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# Defect pair creation through ultraviolet radiation in dense, amorphous $SiO_2$

R. A. B. Devine
*Centre National d'Etudes des Télecommunications, Boîte Postale 98, 38243 Meylan, France*

J. Arndt
*Mineralogisch-Petrographisches Institut, Universität Tübingen, D-7400 Tübingen 1, Federal Republic of Germany*
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Defect creation in 24% densified, high-OH-concentration amorphous $SiO_2$ has been studied using 248-nm excimer laser radiation. Combining laser and $\gamma$-ray radiation data, we find correlated growth of oxygen-vacancy and nonbridging oxygen-hole center defects over a range of concentration from $5\times10^{15}$ to $5\times10^{17}$ cm$^{-3}$. Oxygen-hole centers are created at least 100 times more efficiently in densified, high-OH-concentration $SiO_2$ than in undensified, high-OH-concentration $SiO_2$ for the same 248-nm-radiation dose. It is argued that strained bond cleavage is the dominant mechanism of defect creation by energetic photons in metastably densified oxides. The primary oxygen-vacancy-center creation mechanism by ultraviolet radiation in undensified, high-OH-concentration $SiO_2$ appears to be network-atom-displacement related.

In general, research into radiation effects in crystalline and amorphous $SiO_2$ used in microelectronics applications has centered upon MeV-energy photons while the damaging effects of sub-band-gap photons ($E\sim9$ eV) have been the reserve of those researchers interested in laser-induced breakdown.[1,2] Increasingly, however, low-pressure, high-frequency plasma discharges are being used in various processing steps in microelectronics (dry etching, deposition, resist stripping,...). With these systems one can no longer ignore the possible role played by the intense ultraviolet (uv) emission of the plasma which may extend into the vacuum-uv wavelength range.[3,4] Irrespective of the energy of the photons or ionizing radiation giving rise to damage production there remains the fundamental question, how the radiation interacts with the crystalline or amorphous network to produce defects—whether this proceeds via precursor transformation or "destruction" of the otherwise perfect network.

A considerable amount of work has been done on defect creation in amorphous $SiO_2$ ($a$-$SiO_2$) through $\gamma$- and x-ray radiation.[5] Three "primary" structural defects have been identified, the oxygen-vacancy or $E_1'$ center, the nonbridging oxygen-hole (NBOH) center, and the peroxy radical. Recently, two other defects have been identified,[6] both related to the self-trapping of holes. In most of the studies performed to date using $\gamma$-, x-ray, or laser radiation, the density of the defects studied has been $<10^{16}$ cm$^{-3}$. Such densities are typically of the same order as the highest impurity concentration and only $10^{-6}$ of the total density of Si—O bonds in the network. Given the small size of this latter figure (and ignoring impurity effects) it is difficult to discriminate between defect creation reactions—whether they be due to new structural damage or precursor transformation involving intrinsic growth irregularities. Concentrating on $E_1'$ and NBOH centers the generally invoked defect reactions are

$$O_3{\equiv}Si{-}O{-}Si{\equiv}O_3+h\nu\rightarrow O_3{\equiv}Si^{\circ+}Si{\equiv}O_3+e+O^{\circ}, \quad (1)$$

$$O_3{\equiv}Si{-}Si{\equiv}O_3+h\nu\rightarrow O_3{\equiv}Si^{\circ+}Si{\equiv}O_3+e, \quad (2)$$

$$O_3{\equiv}Si{-}OH+h\nu\rightarrow O_3{\equiv}Si{-}O^{\circ}+H. \quad (3)$$

Without specifying the mechanism coupling the photon energy ($h\nu$) and the physical defect transformation reaction, we note that reactions (2) and (3) involve network growth defects or irregularities while Eq. (1) involves atomic displacement from the perfect network. On the basis of Eq. (3) we might anticipate substantially different NBOH creation efficiencies in low-OH-concentration ($<5$ ppm by weight) and high-OH-concentration ($>1200$ ppm by weight) silicas. It is, therefore, already surprising that a difference in creation efficiency of only 5:1 is observed[7] in $\gamma$-irradiated Suprasil 1 (high-OH-concentration) and Suprasil W1 (low-OH-concentration) in the Mrad-radiation dose range. This may already evidence the possibility of alternative defect reactions to those described by Eq. (3) for the formation of NBOH centers.

In a recent study of $\gamma$-radiation-induced defects in metastably densified $a$-$SiO_2$ samples[7] obtained by application of high pressure and temperatures, we found evidence for an apparent correlation between $E_1'$ and NBOH center creation up to densities attaining $\sim10^{18}$ cm$^{-3}$. This result lead us to hypothesize that an alternative defect reaction leading to simultaneous creation of stable, $E_1'$-like and NBOH centers might be one involving cleavage of strained Si—O—Si bonds:

$$(O_3{\equiv}Si{-}O{-}Si{\equiv}O_3)^{*}\rightarrow O_3{\equiv}Si{-}O^{\circ}+{}^{\circ}Si{\equiv}O_3, \quad (4)$$

 

where recombination is impeded by the network relaxation accompanying bond cleavage. Similar arguments have been advanced, it turns out, to explain x-ray photoemission spectroscopy data obtained on the $Si-SiO_2$ interfacial region[8] where substantial network strain due to lattice mismatch is anticipated and may have been evidenced through optical measurements.[9]

In the work reported here, we have extended our study of densified $a$-$SiO_2$ to include defect creation by subband-gap laser radiation. We compare the relative efficiencies of $\gamma$ and laser radiation in creating defects in both densified and undensified material and further investigate the possibility of correlation $E_1'$ and NBOH center creation.

Studies were carried out on samples of high-OH-concentration Suprasil 1 (OH > 1200 ppm by weight according to manufacturers analysis) densified by 24.1% with respect to normal, undensified Suprasil 1 ($\rho = 2.202$ g cm$^{-3}$). The method of densification and experimental details have been described previously.[10] The samples were in the form of irregular grains ~1.5 mm diam resulting directly from the densification process. Laser irradiation was carried out using a KrF gas filled excimer laser (Lambda Physik MG 101), the 248-nm radiation being slightly focused to produce an energy density per pulse at the sample surface of 300 mJ cm$^{-2}$. Accumulated doses up to 5000 J cm$^{-2}$ were obtained at a pulse repetition frequency of 2 Hz. The energy per pulse was measured using a Gen-Tec joulemeter.

Defects were studied using electron-spin-resonance methods at $X$-band frequencies. $E_1'$ centers were measured at room temperature while NBOH centers were observed at 120-K. Defect densities were ascertained by double numerical integration of the experimental power derivative curves and comparison with the same obtained for a sample of pitch containing a calibrated number of paramagnetic spins ("strong pitch"). In the case of the NBOH centers, correction was made for Boltzmann factor effects in determining the spin density from the 120-K spectra.

In Figs. 1(a) and 1(b) we show the experimentally observed power derivative line shapes observed for the $E_1'$ and NBOH centers for a sample subjected to a total dose of 248-nm radiation of 5000 J cm$^{-2}$. The hyperfine lines associated with the $E_1'$ center shown in Fig. 1(a) were measured in the second-harmonic mode which results in a line shape very similar to a pure absorption shape and having a full width at half peak height of ~0.6 times the peak-to-peak first-derivative linewidth.[11] The hyperfine splitting was measured as 465 G (422 G in undensified Suprasil 1) and the second-harmonic linewidths, 50 and 39 G, respectively, for the low-field and high-field lines. The corresponding second-harmonic linewidths in undensified Suprasil 1 are 45 and 38 G.[12] The results obtained for the hyperfine lines are entirely consistent with our previous observations on densified samples subjected to $\gamma$ radiation.[13] In Fig. 2 we show the growth of the $E_1'$ and NBOH densities as a function of accumulated 248-nm radiation dose (incident on the samples). We observe that, within experimental error, both the absolute value and dose dependence of the two defect center densities is the same. Also, in Fig. 2 we show on an expanded density scale (right-hand scale) the dose dependence of the $E_1'$ density measured in undensified Suprasil 1 rod samples (0.8 cm long, pulse energy again 300 mJ cm$^{-2}$). Consistent with other authors[14] we were unable to detect measurable numbers of NBOH centers in undensified samples.

The first observation we must make is that 248-nm laser irradiation of undensified, high-OH-concentration Suprasil 1 produced no measurable numbers of NBOH centers while $E_1'$ centers were produced. In low-OH-concentration Suprasil W1 we found previously that such radia-

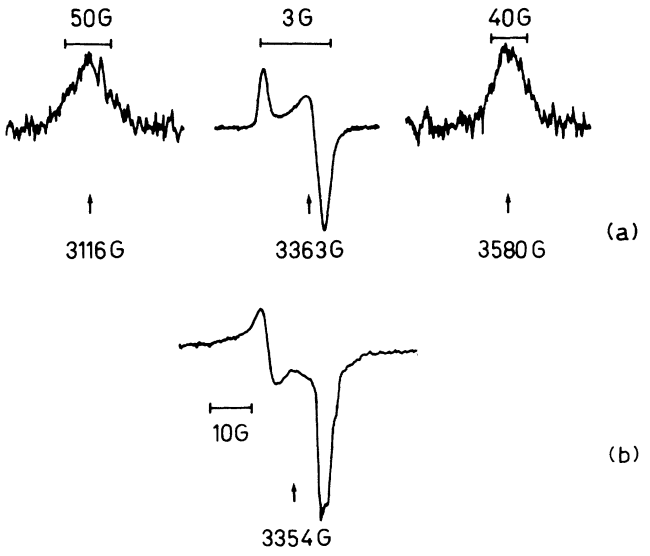


FIG. 1. Experimentally observed electron-spin resonance line shapes for 248-nm laser-irradiated Suprasil 1 densified by 24.1%; the accumulated incident dose was 5000 J cm$^{-2}$. (a) $E_1'$ center at 293 K, the low-field and high-field lines measured in second harmonic mode. (b) NBOH center measured at 120 K.

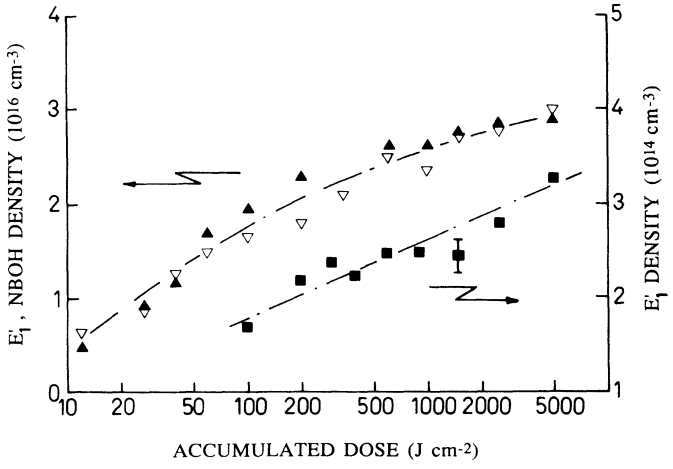


FIG. 2. Growth of the $E_1'$ and NBOH center densities as a function of accumulated dose of 248-nm laser radiation; (▽) $E_1'$ centers in 24.1% densified Suprasil 1, (▲) NBOH centers in 24.1% densified Suprasil 1, and (■) $E_1'$ centers in undensified Suprasil 1.

tion produced both $E_1'$ and NBOH centers. Furthermore, it has been shown recently[15] that 193-nm excimer laser radiation of Suprasil 1 at 77-K produces NBOH centers but no measurable $E_1'$ center density. This latter result contradicts, at first sight, studies on Suprasil 1 using 157-nm laser radiation at room temperature which suggested[14] no NBOH creation but, bearing in mind the rather low annealing temperature of the NBOH centers in undensified Suprasil 1 it may be that these centers annealed to undetectable levels in the 157-nm experiments. The absence of $E_1'$ defects after 77-K irradiation using 194-nm radiation[15] in Suprasil 1 is consistent with our data[16] on 248-nm irradiated Suprasil W1 which indicated that it was necessary to irradiate at temperatures $>150$ K for these defects to be revealed. The data presented here for densified Suprasil 1 irradiated at room temperature clearly indicate substantial NBOH and $E_1'$ creation. To emphasize possible correlation of these defects we replot in Fig. 3 the NBOH and $E_1'$ data obtained by laser radiation and data we obtained previously[7] by $\gamma$ irradiating 13.8% densified Suprasil 1. Within the range of experimental error, the growth of the $E_1'$ and NBOH center defect densities appears correlated in the densified material independent of the ionizing radiation used. Note that this appears to be true over a range of defect densities $\sim 2$ orders of magnitude ($5\times10^{15}$ to $5\times10^{17}$ cm$^{-3}$). Whereas room-temperature laser radiation of undensified Suprasil 1 produces no measurable numbers of NBOH centers (or they have already annealed) and rather low densities of $E_1'$ centers ($2\times10^{14}$ cm$^{-3}$ for 1000 J cm$^{-2}$ of 248-nm radiation), x-ray irradiation performed at 77 K was found[15] to produce both $E_1'$ and NBOH centers in significantly larger numbers, $>10^{15}$ cm$^{-2}$ for 1 Mrad and increasing with dose. Furthermore, NBOH centers were generally created in larger densities than $E_1'$ centers. These results are consistent with our observations[7] on Suprasil 1 irradiated with $\gamma$ rays at room temperature. Since defect-energy calculations[17] place states associated with Si-OH below the $SiO_2$ valence-band edge, larger-than-band-gap-energy photons radiolyse the H rather easily, whereas, the low cross section for two-photon effects renders the process inefficient at 248 nm. This coupled with rapid annealing in undensified material accounts for the difference in NBOH center creation obtained with the sub-band-gap laser radiation.

Various authors[18–20] have demonstrated that laser-induced $E_1'$ defect creation in undensified $a$-$SiO_2$ results from a two-photon absorption modulated process. The fraction, $f_2$, of energy lost in two-photon absorption from an incident beam of intensity $I$ (in MW cm$^{-2}$), is approximately

$$f_2=[1-\exp(-2\alpha z)]I\beta/\alpha\,, \tag{5}$$

where $\alpha$ is the single-photon absorption coefficient [0.002 cm$^{-1}$ at 248 nm (Ref. 21)], $\beta$ is the two-photon absorption coefficient [0.017 cm MW$^{-1}$ at 248 nm (Ref. 22)] and $z$ is the sample thickness in cm. Using Eq. (5) to calculate the energy lost in two-photon excitations we plot in Fig. 4 the observed $E_1'$ density in 24% densified Suprasil 1 as a function of the number of two-photon excitations. We include data taken on undensified Suprasil 1. Also included in Fig. 4 are data obtained on $\gamma$-irradiated samples of undensified and 13.8% densified Suprasil 1. Here we have assumed an electron-hole pair creation efficiency of $8\times10^{12}$ $e$-$h$ pairs cm$^{-3}$rad$^{-1}$. We have previously demonstrated[23] that in undensified, low-OH-concentration Suprasil W1 there appears to be an equivalence, for $E_1'$ creation, between two-photon excitation dependence and $e$-$h$ pair dependence. This equivalence does not appear to be maintained for high-OH-concentration $a$-$SiO_2$.

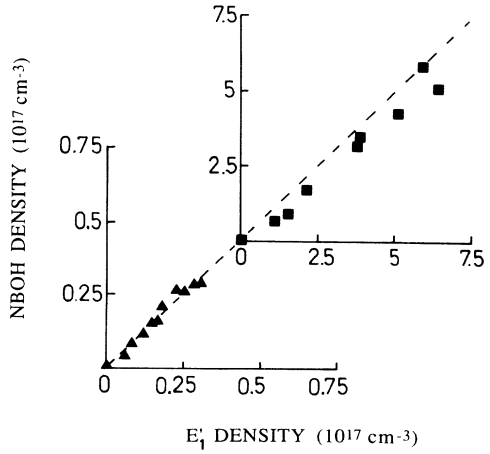


FIG. 3. NBOH center density vs $E_1'$ density measured in (▲) 248-nm laser irradiated, 24.1% densified Suprasil 1 and (■) $^{60}$Co $\gamma$ irradiated, 13.8% densified Suprasil 1.

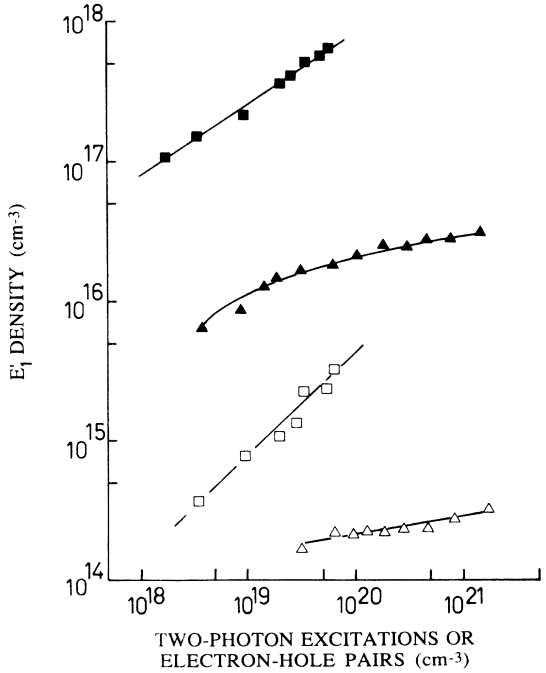


FIG. 4. Variation of the $E_1'$ center defect density in Suprasil 1 as a function of accumulated number of two-photon excitations (248-nm laser) or electron-hole pairs ($^{60}$Co $\gamma$). (△) laser irradiated, undensified; (□) $\gamma$-ray irradiated, undensified; (▲) laser irradiated, 24.1% densified; (■) $\gamma$-ray irradiated, 13.8% densified.

If we crudely compare the enhancement of the $E_1'$ defect creation efficiency in densified $a$-$SiO_2$ with that in undensified $a$-$SiO_2$, we obtain a factor of $\sim 270$ for $\gamma$-ray radiation and 100 for 248-nm laser radiation, again underlining, for the high-OH-concentration case, a difference between effects due to two-photon excitations and those due to $e$-$h$ pairs.

The results presented for 248-nm laser-radiation-induced defect creation in densified, high-OH-concentration $a$-$SiO_2$ give further evidence that in the dense phase there is correlated $E_1'$ and NBOH center generation which we have argued is consistent with strained bond cleavage. This process appears to dominate all other $E_1'$ and NBOH creation processes by $\gamma$-ray or laser radiation in the dense material unless, fortuitously, there exist independent mechanisms which create the two different defects in equal numbers with the same dose dependence. In 248-nm laser-irradiated *undensified* Suprasil 1 we observe $E_1'$ creation but no correlated NBOH creation. Based on the above arguments it may be that annealing of NBOH centers in the undensified material is sufficiently rapid at room temperature to reduce their numbers to an undetectable level. Alternatively, although strained bonds must exist in the undensified network by the very nature of the bonding and bond-angle distribution, it may be that their number is too small for strained bond cleavage there to be relevant. In this case, $E_1'$ creation in undensified material must result either from precursor transformation [Eq. (2)] or network oxygen displacement [Eq. (1)]. It has been suggested[24] that in high-OH-concentration $a$-$SiO_2$ growth defects such as $O_3{\equiv}Si{-}Si{\equiv}O_3$ would be absent or in extremely small concentration since the presence of OH groups in the form of interstitial $H_2O$ would produce hydroxyl terminations (Si-OH). $E_1'$ defect creation by a process such as described by Eq. (2) would then be improbable; this would not be the case for low-OH-concentration $a$-$SiO_2$ where such Si—Si bonds could be compensated to produce chemical balance by the presence of peroxy linkages, $O_3{\equiv}Si{-}O{-}O{-}Si{\equiv}O_3$. At the present time it is not clear what other growth defects might act as $E_1'$ precursors in high-OH-concentration $a$-$SiO_2$ and in this event one might hypothesize that the observed $E_1'$ growth under laser radiation is due to a reaction process such as Eq. (1). Our data then sets a limit on the efficiency of this process in undensified $a$-$SiO_2$.

The results presented indicate strongly enhanced defect creation in densified $a$-$SiO_2$ subjected both to sub-band-gap energy and very high-energy photons. Apart from the general relevance of defect creation due to sub-band-gap radiation these results may be particularly important for applications such as thin-film coatings (sol-gel, chemical vapor deposition, . . .) where deposition at low temperatures is suspected[25] to result in films which are intrinsically densified as compared to high-temperature produced $a$-$SiO_2$.

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