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Dominant role of E' centers in x-ray-induced, visible luminescence in high-purity amorphous silicas

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Detailed measurements of the x-ray-dose dependence of spectrally resolved x-ray-induced luminescence in bulk high-purity a-SiO$_2$ were performed. The dose dependence of the luminescence intensity is compared to that of the paramagnetic E'_γ-center concentration in two types of silicas. Clear experimental evidence is presented that the main features of the 2.6 and 2.75 eV luminescence bands are due to the same radiation-induced defect, and that this defect is related to the E'_γ center.

High-purity, amorphous silicon dioxide (a-SiO$_2$) is an extremely important material used in a wide variety of optical and electronic applications. In environments where high levels of ionizing radiation are present, or where devices are exposed to lower levels of radiation for long periods of time, radiation-induced defects may adversely affect the material. Such defects have been extensively studied using a wide range of experimental techniques, especially electron spin resonance (ESR), luminescence, and optical absorption.[1]

Luminescence bands in high-purity a-SiO$_2$ have been observed with peak centers near 1.9, 2.2, 2.5, 2.7, 3.1, 4.2, and 4.4 eV;[2–5] these bands have been studied by conventional photoluminescence and thermally stimulated luminescence, as well as x-ray-induced[5] and particle-induced luminescence. The emission band centered at approximately 2.7 eV has been seen in numerous experiments on a-SiO$_2$. This line has been observed under ion-beam irradiation,[6] in thermoluminescence after neutron irradiation,[7] by conventional luminescence after neutron irradiation,[8] and in pristine materials when excited by 5.0 to 7.9 eV photons,[3,9–11] or by x-rays.[10] This band has been variously attributed to a twofold coordinated silicon,[10–12] an oxygen vacancy,[9] or a self-trapped exciton.[13]

Several experiments have shown a luminescence band in a-SiO$_2$ with a peak in the 2.2–2.5 eV range[3,14,15,8] which has been attributed[14] to interstitial O_2^- or a self-trapped exciton.[15] Mervic *et al.*[8] found that the 2.2 eV line was very dependent on impurities.

There are many unanswered questions concerning the identification and mechanisms of formation of radiation-induced defects in SiO$_2$, and the picture is unlikely to become complete without a fuller experimental characterization of material properties. While emission bands have been observed in many different experiments, the only study of the x-ray-dose dependence has been that of Marrone,[5] who observed 1.9 and 2.75 eV x-ray-induced luminescence bands in silica core optical fibers.

In this article we present a study of the most intense visible luminescence bands, those at 2.6 and 2.75 eV, in two types of high-purity a-SiO$_2$ over a wide x-ray-dose range and compare the dose dependence of this luminescence with that of the paramagnetic E'_γ defect as measured by ESR. We have also observed lines at 1.9 and 2.2 eV, which will be discussed in another paper. The luminescence is stimulated by x rays and the x radioluminescence (XRL) is measured continuously as the sample is irradiated. In addition to easy applicability to the study of dose dependence, this method differs in other ways from previous luminescence experiments. In the present work, the charge carriers participating in luminescence are excited directly by ionizing radiation and the resulting secondary electrons rather than by visible or ultraviolet photons, as is the case with photoluminescence. This results in a dynamic spectrum of luminescence from several centers, rather than only those excited by a specific absorption band. Defects which might not be observed in postradiation experiments may contribute to the XRL signal.

The high-purity a-SiO$_2$ samples studied were Suprasil-W1 and a material designated in this paper as J8. Both were synthetically prepared, Suprasil-W1, which is oxygen-rich, by an O$_2$ plasma method,[16] and J8, which is oxygen-deficient, by chemical vapor deposition soot remelting.[17] More details about the roles of oxygen in these materials are given by Zhang *et al.*[18,19] Both types of materials are low in hydroxyl content, with [OH] below the detection limit of approximately 3 ppm. All samples were rectangular parallelepipeds approximately $1\times3.5\times8$ mm in dimension.

The XRL was induced by x rays from a conventional molybdenum-anode diffraction tube operated at 45 kV dc and 9 mA. The x rays struck the samples perpendicularly to the 3.5×8 mm face. To improve the uniformity of penetration of the x rays into the sample, an aluminum filter attenuated low-energy x rays from the beam. The average dose rate was 1.5×10^3 rad/s. Light emitted by the sample during irradiation was focused onto the entrance slit of a charge-coupled device spectrograph, which used a grating that allowed the simultaneous observation of the entire visible spectrum. Spectra were accumulated for 60 s and stored in a computer, repeating until the desired total dose had been applied to the sample. A brass sample holder allowed samples to be precisely positioned in the XRL apparatus, keeping the dose rate and light collection efficiency consistent to better than 10% between different experimental runs.

Data were taken until each sample had received a total accumulated dose of at least 400 Mrad, yielding over 4300 spectra per sample. These spectra were then individually de-

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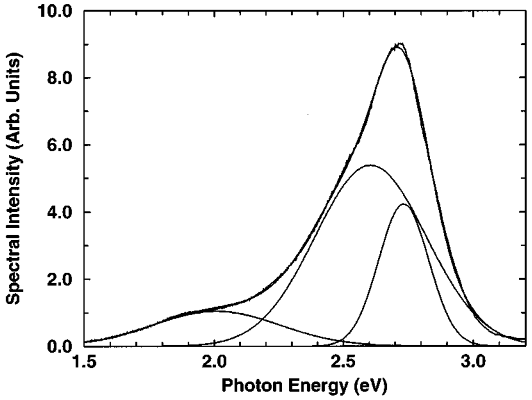

FIG. 1. XRL spectrum of oxygen-deficient a-SiO$_2$, J8, with a total dose of 387 Mrad. Spectrum recorded for 60 s with a dose rate of 1.5×10^3 rads/s. The raw data, individual Gaussian curves, and the sum of the Gaussian curves are shown.

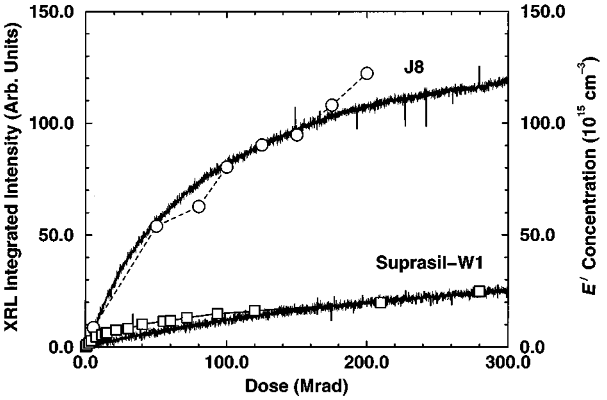

FIG. 3. Comparison of the dose dependence of the 2.6 and 2.75 eV total XRL intensity with E'_γ concentration. The XRL intensities are represented by the continuous lines, while E' concentrations are depicted using circles (○) for J8 and squares (□) for Suprasil-W1.

convoluted into the sum of Gaussian peaks and a linear background using the Levenberg-Marquardt nonlinear least squares method as illustrated by Fig. 1. Next, the parameters describing these peaks (center, width, and intensity) were analyzed as functions of dose and sample type, and compared to the concentration of E'_γ centers as measured by Austin[20] and Zhang,[19] whose samples were cut from the same blocks as those used for the XRL measurements and were irradiated under similar conditions. Control ESR measurements were done to calibrate the doses between the XRL and ESR data. Figure 2 shows the ratio of the integrated intensities of the 2.6 to the 2.75 eV lines as a function of dose for Suprasil-W1 (a) and J8 (b). This ratio is very nearly constant over the entire dose range in both oxygen-deficient and oxygen-excess samples, with the low-dose behavior primarily due to difficulties in fitting broad overlapping curves at low signal levels. The peak positions are the same for the two different materials to within approximately 10%.

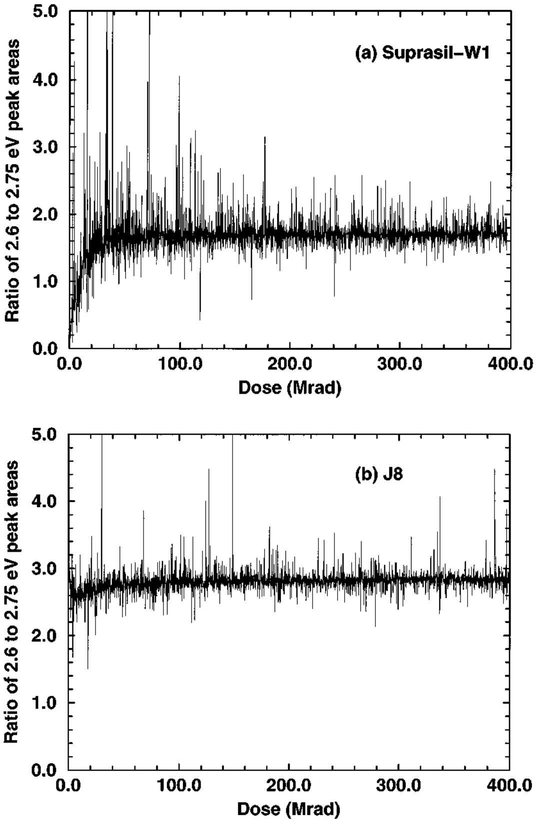

FIG. 2. Ratios of the 2.6 and 2.75 eV integrated peak intensities.

Figure 3 shows the dose-dependent part of the sum of integrated intensities of the 2.6 and 2.75 eV XRL bands for each sample as a function of dose. There is also a zero-dose component in J8, which is about 20% of the high-dose value, which has been subtracted. This subtraction has no effect on the ratio shown in Fig. 2(b). Also plotted in Fig. 3 are the absolute concentrations of the E'_γ centers in these two types of amorphous silica as determined by ESR. The E'_γ is the most common E' variant, which is widely believed to consist of an asymmetrically relaxed oxygen vacancy.[21] A constant scaling factor was applied to scale the XRL data so as to match the luminescence intensity in Suprasil-W1 at 200 Mrad to the E'_γ concentration. It is important to note that *exactly the same factor* was applied to the XRL intensities for both samples, so the only effect of this scaling was to plot the XRL and ESR data on visually compatible scales.

These figures reveal three important facts regarding the physics of the radiation response of high-purity a-SiO$_2$. First, for each sample the 2.6 and 2.75 eV lines have nearly identical dose dependences, which is reflected by the constant ratio of the intensities (Fig. 2). This indicates that these two lines are due to the same defect. Next, Fig. 3 shows that the XRL and E'_γ concentrations scale the same between the two materials; both are approximately five times stronger in oxygen-deficient J8 than in oxygen-rich Suprasil-W1. Finally, Fig. 3 also shows that the dose dependences of the XRL intensities and ESR-active centers are very similar in each material. In J8, the dose dependences of these centers are very nearly identical over the range of available data, with the XRL intensities and E'_γ curves both decreasing in slope with increasing dose. In Suprasil-W1 there is a measurable difference in the dose curves of the XRL and E'_γ intensities below 100 Mrad.

The subtraction of the zero-dose component of the XRL spectrum in J8 requires explanation. Pristine, unirradiated samples of both materials contain no measurable E' or other paramagnetic defects. However, J8, being oxygen deficient, contains neutral oxygen vacancies, known as B_2 centers, at a concentration of approximately 10^{18} cm^{-3}.[17] We propose that there are two or more concurrent physical processes giving rise to the 2.6 and 2.75 eV luminescence during x-ray irradiation. The dose-independent (zero-dose) component of the XRL in J8 is due to de-excitation luminescence at B_2 sites. The dose-dependent part of the XRL is due to recombination luminescence at E' centers. Because E' centers are positively charged, while B_2 centers are electrically neutral, an E' is very likely to attract an electron and yield luminescence, and the luminescence from E' centers will be strongly governed by their concentration. However, for a B_2 center to luminesce it must be excited by an interaction with an energetic electron produced by the ionizing radiation. Therefore, subtraction of the zero-dose signal in J8 represents removing the portion of the XRL arising from neutral B_2 centers, which are structurally similar to the positively charged E' centers. Thus the subtraction has a clear physical meaning.

Now considering the Suprasil-W1 XRL dose behavior, we observe a difference between the XRL and E' signal strengths at low dose. Suprasil-W1 is known to be oxygen rich. While the exact configuration of this excess oxygen is not well understood, it is likely that peroxy linkages, as well as interstitial atomic and molecular oxygen exist within this material. Because oxygen can serve as an electron trap, the number of electrons available to participate in E' recombination luminescence is reduced, particularly at low dose when there are relatively few E' centers existing within the sample. As the dose increases, more E' centers are produced and the excess oxygen becomes relatively less important.

Based upon the experimental data presented, we conclude that the E'_γ center is the dominant center of visible radiative recombination luminescence in high-purity amorphous silicas. While there are several slightly different E' center configurations, all are based upon a three-coordinated silicon.[22] J8, which is oxygen deficient and rich in three-coordinated silicon,[17] has significantly higher levels of XRL and E'_γ centers than Suprasil-W1, which is oxygen rich.[1]

In conclusion, using the technique of XRL, we have presented a detailed study of the x-ray-dose dependence of spectrally resolved luminescence in a-SiO_2. Their correlated dose dependences indicate that the 2.6 and 2.75 eV lines originate from the same defect. We have presented strong evidence that the E'_γ center serves as the site of the 2.6 and 2.75 eV recombination luminescence. The existence of *two* luminescence bands associated with the E'_γ center suggests that the currently accepted theoretical model[21] of the asymmetrically relaxed E' center may be incomplete.

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