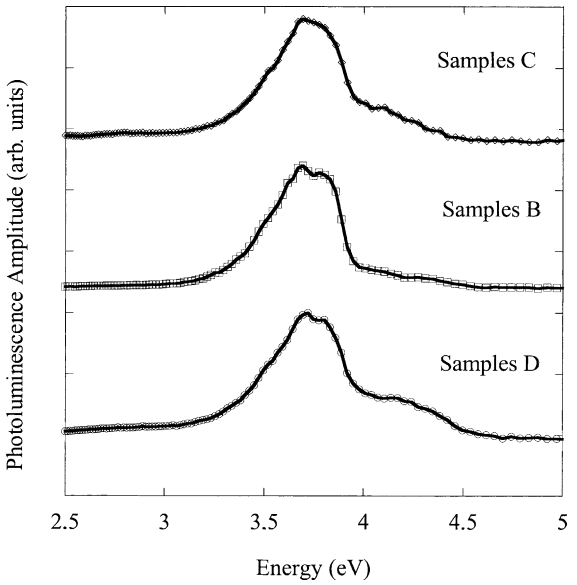

Fig. 2. PL spectra of porous silica excited at 5.6 eV of porous silica synthesized at 600 °C (samples C), porous silica synthesized at 500 °C (samples B) and PEG/SiO_2 hybrid (samples D). Markers are experimental data, line is a guide for the eye.

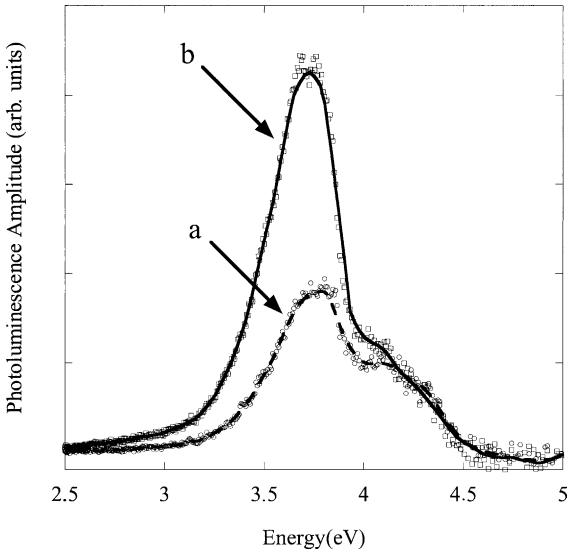

Fig. 3. PL spectra of porous silica (samples A) excited at 5.6 eV: as-grown (a) and water-treated (b). Lines are a guide for the eye.

emission intensities have been normalized to their maxima and baselines arbitrarily shifted.

Fig. 3 shows PL spectra of as grown and water treated porous silica samples A. We observe increases of the 3.7 eV component with respect to the 4.1 eV band in the water treated samples. Both as-grown and water treated samples have Raman activity in the O–H stretching range as shown in Fig. 4. A composite band, whose main peak is located at 3450 cm^{-1} and other components are located at about 3230, 3590 and 3700 cm^{-1} is found. A peak with a smaller width is detected at 3750 cm^{-1} only in as grown samples.

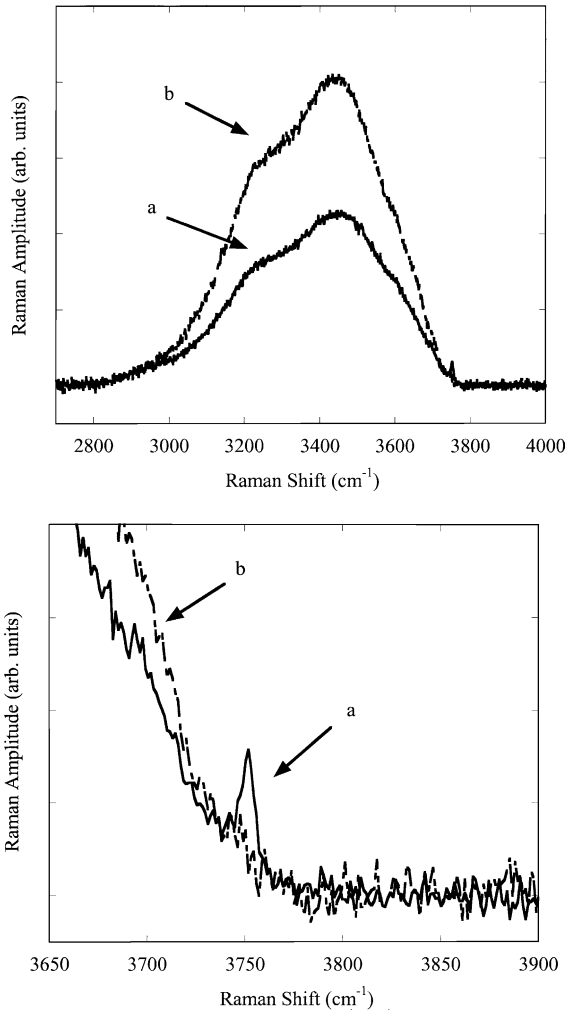

Fig. 4. O–H stretching range Raman spectra of porous silica (samples A): as-grown (a) and water-treated (b). A detail of the isolated silanol vibration band is shown in the lower panel.

4. Discussion

Porous silica prepared via sol–gel route has an open, branched and interconnected pore structure in a 'fractal like geometry' and its surface is naturally terminated in OH groups, forming SiOH groups (silanols) [15,16]. Porous silica UV PL has several similarities with the light emission from oxidized porous silicon [6,9,10]. The origins of PL in porous silica are still debated and several attributions have been proposed: Si–OH complexes [6,8,11], water–carbonyl groups [10], apical-like Si surface centers and surface oxygen deficient centers [9]. Comparing the UV PL of differently synthesized samples, we suggest that the center responsible for the observed activity is a surface center. Indeed, all the analyzed samples, although differing from the chemical composition of the silica walls, display a comparable PL activity, as shown in Fig. 2 where a composite PL in the 2.5–4.5 eV excited at 5.6 eV is observed. In addition, the attribution of the observed PL to a surface center is well confirmed by the dependence of the intensity of the 3.7 eV on the specific surface of porous silica [9].

From analysis of the PL spectra of the porous silica samples, synthesized at different temperatures, we establish that the observed luminescence is not related to organic compounds: samples C, thermally treated at 600 °C are completely calcinated, that is they do not contain any organic residual left in by the sol–gel synthesis and originating from precursors, templates and/or catalysts. Although free of organic residuals, the C samples have a comparable PL activity with the other sets of samples. Moreover, the lack of dependence of the observed emissions on the chemical composition of the matrix (sample D—Fig. 2) supports the attribution of the PL to a non-organic surface center.

The Raman spectra analysis in the O–H stretching mode (Fig. 4) indicates that the water treatment modifies the surface morphology of the samples: a Raman activity is found in the range of the O–H stretching (Fig. 4). The broad band peaked at about 3450 cm^{-1} originate from different sets of OH oscillators present at the silica surface: namely silanols (vicinal and geminal) and water molecules (adsorbed or engulfed in the pores) [16,17]. The fundamental difference in the Raman spectra of the treated samples, with respect of the as-grown ones, is the 3750 cm^{-1} peak. This vibrational band is due to the presence of isolated silanols [16,17], which are absent in the water treated samples. Some minor differences in the O–H stretching band appear due to the presence of water adsorbed at the surface or nested in puddles within the pores.

The presence of water increases the hydrogen bonding between superficial hydroxyls linking previously isolated silanols. As a consequence, the 3750 cm^{-1} vibration disappears. Based on the increase of PL at about 3.7 eV upon water treatment we suggest the observed emissions are not related to isolated silanols but to interacting OH-related centers. The modification induced by the treatment confirms a surface location of the centers emitting in the UV and that the observed activity is related to the hydroxyl concentration and coverage of the inner surface. The unobserved reactivity to the ambient atmosphere, in contrast to previously reported experiments [8], can be explained as follows: the as-prepared samples are already in equilibrium with the OH contained in the air or, at least, they present an equilibrium rate faster than the time technically required to perform measurements. Whatever the explanation, the PL emissions should be ascribed to some surface species whose emission spectrum can be modulated by the OH concentration and even increased as the concentration of hydroxyl at the inner pore surface increases. Further experiments, including chemical and physical treatments, are in progress to verify this interpretation.

5. Conclusion

By exciting at 5.6 eV porous silica emission of a structured PL in the 2.5–4.5 eV range with main contributions at 3.7 and 4.1 eV is observed. Based on the comparative analysis of differently synthesized porous silica samples we attribute the UV fluorescence in sol–gel prepared porous silica to surface centers. We have found that PL emission does not depend on the chemical composition of

the samples but it is related to the chemical and the physical states of the surfaces. We conclude that the observed emissions are not related to water carbonyl groups. Changing the OH coverage of the inner pore surface changes the PL spectrum.

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