SiO_2:Ge photoluminescence: Detailed mapping of the excitation-emission UV pattern

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Photoluminescence (PL) data on SiO_2:Ge samples have been obtained at 9 and 300 K by synchrotron radiation excitation, achieving a detailed mapping of the emission/excitation pattern in the UV and VUV energy range. Emission/excitation PL data have been analyzed by means of two-variables Gaussian components. New PL features have been identified, clarifying the composite nature of the excitation structure. The analysis of the high-energy portion of the collected spectra confirms that the α and β emissions possess several excitation channels. The overall pattern calls for at least three distinct types of PL centers to justify the observed PL components: at about 3.1 and 4.3 eV (excited at 7.3, 6.6, and 5.4 eV), at 4.4 eV (excited at 5.1 eV), and 2.9 and 3.9 eV (excited at about 7.0 and 4.7 eV). [S0163-1829(98)03304-9]

I. INTRODUCTION

Oxygen deficient centers (ODC's) in various configurations play a key role in the absorption and emission ultraviolet (UV) spectra of silica and silica-based oxides.[1] Also photoinduced processes—such optical absorption changes, volume increase, and refraction index modulation–are generally interpreted as arising from defect kinetics involving this type of defects.[2,3] All these facts motivated a wide interest in the definition of the specific structural and electronic ODC configurations. Concerning the native variants of ODC, they appear diamagnetic and undetectable by paramagnetic resonance measurements, so, their detailed characterization has not been achieved until now. Further complications come from the possible presence of both intrinsic and extrinsic ODC in multinary systems, as SiO_2:Ge-based materials, extremely interesting for technological applications in optical fiber communications. ODC structures were proposed to account for the UV absorption in this type of materials. In particular, the absorption bands at about 5.2–5.4 and 7.3 eV [accompanied by two photoluminescence (PL) emissions, the α band at $\sim$4.3 eV and the β band at 3.1 eV] are generally ascribed to ODC. These features have very similar counterparts in irradiated and oxygen-deficient pure silica (absorption bands at 5.0 and 7.6 eV and PL bands at 4.4 and 2.7 eV). Few proposals were made for the local structure of the ODC's responsible for the observed phenomenology: the neutral oxygen vacancy (Si-Si with the related Ge-perturbed variants),[4,5] the twofold coordinated cation (Si^{2+} and related extrinsic variants),[6,7] and the oxygen divacancy.[8] No clear evidence exists favoring an attribution over the others or supporting the coexistence of distinct types of ODC. Evaluations of the expected electronic transitions suggest that both Si-Si and Si^{2+}-like structures could match the experimental findings.[6,9,10] Some refinement of these models is probably needed to explain the role of high energy excitations and details such as the observation of structured features in the PL bands.[11–15]

In order to clarify the detailed features of the excitation/emission pattern of Ge-doped silica, we carried out an accurate spectral mapping of the PL excited by synchrotron radiation. The results show new features and suggest that at least three types of PL centers are to be considered to account for the observed pattern.

II. EXPERIMENTAL PROCEDURE

Samples were obtained from Ge-doped silica glasses (0.03, 2, and 10 at. % Ge) from commercial preforms of optical fibers prepared by the modified chemical vapor deposition (MCVD) method (by FOS, Battipaglia, Italy) and from samples obtained by sol-gel preparation (by GDE, Novara, Italy). Measurements were carried out by employing synchrotron radiation at the SUPERLUMI experimental station of HASYLAB at DESY (Hamburg, Germany) equipped with a 2 m primary monochromator, both at 300 and 9 K. The excitation spectral bandwidth was 0.3 nm. Photoluminescence excitation (PLE) and PL signals were detected by a charge coupled device (CCD) camera with 3 nm of emission bandwidth. Data were corrected for the optical response of the apparatus. Energy density of synchrotron radiation on the sample was of the order of 0.1 J/cm^2 after a complete measurement, with a power density per single pulse of about 0.1 W/cm^2. No photoinduced effect was observed in the PL spectra as a result of the synchrotron excitation, consistently with the very low power density employed compared with the values needed to observe such processes.[3] In fact, comparison between absorption spectra collected before and after luminescence measurements does not evidence any detectable change. Three-dimensional spectra were obtained by collecting PL emission at different excitation energies. Deconvolutions of the spectra were performed by using two-dimensional Gaussian functions:

$$I = I_0 \exp\left[-\frac{1}{2}\left(\frac{E_{\mathrm{emi}} - E_{0(\mathrm{emi})}}{\sigma_{\mathrm{emi}}}\right)^2 - \frac{1}{2}\left(\frac{E_{\mathrm{exc}} - E_{0(\mathrm{exc})}}{\sigma_{\mathrm{exc}}}\right)^2 \right].$$

In one case it was supposed that the mean emission energy increases linearly with the excitation energy (see next section). In this case, the function takes the following form:

$$I = I_0 \exp\left[-\frac{1}{2}\left(\frac{E_{\mathrm{emi}} - (E_{0(\mathrm{emi})} + a(E_{0(\mathrm{exc})} - E_{\mathrm{exc}}))}{\sigma_{\mathrm{emi}}} \right)^2 - \frac{1}{2}\left(\frac{E_{\mathrm{exc}} - E_{0(\mathrm{exc})}}{\sigma_{\mathrm{exc}}} \right)^2 \right],$$

where a is a multiplicative factor. The FORTRAN subroutine MINUIT,[16] running on a VAX 7000/230, was used in all calculations. A complete deconvolution procedure of a three-dimensional (3D) spectrum (about 30 000 experimental points and more than 25 free parameters) required about 1 h of CPU/time, but this time can be greatly reduced (at about 600 s) by analyzing separately the high and low excitation energy regions.

III. RESULTS

All the SiO_2:Ge samples investigated in the present work give quite comparable results whose main features consist of PLE spectra of the well known α and β emissions (at about 4.3 and 3.1 eV, respectively) showing bands at about 5, 6.6, and 7.3 eV (with slightly sample-dependent PLE relative intensities), substantially consistent with all the data reported up to now.[12,13,15,17–19] As an example, Fig. 1 displays surface plots of the excitation-emission features at 9 K in the case of a selected representative sample (SiO_2:Ge with 2 at. % Ge produced by the MCVD method).

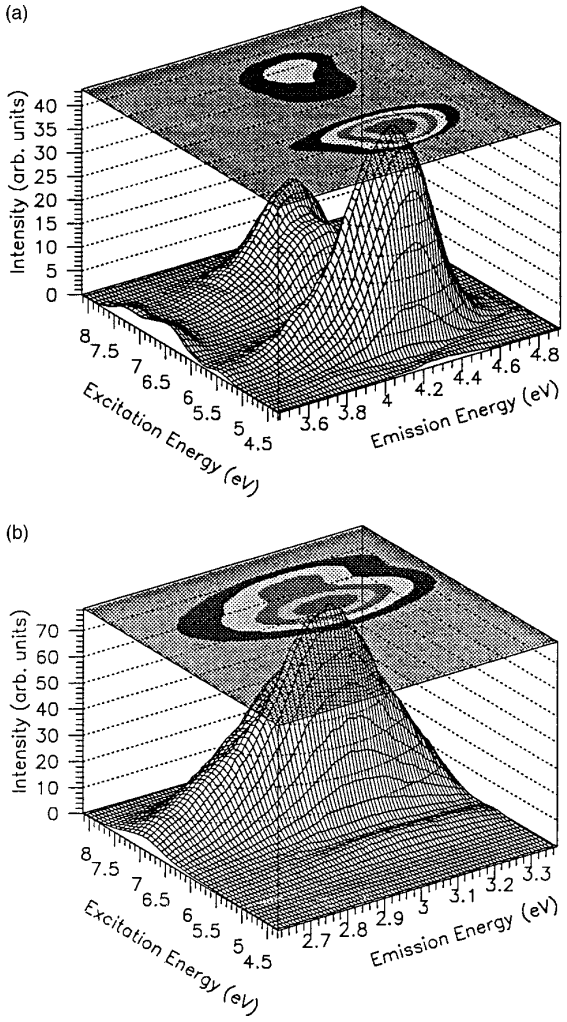

FIG. 1. Three-dimensional view of the 9 K PL spectra (a) in the α region (around 4 eV) and (b) in the β region (around 3 eV), as a function of the excitation energy, in a SiO_2:Ge sample (2 at. % Ge) produced by MCVD. [The feature at high emission energy in (a), linearly drifting from 4.4 to 4.8 eV, is due to reflected excitation light, only partially suppressed to clarify the figure.]

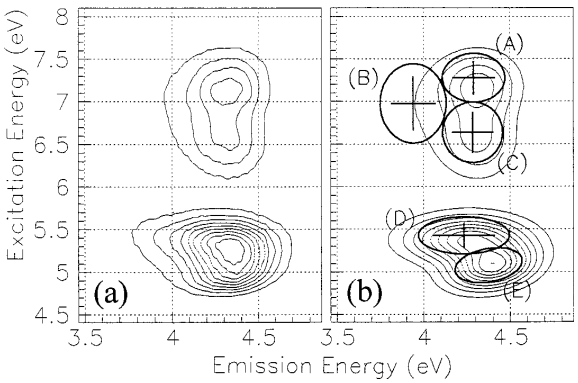

FIG. 2. Contour plot of the experimental data in the α region (a), collected at 9 K for a SiO_2:Ge sample with 2 at. % Ge produced by MCVD, compared with the bidimensional fit in Gaussian components (b). In (b) the centers of the components are indicated together with the isointensity lines giving the FWHM.

The detailed mapping of the excitation-emission pattern shows some previously unobserved features. Figures 2 and 3 show these new findings. In the α emission region, centered at 4.3 eV [Fig. 2(a)], a complex excitation structure is observed around 5 eV. No evident composite feature is observed in the 5 eV excitation range of the β region [Fig. 3(a)]. At higher excitation energies around 7 eV, both α and β bands show unexpected components [besides the previously identified ones at 6.6 and 7.3 eV (Ref. 12)] giving rise to broad low energy tails excited at 7 eV. We remark that most of this evidence would be probably lost by collecting conventional PL (PLE) spectra at a few fixed excitation (emission) energies around the main peaks. This can probably explain why these features were not reported up to now by other authors.

In Figs. 2(b) and 3(b) we report the results of two-dimensional fits of the α and β PL, respectively. The results are summarized in Table I. Concerning the low-energy exci-

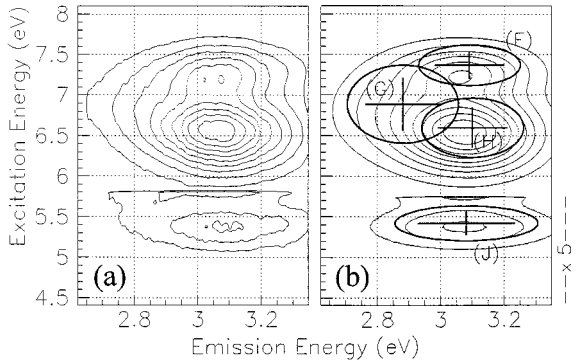

FIG. 3. Contour plot of the experimental data in the β region (a), collected at 9 K for a SiO_2:Ge sample with 2 at. % Ge produced by MCVD, compared with the bidimensional fit in Gaussian components (b). In (b) the centers of the components are indicated together with the isointensity lines giving the FWHM.

TABLE I. Peak energies E (eV), FWHM's (eV), and peak intensity I_0 (a.u.) of the spectral components from the two-dimensional fit of the excitation/emission pattern at 9 K of a SiO_2:Ge (2 at. % Ge) sample produced by MCVD.

α region	Excitation E	Excitation FWHM	Emission E	Emission FWHM	Intensity I_0
A	7.28	0.57	4.29	0.36	183
B	6.98	0.93	3.94	0.38	32
C	6.63	0.71	4.29	0.35	139
D	5.43	0.44	4.23	0.52	338
E	5.07	0.41	4.37	0.37	358
β region	Excitation E	Excitation FWHM	Emission E	Emission FWHM	Intensity I_0
F	7.37	0.50	3.09	0.32	376
G	6.89	0.96	2.88	0.35	213
H	6.60	0.73	3.10	0.32	686
I	5.42	0.43	3.08	0.45	46

tation region around 5 eV, all the numerical analyses showed that,while there is no evident reason to introduce more than one component in the fit of the β PL excited at 5.43 eV (Table I and Fig. 3), the α emission is not well reproduced unless one introduces several bands. However, a rather satisfactory deconvolution [Fig. 2(a)] can also be achieved in a simplifying approach by considering only two components (at 4.23 and 4.37 eV), provided that a small site selective excitation effect is taken into account for one of the two bands, i.e., the component at 4.37 eV excited at lower energy (at 5.07 eV). Such an effect could occur as a result of a sufficiently small homogeneous contribution to the bandwidth. In this respect, the 5.07 eV excitation band is clearly differentiated from the other components, which in turn should possess a homogeneous width comparable with the inhomogeneous broadening arising from the glassy structure of the material [the observation of very similar full width at half maximum (FWHM) in crystalline quartz supports this position[20]]. It is noteworthy that the two-components fit in the α region gives a 5.43 eV PLE band (0.44 eV wide) of the 4.23 eV PL well matching the low energy PLE band of the β emission (at 5.42 eV, with FWHM 0.43 eV).

As regards the high-energy part of the excitation pattern, three structures appear both in the α and β regions, well accounted for by six spectral components with a remarkable accordance of peak energies and FWHM's: three PLE components at about 6.6, 7.0, and 7.3 eV are observed both in the α and β regions with nearly the same FWHM for fixed excitation energy (see Table I for an easy comparison). Moreover, the emission energies of the α (or β) PL excited at 6.6 and 7.3 eV match together. These energies also correspond rather well with the value of the α (or β) PL excited in the low energy region at 5.4 eV, except for a minor shift a few tens of meV.

Two emissions peaked at 2.88 and 3.94 eV, clearly distinct from the α and β ones, are instead excited just below 7.0 eV (at 6.89 and 6.98 eV, respectively). These latter components were never observed. Contributions from these

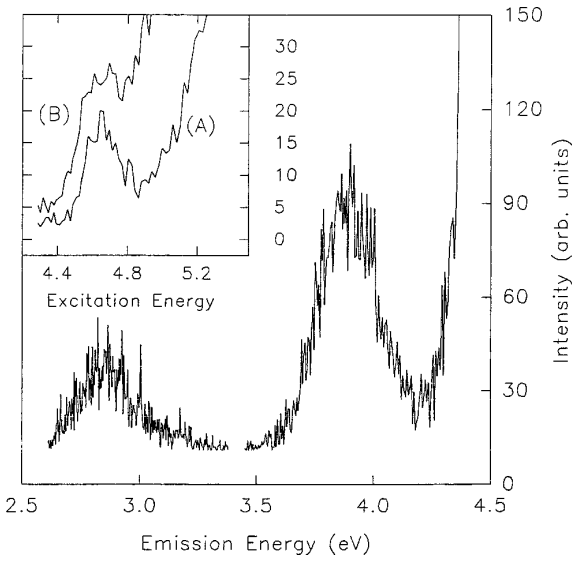

FIG. 4. 9 K PL spectrum excited around 4.6 eV in a SiO_2:Ge sample with 2 at. % Ge produced by MCVD. The spectrum is the average of 10 PL spectra excited within 30 nm around the reported energy. In the inset, PLE spectra of the emissions at (a) 2.9 and (b) 3.9 eV are shown.

emissions by exciting in the low-energy region of the excitation pattern (around 5 eV) are apparently lacking. But, a deeper inspection of the data indicates the presence of PL signals, just above the noise, by exciting below 5 eV: although no reliable analysis of these features seems possible from the surface plot data, clear evidence of their presence can be extracted by averaging several PL or PLE spectra. Figure 4 shows two PL bands peaked at about 2.9 and 3.9 eV, well distinct from the α and β bands and matching the peak energies of the new PL excited in the 7.0 eV band. PLE spectra in the UV region of these new emissions are reported in the inset, both showing a component at 4.7 eV.

IV. DISCUSSION

We will briefly comment the main PL pattern arising from the α and β emissions at 4.3 and 3.1 eV, then the new PL findings will be discussed in the light of their excitation features. Several analogies in Figs. 2 and 3 put in evidence the relevant similarity between the excitation patterns of the β and α bands, confirming a picture consistent with the model attributing these emissions to transitions of the same emitting site[6,10] (provided that more than one excitation channel is possible). The temperature dependence we observed by comparing the data at 9 and 300 K obtained by exciting at 5.4 eV is well consistent with the existence of a thermally activated interconversion process between singlet and triplet excited states.[6,10] On the other hand, energy transfer mechanisms from adjacent defect sites exciting the α singlet state should be responsible for the 6.6 eV excitation channel (according to Ref. 21), while the 7.3 eV component of the PLE spectra could be due to an excited level of the α-β PL sites. Alternative attributions to distinct defect sites admitting conversion towards the excited singlet state of the α-β center[12,22] have been apparently weakened by recent results on the temperature dependence of the PL lifetimes.[14]

Let us now regard the 4.37 eV component excited at 5.07

eV. Its attribution to defect sites clearly distinct from the α-β ODC is supported by the lack of related β-like PL excited at the same energy. Nevertheless, the comparison of results from different samples shows that its intensity is roughly proportional to that of the α band at 4.23 eV. This fact suggests that both defects are linked to the presence of oxygen vacancies induced by Ge doping.

Concerning the previously unobserved emissions peaked at 2.88 and 3.94 eV, the low intensity of these minor components in many of the investigated samples prevents the reliable analysis of possible relations with other bands. Nevertheless, the analysis of a few clear cases shows a wide variability of the ratios between the intensity of the new bands and those of the β components excited at about 6.6 and 7.3 eV. This fact, together with the differences of peak energies between these emissions and the other ones, indicates that the 2.9 and 3.9 eV PL bands are quite disjointed from the α-β pattern. However, looking at Figs. 2 and 3, a remarkable coincidence may be noted between the apparent ''redshifts'' of the 3.9 and 2.9 eV bands from the α and β peak energies at 4.3 and 3.1 eV, possibly suggesting that the unknown components may be attributed to undefined variants of ODC characterized by an energy shift of ≈ 0.3 eV.

In summary, the detailed spectral sampling of the optical emission excited in SiO_2:Ge between 4.5 and 13 eV clearly identifies the following three sets of PL components: (a) the two well known competitive emissions at 3.1 and 4.3 eV (α and β bands) with three excitation channels at 5.4, 6.6, and 7.3 eV forming the predominant spectral structure indicated as α-β pattern; (b) a second minor doublet of emissions at 2.9 and 3.9 eV, appearing as a redshifted α-β pattern, with only two detectable excitation bands at 4.7 and 7.0 eV; (c) the isolated 4.4 eV emission excited only in the 5.1 eV PLE band, lacking of any higher-energy PLE counterpart. The presence of a second α-β-like pattern suggests that variants of the same ODC structure may exist in the Ge-perturbed silica matrix. By contrast, a quite different ODC configuration is to be invoked to account for the 4.4 eV PL. So, distinct ODC structures—such as the already proposed Si-Si- and Si^{2+}-like sites or possibly other undefined ones—should play comparable roles, as well as the respective ''intrinsic'' (Si-like) and ''extrinsic'' (Ge-substituted) variants, in the PL properties of mixed Si Ge oxides.

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