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Time-resolved photoluminescence in amorphous silicon dioxide

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We report time-resolved measurements of photoluminescence in bulk a-SiO_2 using 7.9- and 6.4-eV excitation. Time-resolved spectra have been obtained at room temperature and 25 K, and the intensity and decay rates of various luminescence bands have been measured as a function of temperature. Bands at 1.9, 2.2, 2.7, and 4.3 eV are identified. In addition, there is a very broad luminescence peaking between 3–4 eV but extending to below the 1.5-eV cutoff of our measurements. We have also measured photoluminescence in crystalline quartz and in a thermally grown oxide. Both the 4.3- and 1.9-eV bands are seen in the thermal oxide, but the 2.7-eV band is absent. In the crystal, the 1.9-eV band is absent.

I. INTRODUCTION

In spite of years of research by many different people, there are still a great many things we do not know about the structure and properties of defects in SiO_2. Although several defects have been identified by EPR,[1] the origin of several defect-related luminescence bands remains a mystery. This paper presents the results of measurements of time-resolved photoluminescence (PL) in SiO_2. The work described here is not intended to provide definitive answers, as these measurements were performed as corollary experiments to a more extensive project investigating photoinduced metastable paramagnetic states in a-SiO_2.[2–5] Nonetheless, the results presented here do constitute a careful and fairly complete survey of transient photoluminescence in SiO_2, resulting in both new insights and new questions.

II. EXPERIMENTAL PROCEDURE

To excite the luminescence we used an excimer laser operating on either the F_2 transition at 157 nm (7.9 eV) or on ArF at 193 nm (6.4 eV). As both of these energies are below the band gap of SiO_2 ($\simeq$9 eV), the luminescence results from direct excitation at defects. In particular, from the work of Gee and Kastner[6] we know that the 7.9-eV laser line is within the excitation band of the 4.3-eV defect luminescence.

Samples of Suprasil and Suprasil-W were obtained from Heraeus-Amersil in the form of polished disks of $\frac{1}{8}$-in. thickness. These are high-purity synthetic materials differing mainly in their OH content. Suprasil contains approximately 1200 ppm (by weight) OH, whereas the OH content of Suprasil-W is less than 5 ppm. Both have a total metallic impurity level of about 1 ppm, and a few hundred ppm of chlorine. A sample of crystalline quartz was obtained from Sawyer Research Corp. and polished using standard techniques. Unless otherwise indicated, all the data presented here are for samples in their as-prepared state, i.e., the samples were not exposed to any radiation other than the laser used to excite the luminescence.

For PL measurements at low temperatures the sample was mounted on a liquid-He-cooled cold finger in a chamber maintained at 10^{-8} torr using a completely oil-free pumping system. For excitation with the 7.9-eV vacuum-ultraviolet line of the F_2 laser it is necessary that the entire optical path from the laser to the sample be under vacuum; moreover a *clean* vacuum is necessary to prevent spurious luminescence from contaminants which would otherwise collect on the cold sample. In the case of room-temperature measurements using the 6.4-eV line from ArF the vacuum system was not employed.

The luminescence induced by the 10-nsec laser pulse was dispersed by a monochromator and detected with a fast photomultiplier with an S-20 photocathode. The photomultiplier current was dropped across a load resistor, and the resulting voltage was amplified by a wide band amplifier and then measured with either a transient recorder on a boxcar averager, followed by an interface to a minicomputer. The response of the collection optics was calibrated from 250 to 700 nm using a calibrated tungsten lamp. The output of the laser was monitored during data collection, and the data are corrected for drifts in the laser fluence. For both 7.9 and 6.4 eV the excitation intensity was ~ 1 J/cm^2, at 10-Hz repetition rate.

III. TIME-RESOLVED SPECTRA

We start by presenting the time-resolved luminescence spectra, which give the best overview of the various luminescence processes in SiO_2. Figures 1–4 show the time-resolved PL spectra from approximately 1.5 to 5 eV under various conditions and for various samples. These spectra were taken with the boxcar gate centered at the indicated delay times after the laser pulse. A gate width of $\Delta t/t = 0.1$ was used. The data in the figures have dimensions of photons per unit time per unit photon energy, and are plotted with a 0.05-eV energy resolution. In some cases smooth curves are drawn through the data points at the lower photon energies in order to show more clearly certain relatively sharp features. These curves are guides for the eye connecting the actual data points (taken at 1-nm intervals, with the monochromator set for 4-nm resolution), not fits to the data.

Figures 1(a) and 1(b) are the results for 7.9-eV excitation of Suprasil-W at room temperature and 25 K, respectively. At room temperature there are four distinguishable bands. The 1.9-eV band is most prominent. At the earliest times there is evidence of a band at about 2.2 eV, and there is a prominent band centered at 4.3 eV which is present only at zero delay. At later times a very broad band with a maximum between 3—4 eV can be seen.

There are several changes in the spectrum when the sample temperature is lowered to 25 K, as seen in Fig. 1(b). The intensities of the 4.3- and 2.2-eV bands increase considerably, while the 1.9-eV band and the 3—4-eV luminescence have a weaker temperature dependence. The 2.2-eV band appears to undergo a dramatic sharpening-up as it decays. Finally, there appears a band at 2.7 eV with a decay time of about 5×10^{-3} sec that was not present at room temperature. This band could be readily excited even at room temperature in *neutron-irradiated* samples of Suprasil-W, either by 7.9- or 6.4-eV photons.

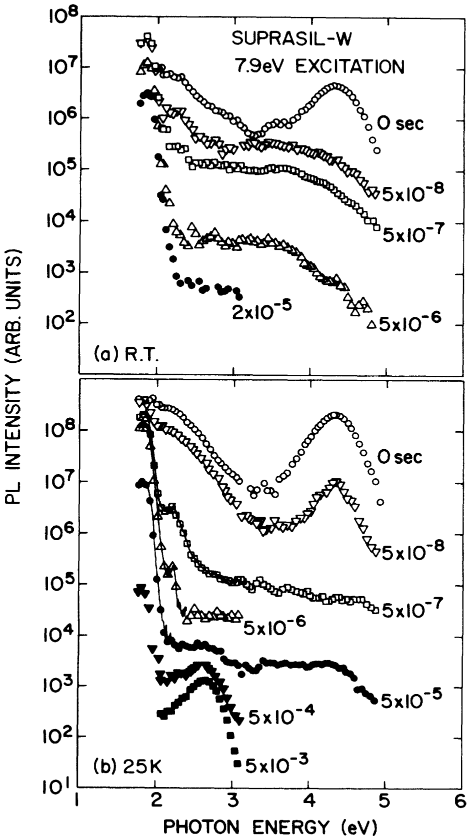

FIG. 1. Time-resolved spectra in Suprasil-W, 7.9-eV excitation. (a) Room temperature. (b) 25 K.

The time-resolved PL spectra for 6.4-eV excitation of Suprasil-W at room temperature are shown in Fig. 2. The spectra look very similar to those from 7.9-eV excitation [Fig. 1(a)] except for the lower intensity of the 4.3-eV band. Note that since the spectra for 7.9-eV excitation were taken with a different optical arranegment from that used for all other spectra in this paper, the absolute magnitudes should not be compared.

In Fig. 3 is shown the time-resolved PL in Suprasil excited at 6.4 eV. The spectra are quite similar to those seen in Suprasil-W, except for the stronger 4.3-eV band. There was, however, some sample-to-sample variation in this band in Suprasil. There is also a band at about 2.2 eV. This cannot be related to the 2.2-eV band noted earlier in Suprasil-W, because of its vastly different decay time. We suspect it to be impurty-related since its intensity varied from sample to sample and even from place to place on the same sample.

Spectra taken with 7.9-eV excitation were generally limited to wavelengths shorter than 700 nm in order to avoid the atomic-fluorine laser lines in this wavelength region. For other excitation energies the spectra could be extended as far at the 800-nm cutoff of the detection system. Doing so allowed the low-energy side of the 1.9-eV band to be measured, and revealed additional luminescence extending farther into the infrared. This can be seen most clearly in the zero-delay spectrum in Suprasil (Fig. 3), but it is also seen in Suprasil-W. The exact shape and extent of this infrared luminescence is not known. The spectra cannot really be trusted in this region of photon energies because the system response is falling off very rapidly. Nonetheless, there *is* measurable luminescence at 800 nm. From measurement of its decay time it was determined that this is *not* simply the low-energy tail of the 1.9-eV

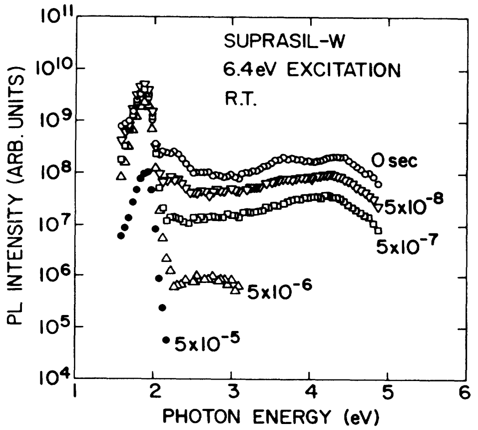

FIG. 2. Time-resolved spectra in Suprasil-W, 6.4-eV excitation at room temperature.

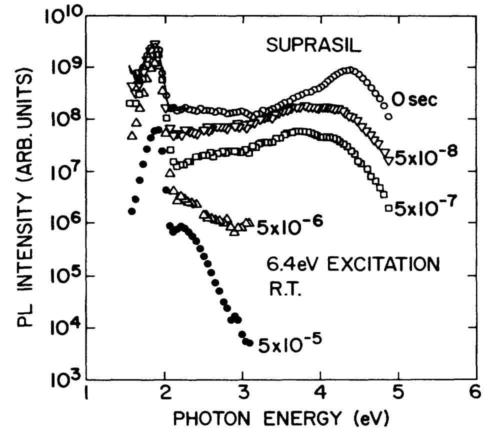

FIG. 3. Time-resolved spectra in Suprasil, 6.4-eV excitation at room temperature.

band, but is rather a continuation of the very broad luminescence seen from 2 to about 4 eV. It would be very interesting to extend these photoluminescence measurements to lower energies.

Time-resolved spectra for crystalline SiO_2 excited at 6.4 eV are shown in Fig. 4. Gee[7] reported that no steady-state PL (using hydrogen-lamp excitation near 7.3 eV) could be detected in crystalline SiO_2 unless the sample was neutron irradiated. The present results for below-gap laser excitation of the as-grown crystal are quite similar to those for Suprasil-W, except for the lower overall intensity and the striking absence of the 1.9-eV band. We note that this spectrum looks much more like the one for 7.9-eV excitation of Suprasil-W than like the spectrum for 6.4-eV excitation. The 4.3-eV band is evident, although shifted down in energy relative to the glass. The fast decay-time nonetheless allows one to be fairly confident in identifying this with the fast 4.3-eV band observed in the glass. On the other hand, Gee and Kastner[8] found that the steady-state PL in the neutron-irradiated crystal occurred at *higher* energy than that in the similarly irradiated glass. The data are somewhat too noisy to allow an accurate assessment of whether the 2.2-eV band is present. There is a band centered near 2.7 eV, which will be discussed below. As in the glass, there is a very broad luminescence extending from about 4 to below 1.5 eV.

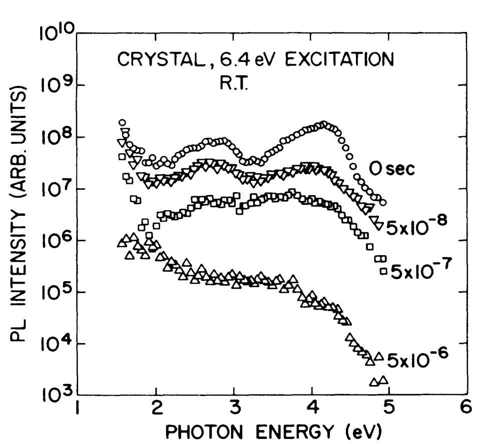

FIG. 4. Time-resolved spectra in crystalline SiO_2, 6.4-eV excitation at room temperature.

In all of the samples and for all excitation energies the luminescence cuts off rather sharply above about 4.5 eV. This is not a reflection of the system response, which is quite flat at high energies. An experiment was performed in which we used a vacuum monochromator, with its output window coated with sodium salicylate phosphor on the inside surface, to detect luminescence beyond the 6-eV air cutoff. Between the 4.3-eV band and the laser line at 7.9 eV, no additional photoluminescence bands were seen.

IV. LUMINESCENCE TRANSIENTS

In this section we present the photoluminescence transients, measured as a function of delay time after the laser pulse, at fixed wavelength. As can be seen from the time-resolved spectra of Sec. III, the 4.3-eV band has a very fast decay time. In fact its decay time could not be measured in our experiments as it is comparable to or shorter than the laser pulse width.

The decay of the very broad 3—4-eV emission is shown in Fig. 5 at various temperatures for 7.9-eV excitation of Suprasil-W. The measurement was performed at 3.9 eV for best sensitivity. The fast component visible at the earliest times is from the 4.3-eV band, the shoulder of which extends to 3.9 eV. For temperatures between about 150 K and room temperature the photoluminescence decay is roughly constant, with a characteristic decay time of

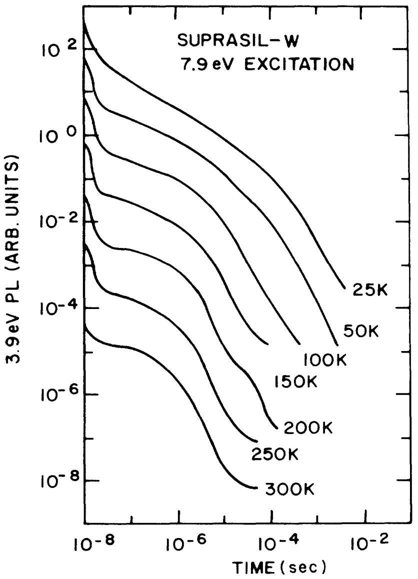

FIG. 5. Luminescence decay at 3.9 eV (319 nm) at the indicated temperatures. 7.9-eV excitation in Suprasil-W. The curves are displaced vertically by factors of 10 for clarity.

about 10^{-6} sec. At lower temperatures the decay begins to broaden markedly, and at 25 K is approximately a power law of $t^{-0.7}$ extending to 10^{-4} sec, followed by a steeper power law (roughly t^{-2}).

Luminescence transients at 3.9 eV from 6.4-eV excitation (room temperature) for Suprasil-W, Suprasil, and crystalline quartz are shown in Fig. 6. The dominant rate is the same as for 7.9-eV excitation, and is the same for all samples (possibly slightly faster in Suprasil).

Figure 7 shows the PL transients at 2.7 eV in Suprasil-W (7.9-eV excitation) at various temperatures. In this figure only the slowest component of the photoluminescence, with a decay time of about 10 msec, is the 2.7-eV band. The rest is from overlapping bands. The component before about 10^{-7} sec, becoming more apparent as the temperature is lowered, is from the 2.2-eV band. From about 2×10^{-7} sec to 10^{-4} sec the broad 3—4-eV luminescence is seen.

Semilog plots of the 2.7-eV component are shown in Fig. 8. Notice the very unusual temperature dependence. The 2.7-eV photoluminescence is *weaker* at 25 K than it is at 50 K, but its decay rate is the same at all temperatures. The upward curvature at short times in the 25 K data is from the 3—4-eV luminescence. Although not shown here, the 2.7-eV photoluminescence was followed out to about 50 msec. Its decay is accurately exponential, with a time constant of 9.5 msec. Such a purely exponential decay is unusual for a glass.

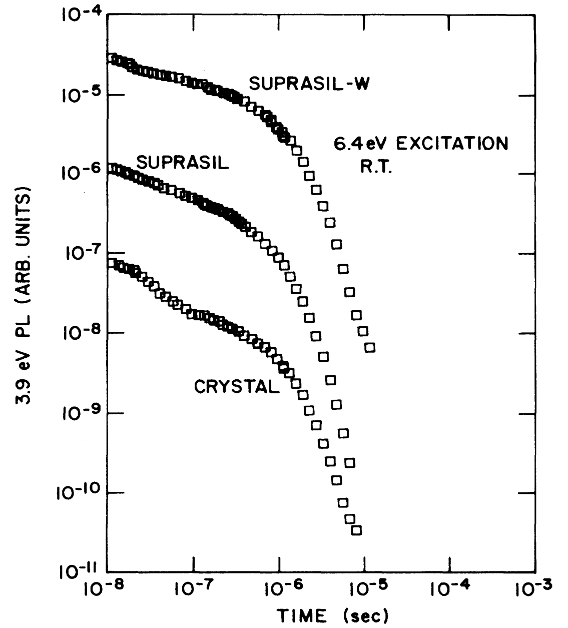

FIG. 6. Luminescence decay at 3.9 eV for 6.4-eV excitation at room temperature in Suprasil-W, Suprasil, and crystalline quartz. The curves are displaced vertically by arbitrary amounts.

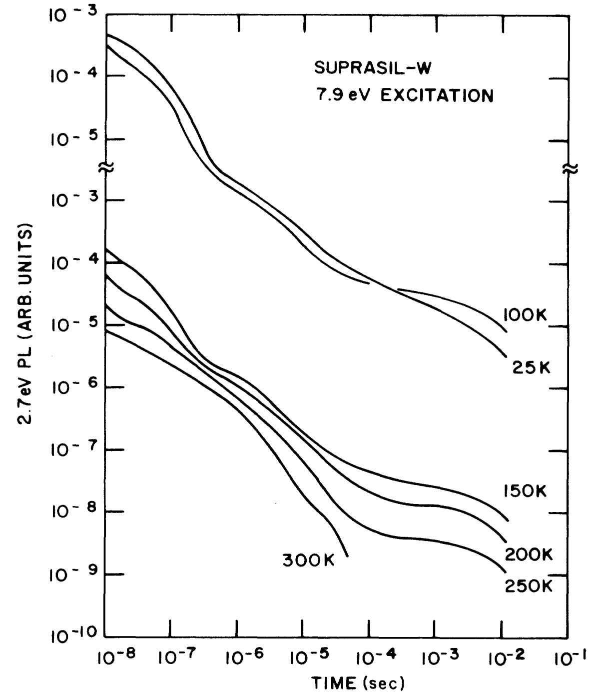

FIG. 7. Luminescence decay at 2.7 eV (459 nm) in Suprasil-W under 7.9-eV excitation at various temperatures. The upper two curves have been displaced vertically by a factor of 1000 for clarity.

Semilog plots of the decay of the 2.2-eV band at various temperatures are shown in Fig. 9 for 7.9-eV excitation of Suprasil-W. While the dominant decay time of between 60—80 nsec is roughly constant as a function of temperature, the decay is not a pure exponential at any temperature.

Figure 10 shows the decay of the 1.9-eV band. While the decay is clearly characterized by a single dominant rate, it is not purely exponential as can be seen in Fig. 11. There is some change in the decay as the temperature is varied.

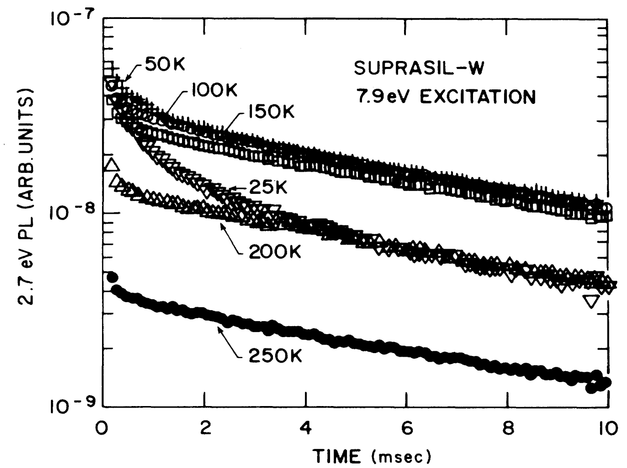

FIG. 8. Semilog plot of the 2.7-eV luminescence decay at various temperatures, for 7.9-eV excitation of Suprasil-W.

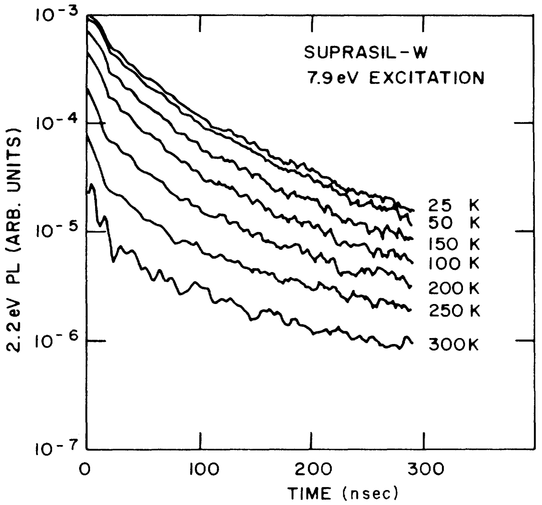

FIG. 9. Semilog plots of the decay of the 2.2-eV luminescence band at various temperatures, for 7.9-eV excitation of Suprasil-W. The data were taken at 2.3 eV (539 nm) for increased sensitivity.

V. TEMPERATURE DEPENDENCE

The temperature dependence of the magnitudes of the various PL bands, for 7.9-eV excitation of Suprasil-W, is shown in Figs. 12 and 13. The temperature dependences of the 4.3-, 3—4-, and 2.7-eV luminescence (Fig. 12) are most unusual in that the intensity first increases as the temperature is raised from 25 to 50 K, after which it decreases with increasing temperature. This nonmonotonic behavior is not seen in the 2.2- and 1.9-eV bands (Fig. 13). The contrasting temperature dependence of the 2.7- and 2.2-eV bands can be discerned quite clearly in Fig. 7 (in this figure the 2.2-eV band is visible at short times, the 2.7-eV band at long times), and it can be seen in Fig. 5 that the decay curve for the 3—4-eV luminescence changes shape as the temperature is lowered below 100 K.

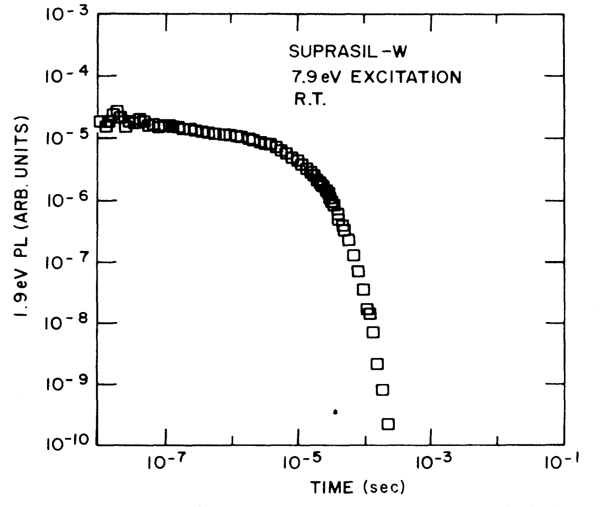

FIG. 10. Decay of the 1.9-eV PL in Suprasil-W (7.9-eV excitation) at room temperature.

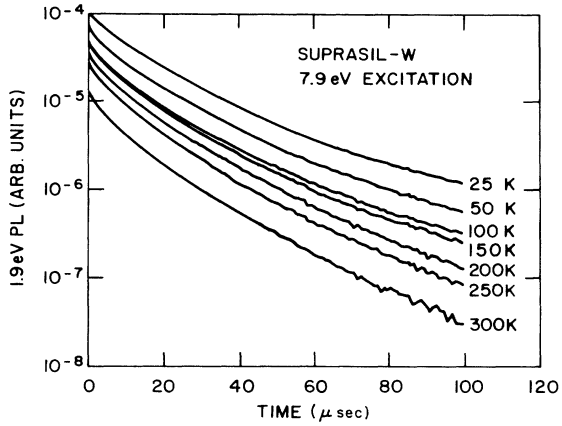

FIG. 11. Semilog plots of the decay of the 1.9-eV band in Suprasil-W (7.9-eV excitation) at various temperatures.

The data in Figs. 12 and 13 were obtained by integrating the PL transients displayed earlier. The 4.3-eV data results from integrating the luminescence signal over a 16-nsec window centered at $t=0$. This corresponds roughly to the width of the laser pulse. The relatively small number of sample points (the data were recorded digitally with 2-nsec resolution) accounts for the greater scatter of the 4.3-eV data compared to the data for the other bands. In extracting the magnitude of the 4.3-eV

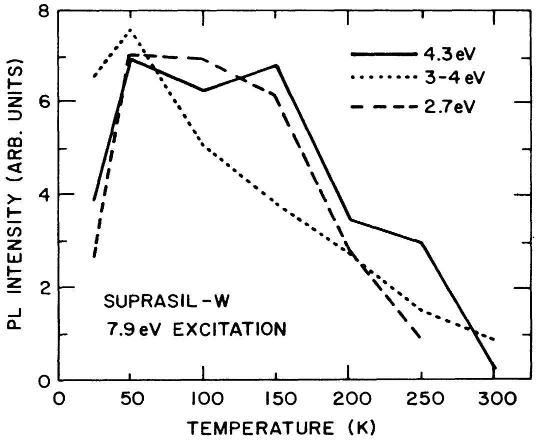

FIG. 12. Temperature dependence of the luminescence bands in Suprasil-W (7.9-eV excitation). Solid line, 4.3-eV band. Values are proportional to the integral of the data over a 16-nsec window centered at $t=0$. Dotted line, 3—4-eV band. Values are proportional to the integral of the luminescence transient for times greater than 20 nsec. Dashed lines, 2.7-eV band. Values are proportional to the integral of the luminescence transient for times between 5 and 10 msec. The 2.7-eV band is unmeasurably small at 300 K.

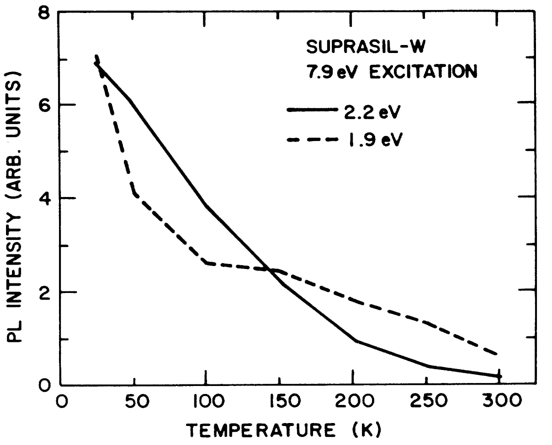

FIG. 13. Temperature dependence of the luminescence bands in Suprasil-W (7.9-eV excitation). Solid line, 2.2-eV band. Values are proportional to the integral of the luminescence transient for times from 2×10^{-9} to 2×10^{-7} sec. Dashed line, 1.9-eV band. Values are proportional to the integral of the luminescence transient for times from 2×10^{-7} to 10^{-4} sec.

PL, the baseline was taken as the magnitude of the photoluminescence just after the fast 4.3-eV signal in order to subtract off the contribution of the 3—4-eV luminescence which follows at later times.

For the other energies a broader time window is available. For the 3—4-eV PL the data of Fig. 5 were integrated for times greater than 20 nsec. For 2.7 eV the data of Fig. 8 were integrated from 5 to 10 msec. For the 2.2-eV band the data of Fig. 9 were integrated from 2×10^{-9} to 2×10^{-7} sec. Finally, for the 1.9-eV band the data of Fig. 11 were integrated from 2×10^{-7} to 10^{-4} sec.

VI. DISCUSSION

Some preliminary measurements of time-resolved PL under 7.9-eV excitation were reported by Gee.[7,9] The 4.3- and 2.7-eV bands were observed to increase after neutron irradiation, while the 1.9-eV band did not. Perhaps the most interesting observation reported by Gee and Kastner was that while only the 3—4- and 4.3-eV bands could be seen under steady-state excitation by a hydrogen-discharge lamp (exciting at 7.6 eV), the other bands become apparent when the 7.9-eV F_2 laser was used.[6–8] In part this may be due to the increase sensitivity afforded by the more intense laser source, but in the case of the 1.9-eV band we know[10] that the luminescence center is being *created* by the intense photon flux, and the same might be true for the other bands.

The photoinduced 1.9-eV luminescence center was first observed in response to 7.9-eV irradiation,[10] but we have subsequently found that it can be generated equally well by 6.4- or 5.0-eV photons. The generation spectrum falls off below this energy, however, since 3.7-eV photons, although capable of exciting the 1.9-eV PL once the centers are in place, are unstable to create the centers. The spectrum of the 1.9-eV PL for various excitation energies is shown in Fig. 14. The spectra were measured at a delay time of 5 μsec, comparable to the inverse decay rate of the luminescence (see Fig. 10) and with 4-nm resolution, which corresponds to an energy resolution of approximately 0.01 eV in this range of photon energies. Figure 14(a) shows the luminescence measured with 5.0-eV excitation in virgin samples (i.e., no previous exposure at photon energies higher than 5.0 eV). After the luminescence centers are created by the 5.0-eV irradation, they can then be excited by 3.7-eV photons with the result shown in Fig. 14(b). Figure 14(c) results from 6.4-eV excitation. The magnitudes of Figs. 14(a)—14(c) are normalized to the incident laser flux. Figure 14(d) shows the spectrum of the 1.9-eV PL in Suprasil-W resulting from 7.9-eV excitation. The magnitude of this spectrum should not be compared to the spectra shown in Figs. 14(a)—14(c), since Fig. 14(d) was obtained with a different optical arrangement. The data in Fig. 14(d) only extend down to 1.77 eV (700 nm) because of interference from the atomic-fluorine laser lines. The peak of the luminescence in this case is shifted down by about 0.02 eV from its value at the other excitation energies. Apart from this, the luminescence energy is remarkably insensitive to the excitation energy, as is the decay rate and the unusually skewed line shape.

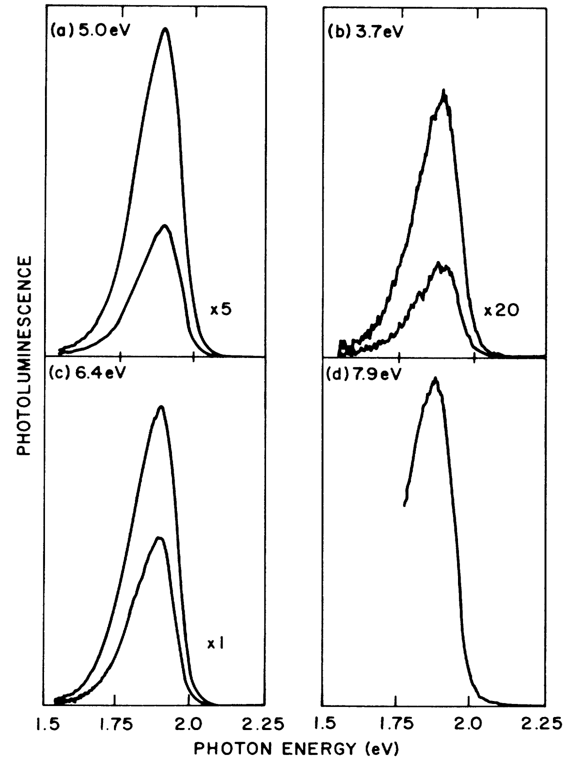

FIG. 14. Spectrum of the 1.9-eV luminescence band. (a) 5.0-eV excitation, virgin samples. (b) 3.7-eV excitation after previous 5.0-eV irradiation. (c) 6.4-eV excitation. (d) 7.9-eV excitation. In each case the upper (more intense) spectrum is from Suprasil-W, and the weaker spectrum is from Suprasil. For 7.9-eV excitation only Suprasil-W is shown.

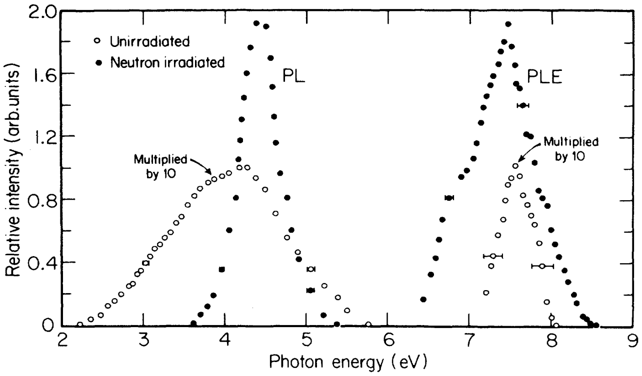

FIG. 15. Steady-state photoluminescence results of Gee and Kastner.[6] The material is Suprasil, and the spectra were taken at 15 K. The curves labeled PLE are the photoluminescence excitation spectra.

Particular significance was attached to the 4.3-eV luminescence band by Gee and Kastner[6] who attributed this luminescence band to an intrinsic defect because its strength could be enhanced by neutron irradiation. They also noted a similarity to the photoluminescence in the semiconducting chalcogenides, i.e., the luminescence energy scaled with the band gap and its temperature dependence scaled with the glass transition temperature. The time-resolved measurements presented in this paper provide additional insight into this band. The data of Gee and Kastner[6] are reproduced in Fig. 15, while for comparison Fig. 16 shows the present time-resolved measurements. Figure 16 is the same data as in Fig. 1(a), plotted on a linear scale. While Gee and Kastner noted the narrowing and shifting of the luminescence band upon neutron irradiation, it is immediately apparent from Fig. 16 that there are really two *completely distinct* luminescence processes. The zero-delay luminescence in the unirradiated sample has the same spectrum as seen by Gee and Kastner in the neutron-irradiated sample, while the spectrum at longer times more closely resembled the steady-state spectrum seen in the unirradiated material. Gee and Kastner's spectrum for unirradiated Suprasil in fact shows a peak at 4.3 eV and a shoulder at about 3.9 eV, so it can easily be believed that this spectrum really is made up of the two overlapping bands that are revealed in the time-resolved measurement.

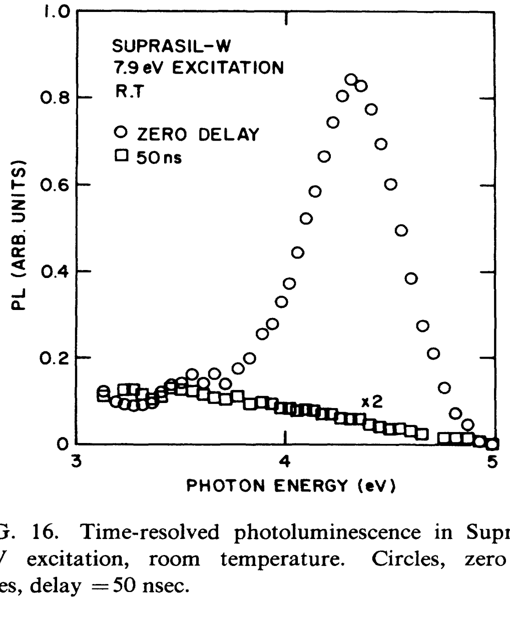

FIG. 16. Time-resolved photoluminescence in Suprasil-W. 7.9-eV excitation, room temperature. Circles, zero delay; squares, delay =50 nsec.

It may therefore be concluded that only the 4.3-eV band grows with neutron irradiation (or at least it grows by a much greater amount than does the 3–4-eV band). This was confirmed by our own measurements of transient photoluminescence from a neutron-irradiated sample, where using 7.9-eV excitation we could discern only the fast 4.3-eV band whose strong intensity at zero delay precluded observation of the weaker longer-lived luminescence.

We turn now to a discussion of the 2.7-eV band. As can be seen from the figures presented earlier, this band is strongly temperature quenched, being unmeasurable at room temperature. Skuja, Streletsky, and Pakovich[11] reported a very different temperature dependence in neutron-irradiated Suprasil-like a-SiO$_2$. For excitation at 5 eV, they found that the time-integrated intensity of the 2.7-eV band *increased* with increasing temperature above 100 K, while the 4.3-eV band decreased. They interpreted this as thermally activated spin conversion, with the 4.3- and 2.7-eV luminescence bands being the singlet-singlet and triplet-singlet transitions, respectively, at a single defect. We emphasize that their measurement of the decay time of this band is in complete agreement with our own; only the temperature dependence of the intensity is different.

It appears, therefore, that neutron-induced defects give luminescence with a very different temperature dependence from the native defects in the as-prepared material, even though the luminescence is the same in every other aspect, such as energy and decay time. The most obvious source for a difference in the temperature dependence is some difference in the local environment which could give rise to a different branching ratio to a nonradiative decay channel, for example. While this could easily result in a change in the *magnitude* of the slope of the intensity-versus-temperature curve, such a mechanism seems less likely to be able to account for a change in the *sign* of this slope. Moreover, the fact that the decay is exponential suggests that the luminescence center is not strongly influenced by the details of the local environment. We would therefore like to suggest another possibility here.

We have previously demonstrated[2,5–10] that below-gap optical excitation, such as that used to excite the photoluminescence, will cause metastable changes in the configuration of defects in a-SiO$_2$. These changes are observable by electron paramagnetic resonance (EPR) and by photoluminescence. Once the possibility of photoinduced metastable defects is acknowledged, it becomes reasonable to suspect that there could also be transient, short-lived centers produced by optical excitation. These would of course not be detected in a post-irradiation EPR experiment, but we have previously reported evidence of such centers in photoluminescence.[10] A plausible origin for the discrepancy between our results and those of Skuja *et al.*[11] is that photoluminescence on an annealed (i.e., unirradiated) sample may not in fact probe a fixed number of defects. Rather, the excitation creates new centers, which then rapidly anneal near room temperature, and it is the temperature dependence of this more complicated process which is really reflected in our photoluminescence data.

Clearly, the data presented here are not sufficient to prove this hypothesis. Nonetheless, there is other evidence to support the idea that a transient defect of some sort is involved in the 2.7-eV photoluminescence. Tanimura *et al.*[12] studied electron-beam-induced luminescence near 2.8 eV in both crystalline and amorphous SiO_2, and found it to correlate strongly with a transient volume change consistent with a transient vacancy-interstitial pair formation. This was supported by the work of Hayes *et al.*[13] who measured optically detected magnetic resonance of the 2.8-eV x-ray-induced luminescence in crystalline quartz. Our measurements of photoluminescence in crystalline quartz (Fig. 4) shows a band at about 2.8 eV, and its lifetime agrees well with the value found by Tanimura *et al.*[12] if we extrapolate their results to room temperature. The evidence presented here would therefore seem to suggest that below-gap optical excitation may be able to create the same sort of transient defects in a-SiO_2 as are produced by electron-beam or x-ray excitation. This would indeed be a remarkable result.

To explain the radiolytic formation of transient defects as seen by Tanimura *et al.*, Griscom[14] has recently put forth a model involving intrinsic self-trapping of an exciton formed from an electron in the conduction band and a hole in the lower valence band, i.e., that part of the valence band which arises from the Si—O bonding orbitals. Such an exciton requires at least 15 eV to produce. The same model might account for the present results, if a two-photon process is invoked. Alternatively, a smaller amount of energy might suffice if the electron were excited directly into a defect state in the gap, rather than into the conduction band as is the case in Griscom's model. The $O_3^+(Si_2O)$ center, an overcoordinated oxygen bonded to two silicons and one other oxygen, is a likely candidate since calculations[15] show that it gives an empty state in the lower half of the gap.

Another puzzling result concerning the 2.7-eV photoluminescence comes from studies of thin SiO_2 films. We have performed preliminary measurements on a thin-film sample of a-SiO_2 thermally grown on silicon. The sample was grown in steam at 1100 °C on 300 Ω cm p-type silicon to a thickness of about 1 μm. Both the 4.3- and 1.9-eV bands were seen clearly, under 7.9- or 6.4-eV excitation, recognizable by their distinct spectral and temporal characteristics which were the same as in the bulk glass samples. However, the 2.7-eV band was *not* seen, even at low temperature.

Other investigators have reported conflicting information regarding this band. McKnight and Palik[16] reported seeing the 2.7-eV band in thermal oxides using electron-beam excitation, whereas Koyama[17] reported a similar experiment where he did not see the 2.7-eV band. While the connection between photoluminescence and cathodoluminescence is of course not straightforward, these results clearly show that the 2.7-eV band is highly sample dependent. It may therefore be hoped that this band, which is clearly defect-related, could be used as a monitor of oxide quality in electronic device applications.

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