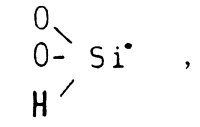
Extrinsic- and intrinsic-defect creation in amorphous SiO_2

R. A. B. Devine and J.-M. Francou
Centre National d'Etudes des Télécommunications, Boîte Postale 98, 38243 Meylan CEDEX, France
(Received 22 November 1989; revised manuscript received 12 February 1990)

We have studied the creation efficiency of various intrinsic and extrinsic defects in high-[OH] amorphous silica subjected to the ultraviolet emission from an O_2 plasma or ^{60}Co γ-ray radiation. Both oxygen-vacancy- and nitrogen-related defects are observed following γ-ray irradiation or ultraviolet exposure. The wavelength range responsible for defect creation is estimated to be $200 \lesssim \lambda \lesssim 300$ nm ($4 \lesssim E_{\text{photon}} \lesssim 5.9$ eV). The ultraviolet power output of the plasma estimated by comparing defect yields with those from a Hg lamp ($\lambda = 185$ and 254 nm) suggests $200 \lesssim P \lesssim 900$ mW cm^{-2} for a plasma power density ~ 300 mW cm^{-3}. Nonbridging oxygen-hole centers and hydrogen-related defect centers as well as methyl radical (CH_3) defects are observed after γ-ray irradiation but not after ultraviolet exposure. The efficiency of creation of the various defects is material dependent.

INTRODUCTION

The creation or "revelation" of defects in amorphous SiO_2 (a-SiO_2) by sub-band-gap (8.9-eV) radiation from intense light sources such as excimer lasers has been the subject of a number of recent studies.[1-5] These studies have been carried out with the objective of elucidating the nature and mechanisms of creation of both intrinsic and extrinsic defects and this by using different types of radiation such as neutrons, electrons, γ's, optical photons, etc. In particular, extensive studies have been made on the oxygen-vacancy (E_1') defect since this is one of the most well-documented[6] intrinsic network defects. It is now generally accepted that sub-band-gap radiation may transform existing E_1' precursors such as the B_2 center[7] ($O_3 \equiv Si—Si \equiv O_3$) or create new centers through oxygen displacement via a still ill-defined process probably involving exciton relaxation.[8] At optical wavelengths the excitons may be created by a two-photon process. As far as extrinsic defects are concerned, studies[1] on high-[OH] a-SiO_2 subjected to 7.9-eV laser radiation have evidenced the presence of nitrogen (N) -related defects attributed to an $O_3 \equiv Si—O—N—O—Si \equiv O_3$ or $O_3 \equiv Si—O—N—Si \equiv O_3$ structure. These defects have also been revealed in studies[9] using 100-keV x rays to irradiate high-[OH] oxides. Here, the defect structure was interpreted as similar to the Si A center,[10] except that the interstitial O atom bonded to two nearest Si neighbors is replaced by a N interstitial loosely bonded to all four Si first-nearest neighbors. Such a model has been used previously[11] to describe N-related centers in laser-annealed, N-implanted Si. The absence of N centers in 6.4-eV-laser-irradiated high-[OH] silica has been taken[9] as evidence that N revelation processes require the cross-band-gap excitation of free electrons followed by their trapping at positively charged, nonmagnetic precursor sites. Other extrinsic defects which have been studied[12,13] are the deuterium (D) center observed following ^{60}Co γ or n irradiation of deuterium-exchanged, high-[OH] a-SiO_2, the hydrogen-related E_1' defect center[12,14]



and the methyl radical,[15] $CH_3^{\bullet}$. Note that in the case of the deuterium center the D is assumed to substitute for the hydrogen.

The present work has been motivated by a need to understand the damage processes in a-SiO_2 resulting from exposure to the intense ultraviolet (uv) emission from a radiofrequency (rf) plasma. Such plasmas, having rf power densities in the hundreds of mW cm^{-3} region, are being increasingly used in current technological applications where plasma-assisted chemistry enables one to lower processing temperatures. Examples are dielectric-metal deposition, oxidation, and dry, chemical etching. To establish a basis for comparison, we have studied in some detail defect creation in high-[OH] a-SiO_2 as a result of ^{60}Co γ radiation. Defect densities (and types) observed in samples subjected to intense plasma uv radiation have been compared with the radiation results.

EXPERIMENT AND RESULTS

Two forms of samples have been used in our experiments, 4-mm-long cylinders cut from 4-mm-diam rods and 2.5-cm-long, 2.5-mm-wide strips cut from a 0.5-mm-thick microscope slide. Both materials, purchased at the same time, were commercially available Suprasil 1 (Heraeus, France)—the processing differences were, apparently, that the rod was hot-drawn from a starting ingot, while the slides were cut directly from the ingot and then polished. γ irradiation of the samples was carried out at room temperature in a ^{60}Co source at a rate of 0.55 Mrad h^{-1}. Oxygen plasma exposures were carried out in

a prototype[16] remote-source etching reactor with an O_2 pressure of 1.5 mTorr. The rf frequency was 13.56 MHz and the power, 1000 W, corresponded to a plasma power density of 280 mW cm^{-3}. Samples were placed on a baseplate remote from the plasma source and unpolarized with respect to it to avoid possible ion-damage effects. We have previously demonstrated in substoichiometric oxide[17] that, in this mode, superficial ion damage, if any, is undetectable. Paramagnetic defect densities were determined using electron-spin-resonance (ESR) measurements made with a Bruker ER 200D X-band spectrometer with noise-averaging facilities. Absolute defect densities were ascertained by comparing the double numerical integration of the observed derivative power absorption spectrum with that obtained from a standard, strong-pitch sample containing a known number of paramagnetic spins. Most measurements were made at room temperature, while some [to compare nonbridging-oxygen–hole (NBOH) center creation efficiency] were performed at 120 K.

We have been able to observe the creation of E_1', N-, H-, and NBOH-related centers and the methyl radical, $CH_3^{\bullet}$, defects. Consistent with the observations of other authors,[9] we have observed that the creation of the N center is material dependent—the center was not detected in the 4-mm—rod samples, but was easily observed in the slide material. In Fig. 1 we show the experimental spectrum observed at room temperature for a slide sample irradiated to an accumulated γ dose of 32 Mrad. Not shown in Fig. 1 are a pair of hyperfine lines separated by 74 G which are due to the H-related center; they were observed only in γ-irradiated slide samples. In Fig. 2 we show the central portion of the spectrum presented in Fig. 1 for samples irradiated with a dose of 5 Mrad [Fig. 2(a)] and 52 Mrad [Fig. 2(b)]. We identify the spectra in Fig. 1 as being due to a central E_1' resonance and two sets of lines (Figs. 1 and 2), at least one being a triplet due to hyperfine interactions of a paramagnetic center with nuclei having nuclear spins of $I=1$. Following other authors,[1,2,9,12] these are the N-related defects (outermost hyperfine lines). In Fig. 3 we show the experimental spectrum for a sample irradiated with 52 Mrad of ^{60}Co γ rays–the central part of the spectrum containing the E_1' resonance has been excluded. We see that the 22.9-G doublet shown in Fig. 1 is, in fact, part of a quadruplet having equispacing of 22.9 G, which has been previously[15] identified as due to methyl, $CH_3^{\bullet}$, radicals. From the data presented in Figs. 1–3, we extract the resonance g factors, hyperfine parameters, and hyperfine linewidths given in Table I. In Figs. 4(a) and 4(b) we plot the N, $CH_3^{\bullet}$, and E_1' defect densities in Suprasil 1 slide material

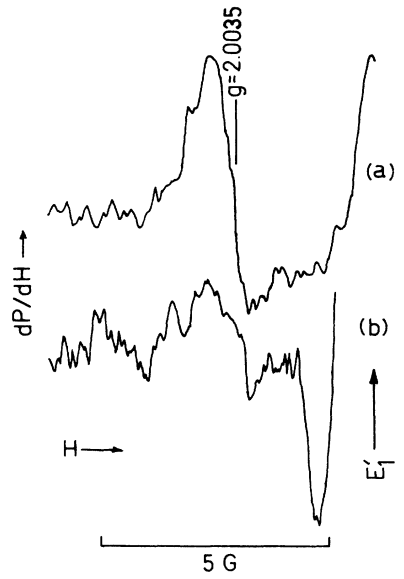


FIG. 2. Amplified view of the central part of the experimental derivative power absorption spectrum in Suprasil 1 slide material for two γ doses: (a) 5 Mrad and (b) 52 Mrad. For the gain used the E_1' resonance is largely off scale. The amplitude of the resonance having a g factor of 2.0035, identified as the central line of the N-center triplet, decreases with increasing dose, as does the amplitude of the outer pair.

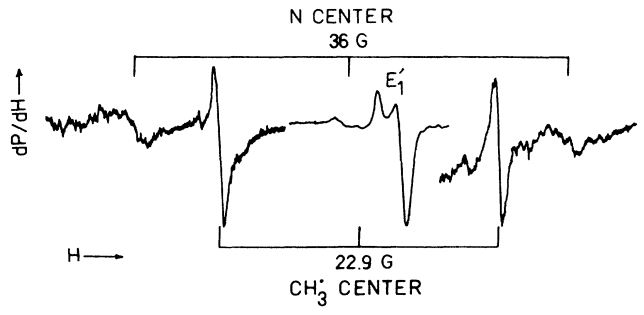


FIG. 1. Experimental derivative power absorption (dP/dH) spectrum as a function of magnetic field, H, for a Suprasil 1 slide sample irradiated with a dose of 32 Mrad of ^{60}Co γ irradiation. The gain used to record the central portion of the spectrum was reduced by a factor of 21. The defect centers visible are the N, E_1', and $CH_3^{\bullet}$ radical.

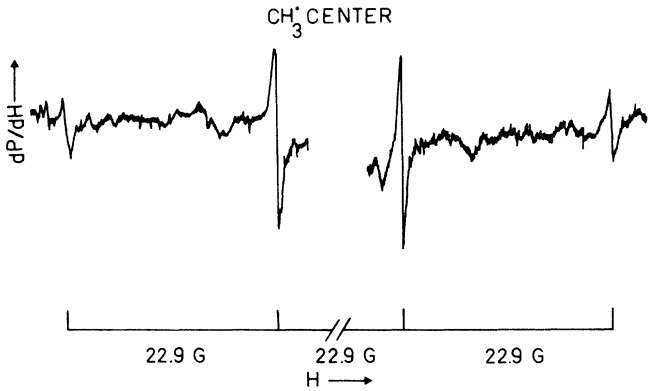


FIG. 3. Experimental hyperfine spectrum of the methyl-radical, $CH_3^{\bullet}$, defect observed in Suprasil 1 slide material following 52 Mrad of ^{60}Co γ irradiation. The peak-to-peak line amplitudes are in the approximate ratio 1:3:3:1. The central, intense E_1' resonance has been omitted.

TABLE I. Resonance g factors, hyperfine line splittings, and hyperfine linewidths for various defects in Suprasil 1 samples.

Center	Central g factor	Hyperfine splitting (G)	Hyperfine linewidth (G)
N	2.0030[a]		2.5[a]
	2.0035	36	2.9
	2.004[b]		
$CH_3^{\bullet}$	2.0027[c]	22.9	0.5

[a]Reference 9.
[b]Reference 1.
[c]From the midpoint field of the two central hyperfine lines.

TABLE II. Densities (per cm^3) of defects observed in Suprasil 1 slide and rod samples exposed to ^{60}Co γ irradiation. The $CH_3^{\bullet}$ radical and H-related defects resulted from 52 Mrad of radiation, while the NBOH centers resulted from 5 Mrad of radiation. NM denotes not measurable.

Defect	Rod	Slide
$CH_3^{\bullet}$	$(1.2\pm0.6)\times10^{13}$	3.1×10^{13}
H-related	NM	6×10^{12}
NBOH	1.2×10^{15}	1.9×10^{14}

as a function of accumulated γ dose. The densities of the N and $CH_3^{\bullet}$ defects were ascertained by integrating the hyperfine spectra and assuming an equal weight ($\frac{1}{3}$) for each hyperfine line of the N spectrum and a 1:3:3:1 ratio for the $CH_3^{\bullet}$ hyperfine spectrum.[15] Note, from Fig. 4(a) and the decrease in intensity of the $g=2.0035$ resonance with γ dose shown in Figs. 2(a) and 2(b), that the triplet nature of the spectrum and its identification with the N center is confirmed. For comparative purposes, we measured the $CH_3^{\bullet}$- and H-related defect densities in Suprasil 1 rod and slide material after 52 Mrad of γ irradiation—the results are presented in Table II. As shown in Fig. 4(a), the N-center density showed a maximum as a function of dose of $\sim8\times10^{13}$ cm^{-3}, approximately 1 order of magnitude larger than the value found[12] in 10-Mrad, x-irradiated Suprasil 2 and 1 order of magnitude smaller than the density observed in Suprasil 1 subjected to 7.9-eV photons from an excimer laser[1] (note the samples were again flat, polished plates).

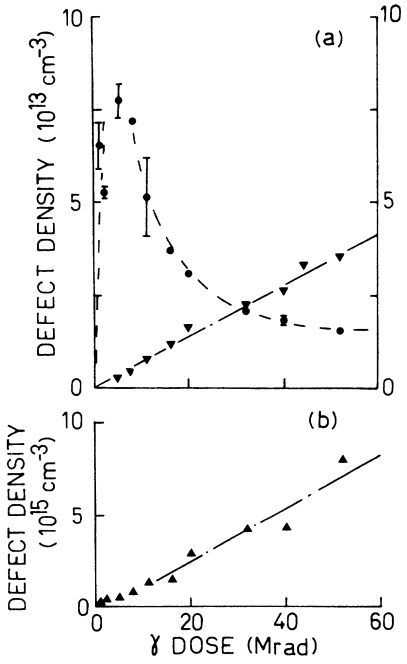


FIG. 4. Variation of the defect density as a function of accumulated γ dose in Suprasil 1 slide samples. (a) ●, N centers; ▼, $CH_3^{\bullet}$ radicals. (b) ▲, E_1' centers.

O_2-plasma exposures were carried out for 10 min—only slide material was used because of convenience of form. We obtained an E_1' density of 1.8×10^{14} cm^{-3} and a N density of $\sim6\times10^{13}$ cm^{-3}. H- and $CH_3^{\bullet}$-center resonances were not detected. Comparison of the defect densities observed with the γ data presented in Fig. 4 suggests that the uv exposure is equivalent to a γ dose of 5 Mrad. In Fig. 5 we show experimental resonance curves obtained at 120 K in O_2-exposed slide material [Fig. 5(a)], 5-Mrad-irradiated slide material [Fig. 5(b)], and 5-Mrad-irradiated rod material [Fig. 5(c)]. The rod material shows a NBOH defect density ~6.5 times the intensity of the slide material for the same dose (account taken of amplifier-gain differences, etc.). The O_2-exposed material showed no detectable NBOH-center creation, even though the E_1' and N density observed at room temperature in the uv-exposed and 5-Mrad-irradiated slide material was essentially identical. The E_1' density in the rod sample exposed to 5 Mrad was ~4.5 times that observed in the slide material for the same dose and in the slide exposed to the uv. Based on the numbers for the comparative creation efficiency of E_1' and NBOH-center defects in slide and rod material subjected to the same γ dose, it is conceivable that the creation of the two defects is correlated in this type of material. This is clearly not the case when using the uv radiation.

We have examined the uv emission from the O_2 plasma by connecting a vacuum monochromator directly to the plasma reactor via a MgF_2 lens. The observed emission spectrum consisted mainly of an intense 130-nm O* line followed by a broad band starting around $\lambda=200$ nm, as expected for the O_2^+ molecule.[18] By placing a 0.5-mm-thick Suprasil slide between the plasma source and the monochromator, we demonstrated that the transmitted intensity of the 130-nm line was attenuated by >50 times. Subsequently, by exposing a five-slice pile of Suprasil 1 samples to the uv plasma and then performing a crude defect profiling by measuring the defect density in each slice, we ascertained that the radiation provoking the defects in the slide material passed uniformly through the five slices. On this basis, we discount the possible role of the 130-nm radiation. The present data then demonstrate that E_1'- and N-center defects are created and/or

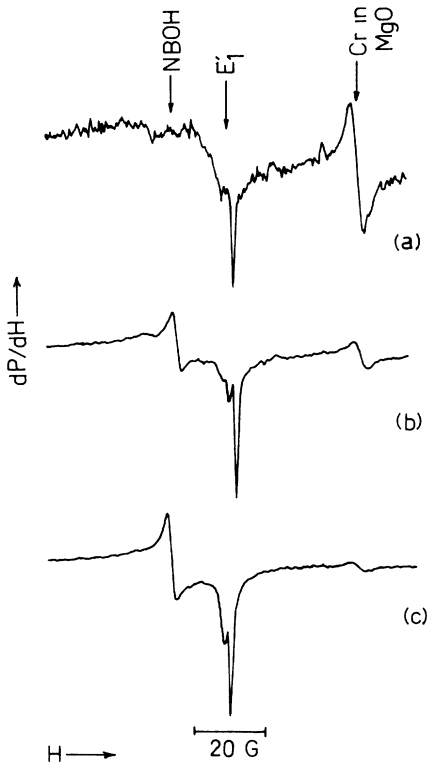


FIG. 5. Experimental derivative power absorption spectra observed at 120 K in (a) Suprasil 1 slide exposed to a 1-kW O_2 plasma for 10 min, (b) Suprasil 1 slide irradiated with 5 Mrad of ^{60}Co γ radiation, and (c) Suprasil 1 rod irradiated with 5 Mrad of ^{60}Co γ radiation. The Cr-in-MgO spectrum derives from a reference sample installed in the microwave cavity. The NBOH-center density in (c) is approximately 6.5 times that in (b). In both (b) and (c) the full NBOH spectrum is distorted by the presence of the E_1' signal.

revealed by radiation having $\lambda \gtrsim 200$ nm ($E_{\text{photon}} \lesssim 5.9$ eV) in the O_2 plasma.

DISCUSSION

It is unlikely that the intensity of the emission in the uv plasma for $\lambda > 200$ nm is adequate to produce a significant number of defects by the kind of two-photon processes observed[3] for the case of intense uv laser radiation. Inspection of published[3] data on laser- and Hg-lamp-irradiation-induced defects in fused silica clearly suggests that for low-intensity sources E_1' defects result from some form of precursor transformation. The most probable precursor in a dry (low-[OH]) oxide is the B_2 center,[7] while in high–OH-content oxide it may be a H-related bond ($O_3 \equiv Si—H$). Calculations[19] place the energies of both the Si—H and B_2 center close to the valence-band edge, while the E_1' center lies ~ 5 eV above it. The mechanism by which the Si—H bond sheds a H or the B_2 center loses an electron remains unclear given the small photon energy we have used with respect to the band gap. We do note that XeCl-laser radiation (4-eV photons) failed[3] to reveal E_1' centers in dry oxide. On this basis and on the basis of the band calculations, we hypothesize that in the case of O_2-plasma exposure E_1' defects are revealed by photons for which $200 \lesssim \lambda \lesssim 300$ nm ($4 \lesssim E_{\text{photon}} \lesssim 5.9$ eV). It has been demonstrated that a Hg-lamp emission ($\lambda = 185$ and 254 nm) reveals similar E_1' densities in dry silica to those we have observed through plasma exposure in high-[OH] silica. If we compare plasma- and lamp-exposure times for the same defect yield, take account of the measured emission intensity in the two lines of the Hg lamp, and assume that the defect revelation is as efficient in low- and high-[OH] silicas, then we can estimate a range for the uv-emission intensity in the O_2 plasma. At the lower end (185 nm) the uv intensity would correspond to 200 mW cm^{-3} and at the higher end (254 nm) 900 mW cm^{-3}. These are clearly very approximate estimates, but they demonstrate that these plasmas are intense uv sources.

The creation of the methyl radical in a-SiO_2 by ionizing radiation (^{60}Co γ or x ray) has been studied in some detail using spin-resonance methods.[15] The anticipated ratio of the amplitudes of the four lines forming the hyperfine spectrum is 1:3:3:1; this we observe at room temperature, as shown in Fig. 3. The density of defects observed after 52 Mrad of ^{60}Co γ radiation is $(1–3) \times 10^{13}$ cm^{-3}; this is consistent with the value of 6×10^{13} cm^{-3} found following 46 Mrad observed by other authors[15] given the fact that the number of these centers present clearly depends on the methods used to manufacture the silica.

Our data on N-defect creation reveal no further information on the nature of the defect itself—we are only able to ascertain that for the slide material that we have studied the defect density maximizes, $\sim 10^{14}$ cm^{-3}, at a γ dose of ~ 5 Mrad. Further irradiation eliminates the defect. The generation of these defects in samples exposed to the O_2 plasma is contrary to the arguments put forward on the basis of 6.4-eV-photon laser irradiation. There,[2] no N centers were observed (although the sample was Suprasil 2), while 7.9-eV-photon irradiation of Suprasil 1 has been shown to reveal N centers,[1] as did 100-keV x-ray irradiation of the Suprasil 2 sample.[9] It was assumed that photons having energies > 6.4 eV were therefore necessary to reveal N centers. The present results on Suprasil 1 clearly indicate that photon energies < 5.9 eV can reveal N centers. If the positively charged, nonmagnetic precursor model[9] is correct, then our results indicate that direct pumping of electrons from the valence band to the defect precursor level must be possible with the range of photon energies we have used. This presumably places the precursor level < 5 eV above the valence-band edge.

Before leaving the subject of N-related defects, we examine the dose-dependent behavior shown in Fig. 4. In general, the irradiation-induced growth of the commonly observed defects such as the E_1' center is a monotonic increase as a function of dose. This has been modeled previously.[20] To explain the peak behavior shown in Fig. 4, we consider the following model: we assume that there exist initially N_i N defect precursors which transform under γ-irradiation dose, D, into N centers via a physical process we do not need to consider. Not only do the pre-

cursors transform to N centers under irradiation, but there is a finite possibility that they are "lost" for defect production through a process such as radiolysis (of the kind purported for H during the production of NBOHC's,[21] for example). Under these conditions the precursor concentration becomes a function of dose, $N_i(D)$. We may write two rate equations, one for the variation of the N-center density with dose, $d[\mathrm{N}]/dD$, and one for the precursor variation, dN_i/dD:

$$\frac{d[\mathrm{N}]}{dD}=\sigma_c N_i-(\sigma_{A_1}+\sigma_{A_2})[\mathrm{N}]\ ,$$

$$\frac{dN_i}{dD}=-\sigma_c N_i-\sigma_R N_i+\sigma_{A_i}[\mathrm{N}]\ .$$

Here we assume that precursors are lost with a cross section σ_R, some transform to N centers with a cross section σ_c, and some are recovered by reverse transformation of already formed N centers through a cross section σ_{A_1}. The N centers are produced by transformation of precursors with the cross section σ_c and are lost either via some change which does not involve return to the precursor state (with a cross section σ_{A_2}) or via reconversion back to the precursor (e.g., by trapping a hole at a site where previously the trapping of an electron produced the N center). Manipulation of the equations leads to the second-order equation:

$$\frac{d^2[\mathrm{N}]}{dD^2}=-(\sigma_c+\sigma_R+\sigma_{A_1}+\sigma_{A_2})\frac{d[\mathrm{N}]}{dD}$$
$$-(\sigma_R\sigma_{A_1}+\sigma_R\sigma_{A_2}+\sigma_c\sigma_{A_2})[\mathrm{N}]\ , \qquad (1)$$

whose solution is

$$[\mathrm{N}]\propto\exp(-\beta D/2)\sinh[(\beta^2-4\alpha)^{1/2}D/2]\ , \qquad (2)$$

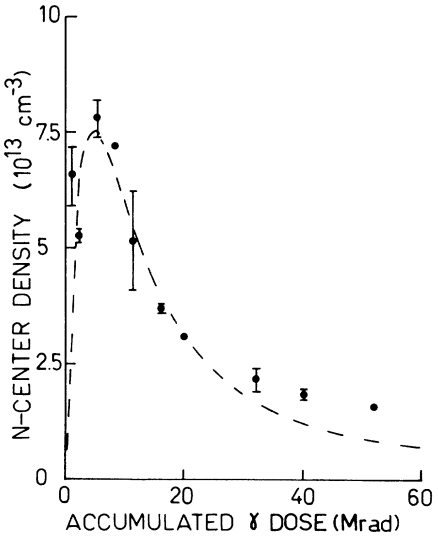


FIG. 6. Experimental data on the γ-dose-dependent N-center density in Suprasil 1 slide material (●) reproduced from Fig. 4. The dashed line shows the predictions of the model [Eq. (2)] with $\beta=6.4\times10^{-7}$ rad^{-1} and $\alpha=3.7\times10^{-14}$ rad^{-2}.

where $\beta=\sigma_c+\sigma_R+\sigma_{A_1}+\sigma_{A_2}$ and $\alpha=\sigma_R\sigma_{A_1}+\sigma_R\sigma_{A_2}+\sigma_c\sigma_{A_2}$. We have used our solution to fit the data in Fig. 4, and the result is shown by the dashed line in Fig. 6. The fit requires a value of 6.4×10^{-7} rad^{-1} for β and a value of 3.7×10^{-14} rad^{-2} for α. We will not dwell on the validity or nonvalidity of these values, but will simply note that the model we propose, including precursor transformation via some process such as radiolysis which does not result in N-center production, gives an adequate description of the experimentally observed γ-dose dependence.

Finally, we return to the data on H-center creation through γ irradiation. We note that in high-[OH] silica there are $\sim9\times10^{19}$ OH molecules cm^{-3} and 2.2×10^{22} SiO_2 molecules cm^{-3}. We observed that 52 Mrad of ^{60}Co γ irradiation in the slide material produced a density of 6×10^{12} H-related centers per cm^3. This indicates that only $\sim7\times10^{-8}$ of the H atoms present in the silica are involved in H-related defect creation after 52 Mrad of γ irradiation. NBOH-center creation is also assumed to be related to the amount of OH groups present in the "as-produced" material, and for the same γ dose one obtains $\sim7\times10^{15}$ cm^{-3}, suggesting that $\sim8\times10^{-5}$ of the OH groups present "transform" to defects. Comparison of the fractions for the two defects suggests that H-related centers may result from a multistep creation process rather than from a direct precursor transformation such as that proposed for NBOHC creation.[21]

Our experiments have shown that N centers can be revealed in some types of high-[OH] a-SiO_2 even by uv photons having energies <5.9 eV. In materials where N defects have been observed, we have also found that for the same dose of ^{60}Co γ irradiation less E_1' and NBOH centers are observed than in the (nominally) same material, but where no N centers were detectable. A reduction in E_1' and NBOHC creation might be anticipated if the material showing the N center contained a lower OH content, always assuming that NBOH centers arise through radiolysis of Si-OH linkages.[21] However, in such a case one might intuitively expect a similar increase in H-center density observable in the non-N-revealing material, whereas our data clearly show the inverse to be the case. Although the uv emission from the O_2 plasma revealed E_1' and N defects, it did not reveal measurable numbers of NBOH centers. It has been previously demonstrated[5] that NBOH centers do result from 4.8-eV excimer-laser irradiation of Suprasil W1. One must conclude that either this results from a two-photon process (for this photon energy), requiring the kind of intensities one obtains in excimer-laser pulses, or that an annihilation process is present in Suprasil 1 (the silica we have studied), which eliminates the defects as they form under uv irradiation.

CONCLUSIONS

We have studied the creation of E_1', N, H, NBOH, and $CH_3^{\bullet}$ defects in Suprasil 1 samples subjected to ^{60}Co γ irradiation or uv radiation from a rf-excited O_2 plasma. The intense uv emission from an O_2 plasma is observed to generate E_1'- and N-center defects in slide material, but

no measurable densities of NBOH, H-related, or $CH_3^{\bullet}$ radical centers. The range of "active" uv photon energies available in the plasma is found to be $4 \lesssim E \lesssim 5.9$ eV, demonstrating that sub-band-gap photons can reveal the N centers, contrary to previous assumptions. Finally, we observe that N-center production as a function of γ dose shows a clear maximum. We interpet this behavior in terms of a model in which N-center precursors are either transformed by the γ irradiation into N centers or eliminated, such as, for example, might occur in a radiolysis process.

ACKNOWLEDGMENTS

We gratefully acknowledge the help of Dr. J. Pelletier with the optical-emission measurements on the O_2 plasma and Dr. D. Griscom for advice on the methyl-radical spectrum.

[1]J. H. Stathis and M. A. Kastner, Phys. Rev. B **29**, 7079 (1984); J. H. Stathis, Ph.D. thesis, Massachusetts Institute of Technology, 1986 (unpublished).

[2]T. E. Tsai, D. L. Griscom, and E. J. Friebele, Phys. Rev. Lett. **61**, 444 (1988).

[3]K. Arai, H. Imai, H. Hosono,Y. Abe, and H. Imagawa, Appl. Phys. Lett. **53**, 1891 (1988).

[4]R. A. B. Devine, Phys. Rev. Lett. **62**, 340 (1989).

[5]R. A. B. Devine, C. Fiori, and J. Robertson, Mater. Res. Soc. Symp. Proc. **61**, 177 (1986).

[6]D. L. Griscom, Nucl. Instrum. Methods Phys. Res. Sect. B **1**, 481 (1984).

[7]R. Tohmon, Y. Shimogaichi, H. Mizuno, Y. Ohki, K. Nagasawa, and Y. Hama, Phys. Rev. Lett. **62**, 1388 (1989).

[8]N. Itoh, K. Tanimura, and C. Itoh, in *The Physics and Technology of Amorphous SiO_2*, edited by R. A. B. Devine (Plenum, New York, 1988), p. 135.

[9]T. E. Tsai, D. L. Griscom, and E. J. Friebele, Phys. Rev. B **38**, 2140 (1988).

[10]H. J. Stein, J. Electrochem. Soc. **132**, 668 (1985).

[11]K. L. Brower, Phys. Rev. Lett. **44**, 1627 (1980).

[12]T. E. Tsai and D. L. Griscom, J. Non-Cryst. Solids **91**, 170 (1987).

[13]J. Vitko, Jr., J. Appl. Phys. **49**, 5530 (1978).

[14]A. H. Edwards and G. Germann, Nucl. Instrum. Methods Phys. Res. Sect. B **32**, 238 (1988).

[15]E. J. Friebele, D. L. Griscom, and K. Rau, J. Non-Cryst. Solids **57**, 167 (1983).

[16]R. W. Boswell and D. Henry, Appl. Phys. Lett. **47**, 1095 (1985).

[17]R. A. B. Devine, J.-M. Francou, A. Inard, and J. Pelletier (unpublished).

[18]R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, 4th ed. (Chapman and Hall, London, 1976), p. 255.

[19]J. Robertson, in *The Physics and Technology of Amorphous SiO_2*, edited by R. A. B. Devine (Plenum, New York, 1988), p. 91.

[20]R. A. B. Devine and A. Golanski, J. Appl. Phys. **54**, 3833 (1983).

[21]D. L. Griscom, in *The Physics and Technology of Amorphous SiO_2*, edited by R. A. B. Devine (Plenum, New York, 1988), p. 125.