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LETTER TO THE EDITOR

Photoluminescence band at 4.4 eV in oxygen-deficient silica: temperature effects

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Abstract. We report experimental results on the spectral properties and time behaviour of the 4.4 eV photoluminescence (PL) band in oxygen-deficient silica (a-SiO₂). Our measurements, performed both at $T = 300$ K and $T = 10$ K, show that at room temperature the PL features are independent of the particular excitation energy (5.0 eV, 6.8 eV and 7.6 eV) whereas at low temperature, upon excitation at 7.6 eV, the decay of the PL emission is faster than for lower excitation energies. This shortening of the PL lifetime is consistent with previously reported data, which were explained by hypothesizing an interconversion mechanism between two structural configurations of the same oxygen defect. Nevertheless, our results do not support the proposed mechanism and we tentatively suggest a different interpretation of the experimental data.

It is well known that non-stoichiometric oxygen-deficient silica (a-SiO₂) shows a photoluminescence (PL) band centred at about 4.4 eV, whose excitation spectrum (PLE) extends into the UV and vacuum-UV regions [1–4]. Measurements of its decay time, of the order of nanoseconds [4–7], characterize this PL emission as related to a singlet–singlet transition.

In spite of these optical features being well established, a structural model accounting for them is not yet universally accepted. At present two models are mainly considered, in which either an oxygen vacancy $\equiv\text{Si}-\text{Si}\equiv$ [1] or a twofold coordinated silicon O– $\dot{\text{S}}\text{i}$ –O [2, 8] is respectively proposed as the oxygen deficient centre (ODC) responsible for the 4.4 eV PL band.

More recently, Nishikawa *et al* [4] have investigated the kinetics of this PL band at $T = 45$ K, by exciting at 5.0 eV, 6.9 eV and 7.6 eV. They measured its lifetime to be $\tau = 4.2$ ns for the first two excitation energies, while a shorter decay time ($\tau = 2.1$ ns) was detected for the highest excitation energy (7.6 eV). On the basis of this experimental evidence, those authors, though not giving a specific structural interpretation, hypothesized that the ODC exists in two distinct configurations, probably the relaxed and the unrelaxed oxygen vacancy [9]. The energy level scheme representing the two configurations, as suggested in [4], is reported in figure 1. As shown, in the first configuration (C₁) 5.0 eV and 6.9 eV are the energies of the singlet–singlet transitions between the ground state (S₀) and the first (S₁) and the second (S₂) excited states, respectively. In this scheme, the PL emission is ascribed to the inverse transition S₁–S₀ and its lifetime, disregarding the non-radiative relaxation rate K_{NR} , is essentially $\tau \approx (K_R)^{-1}$, where K_R is the radiative decay rate. In configuration C₂, 7.6 eV is the transition energy between the levels S'₀ and S'₁. It was proposed that a conversion from C₂ to C₁, with a rate K_C , is activated upon excitation at 7.6 eV, and that this process is counteracted by a back-conversion (C₁ → C₂) acting

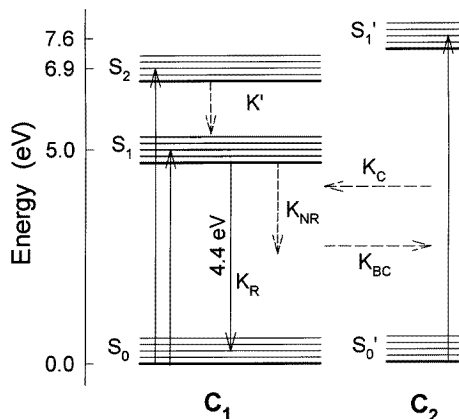


Figure 1. The energy level scheme of the two-configurations model [4]. In this scheme two configurations C_1 and C_2 are considered: the 4.4 eV PL ($S_1 \rightarrow S_0$) is excited at 5.0 eV ($S_0 \rightarrow S_1$) and 6.9 eV ($S_0 \rightarrow S_2$) in the first configuration and at 7.6 eV ($S'_0 \rightarrow S'_1$) in the second one. The rates K_C (direct conversion $C_2 \rightarrow C_1$) and K_{BC} (back-conversion $C_1 \rightarrow C_2$) account for the interconversion process between the two configurations upon 7.6 eV excitation.

at the rate K_{BC} . Consequently the 4.4 eV PL emission, when excited at 7.6 eV, decays with a shorter lifetime $\tau \approx (K_R + K_{BC})^{-1}$ because of the additional contribution of the back-conversion process, which reduces the population of the excited state S_1 . Further measurements performed at $T = 10$ K by Nishikawa *et al* [10] have shown essentially the same lifetime as for $T = 45$ K, so suggesting a poor dependence of the K_{BC} rate on the temperature, at least in the low-temperature range.

Here we report experimental results on the PL emission at 4.4 eV, on its excitation spectrum and on its lifetime, at two different temperatures, $T = 300$ K and $T = 10$ K. The aim of our experiments is to point out how the non-radiative relaxation mechanisms, which are expected to depend on the temperature, affect the PL band at 4.4 eV in the frame of the model previously described [4].

Our measurements were carried out in an 'as-grown' oxygen-deficient silica sample (natural dry, type I) [11], featuring the well known $B_{2\alpha}$ absorption band [1], centred at 5.05 eV with a full-width half maximum of 0.36 eV. The PL emission was investigated for the excitation energies in the range 4.5–8.5 eV, using the synchrotron radiation (SR) at the superlumi experimental station on the I-beamline of HASYLAB at DESY (Hamburg, Germany) [12]. PL and PLE spectra were detected under multi-bunch operation, with excitation and emission bandwidths of 0.25 nm and 5.0 nm, respectively. The PL decay times were measured under single-bunch operation, by scanning 192 ns between adjacent SR pulses, 0.5 ns wide. The measurements at $T = 10$ K were performed by using a sample chamber with a helium-flow cryostat.

In figure 2, the PL spectra excited at 6.8 eV (dashed curves) with the corresponding PLE profiles (solid curves) are reported for $T = 300$ K (figure 2(a)) and $T = 10$ K (figure 2(b)). As shown, the PL emission at both temperatures has nearly the same profile, even if the intensity is higher by a factor of three at lower temperature. The same shape and intensity ratio were found in the PL band excited at 5.0 eV. Also the PLE spectra are similar and show, for both temperatures, two maxima centred at about 5.0 eV and 6.8 eV. Nevertheless, some differences can be singled out in the region 6.0–8.4 eV, as the PLE spectrum detected at $T = 10$ K is broader and slightly shifted towards higher energy with respect to the one

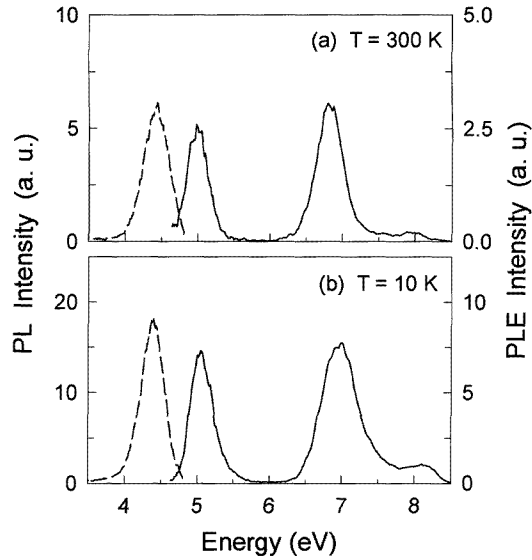


Figure 2. The PL emission spectra excited at 6.8 eV (dashed lines) and PL excitation spectra detected at 4.4 eV (full lines) in our oxygen-deficient sample: (a) $T = 300$ K; (b) $T = 10$ K.

detected at $T = 300$ K.

The dependence of the PL emission on the temperature is still more evident when its time behaviour is considered. In figure 3, the PL intensity at 4.4 eV is reported as a function of the delay time with respect to the SR excitation pulse, for $T = 300$ K (figure 3(a)) and $T = 10$ K (figure 3(b)). For both temperatures, the three experimental curves refer to the excitation energies 5.0 eV, 6.8 eV and 7.6 eV, from the top to the bottom, respectively. As shown, for any excitation energy the time decay of the PL intensity is well described by a single-exponential law, $I_{PL}(t) \propto \exp(-t/\tau)$. By a best-fit procedure we find $\tau = 4.1 \pm 0.1$ ns for the three decay curves at $T = 300$ K. As shown in figure 3(b), on lowering the temperature the measured PL lifetimes change appreciably. In particular, for both excitations at 5.0 eV and 6.8 eV, τ increases up to $\tau = 4.7 \pm 0.1$ ns, whereas, when excited at 7.6 eV the PL emission decays faster, with a lifetime $\tau = 3.1 \pm 0.1$ ns.

Our results, as for the excitation at 5.0 eV and 6.8 eV of the 4.4 eV PL band, are consistent with the energy level scheme describing the C_1 configuration (figure 1). In this frame, the temperature behaviour of both PL intensity and τ , as evidenced in figures 2 and 3, can be ascribed to the temperature dependence of the non-radiative relaxation processes between S_1 and S_0 . In fact, the decay time of the PL emission is determined by both the radiative K_R and the non-radiative K_{NR} rate, according to the relation $\tau = (K_R + K_{NR})^{-1}$ [13]. Because of the expected decrease of K_{NR} with decreasing temperature, τ is expected to lengthen in agreement with the experimental behaviour of the lifetime of the 4.4 eV PL shown in figure 3, for excitation at 5.0 eV and 6.8 eV. In particular, from the experimental data at $T = 10$ K, where K_{NR} can be neglected and τ tends to the value $\tau \approx (K_R)^{-1}$, we derive $K_R \approx 2.1 \times 10^8$ s $^{-1}$ and, by fixing K_R , we fit the experimental values of τ at $T = 300$ K by $K_{NR} \approx 3 \times 10^7$ s $^{-1}$.

When the 4.4 eV PL band is excited at 7.6 eV, we find a different dependence of its decay time on the temperature, as τ is shorter at $T = 10$ K ($\tau = 3.1 \pm 0.1$ ns) than at

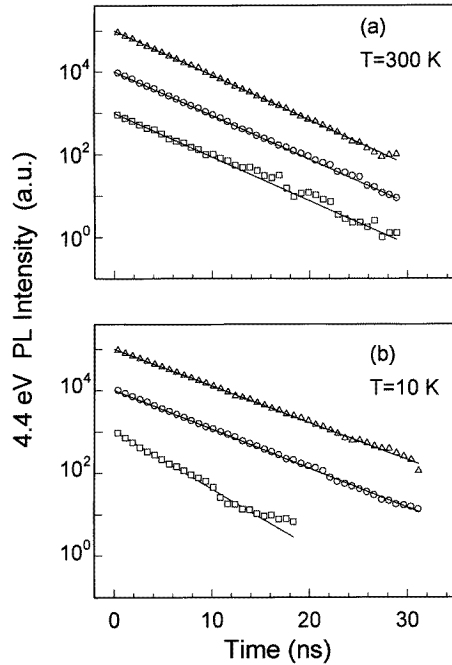


Figure 3. Decay profiles of the 4.4 eV PL band excited at 5.0 eV (Δ), 6.8 eV (\circ) and 7.6 eV (\square) in our oxygen-deficient sample: ((a) $T = 300$ K; (b) $T = 10$ K. The initial values of the decay curves are arbitrarily scaled by decades; full lines plot the exponential functions with the lifetime τ determined by a best-fitting procedure.

$T = 300$ K ($\tau = 4.1 \pm 0.1$ ns). The results obtained at $T = 10$ K (figure 3(b)) agree with previously reported ones showing that, at $T = 45$ K, the 4.4 eV PL band excited at 7.6 eV had a lifetime shorter than the one detected when the same band was excited at lower energies [4].

In spite of this agreement, our experimental data do not seem to support the model proposed by those authors, that is the mechanism of interconversion between two configurations of the same ODC upon excitation at 7.6 eV. In fact, in the frame of this model, K_{BC} would increase with increasing temperature, because the conversion probability between two configurations of the same defect should be enhanced by the presence of a larger spectrum of vibrational modes at higher temperature. In contrast, by taking into account the interconversion mechanism, we derive a back-conversion rate $K_{BC} \approx 1.1 \times 10^8 \text{ s}^{-1}$ at $T = 10$ K, while at $T = 300$ K the rate K_{BC} is so low that, within the experimental uncertainties, we can only determine an upper limit for its value, that is $K_{BC} \leq 6 \times 10^6 \text{ s}^{-1}$.

The above reported results do not allow us to infer a structural model for the ODC responsible for this emission. We can merely hypothesize that the 4.4 eV PL, when excited at 7.6 eV at low temperature, is due to the superposition of the PL emission of an ODC and of another distinct defect. This hypothesis is actually supported by the shapes of the PLE spectra in the region 6.0–8.4 eV, shown in figure 2. In fact, the broadening and the shift towards higher energy observed in the PLE profile at $T = 10$ K could be explained by the presence of another PLE band centred at about 7.6 eV and associated with the second defect. The PL activity of the second defect could be detectable only on lowering the temperature, because of the quenching of non-radiative relaxation mechanisms that are instead effective

at room temperature. So, at $T = 300$ K, we excite the 4.4 eV PL in the tail of the PLE band centred at 6.8 eV by 7.6 eV photons and one measures the same lifetime ($\tau = 4.1 \pm 0.1$ ns) independently of the excitation energy. On the other hand, at $T = 10$ K, we excite both defects by the same energy (7.6 eV) and the PL emission detected at 4.4 eV collects both contributions, and the shortening of the lifetime ($\tau = 3.1 \pm 0.1$ ns) could be ascribed to a faster decay of the PL emission of the second defect. Further experimental work is in progress.

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