Multiple Interconversions of the E' and Oxygen-Hole Defect Centers in High-Purity Amorphous Silica during Anneal-Interrupted x Irradiation

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Multiple interconversions of E' centers and peroxy radicals have been observed for the first time by means of anneal-interrupted x-irradiation experiments. It is shown that each of these defects can serve as the precursor of the other; under thermal anneal an E' center can convert to a peroxy radical due to the capture of an oxygen molecule, and under irradiation the peroxy radical can covert to an E' center due to irradiation-induced release of oxygen. The results for the defect production and anneal behavior are well described in terms of simple stretched-exponential defect-reaction kinetics.

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Radiation-induced defects in wide-gap materials such as ionic crystals, quartz, and oxide glasses have a significant effect on their electronic and optical properties [1,2]. It has been established that Frenkel-type defect pairs are produced by ionizing radiation in both types of materials. In high purity crystalline and amorphous silicon dioxide, and silica-based optical fibers, the most important radiation-induced defects are the E' center (an unpaired spin on a three-coordinated silicon atom, $\equiv Si\bullet$) and oxygen hole centers (an unpaired spin on a nonbridging oxygen atom, $\equiv Si—O\bullet$, or a peroxy radical, $\equiv Si—O—O\bullet$) [3–8]. The E' center can be considered as a relaxed and recharged oxygen vacancy, and the peroxy radical can be considered as an analog of an oxygen interstitial [2,4]. We present for the first time strong evidence for an unusual interrelation between E' centers and peroxy radicals in amorphous silicon dioxide (a-SiO_2) which is in marked contrast to the behavior of vacancies and interstitials in ionic solids. The mechanisms responsible for the production and annealing of these defects are among the most actively studied problems in the physics of a-SiO_2 [5,7,9–11]. The radiation response of these materials is strongly dependent on stoichiometry and hydroxyl concentration [OH]. In general, low [OH] materials, "dry," and high [OH] materials, "wet," have quite different behaviors, as do oxygen-excess and oxygen-deficient materials. The relations among the different defect centers are obviously important for a full understanding of radiation processes in these materials. There is previous experimental and theoretical evidence that E' centers can serve as precursors for oxygen-hole centers (OHC) in dry, oxygen-excess a-SiO_2 [5,12,13].

We report in this Letter the results of a novel set of experiments involving multiple anneal-interrupted x-irradiation cycles in dry, oxygen-excess a-SiO_2. We observed not only the conversion of E' centers into OHC, but also for the first time the reverse process, i.e., the conversion of OHC into E' centers; in fact, we observe for the first time the *multiple* interconversions of E' and oxygen-hole centers in this material. Our experiments give clear evidence that oxygen-hole centers can serve as precursors for E' centers.

Suprasil W1 was chosen as the material to be studied [14]. This material has been found to have low impurity content [15], with [OH] <3 ppm. Electron paramagnetic resonance (EPR) experiments on the unirradiated samples gave no signals. The $10 \times 3 \times 1$ mm^3 samples were irradiated at room temperature by x rays from a W-target tube, operated at 45 kV and 20 mA. The x-ray exposures were made at a constant distance of 2 cm from the external beryllium window of the tube, with the x rays incident normal to the 10×3 mm^2 sample face. The dose rate at the front surface was 1.2 Mrad/h; due to the attenuation of x rays in the material, the volume-average dose rate was about $q = 0.6$ Mrad/h. The room-temperature EPR signals due to radiation-induced E' centers and OHC were measured at 9.5 GHz as a function of accumulated dose to determine the concentration of these defect centers. For an absolute calibration of the spin signals (with accuracy about 50%), the EPR spectrum of each type of center was obtained under nonsaturation condition, numerically integrated, and compared to a standard sample. The standard sample was a 1.0 mM toluene solution of the stable nitroxyl radical tempone, which had a geometrical shape similar to that of the silica samples. Two types of experiments were performed. In the first type of experiment, the samples were removed briefly from the x-ray machine at about every 0.5 Mrad of SiO_2 dose, and the EPR signals were measured. When not being irradiated or in the EPR spectrometer, the samples were stored in liquid nitrogen. In this manner, the EPR signal vs accumulated dose was measured up to 35 Mrad volume-average dose. In the second type of experiment, after the EPR signals had been measured to certain accumulated doses in the sample, the irradiation was interrupted by a soft anneal (10 min at 225 °C). Immediately after the anneal, the EPR signals were measured, and then the previously described irradiation-anneal cycle was repeated. These anneal-interrupted experiments were continued for several

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cycles. Three cycles, I, II, and II, are shown in figures below.

Figure 1(a) shows the concentration of E' centers $[E']$ in Suprasil W1 as a function of accumulated dose (Mrad SiO_2) for both the uninterrupted and anneal-interrupted experiments. The accumulated dose is proportional to the irradiation time t by $D = qt$. The solid symbols show the results for the uninterrupted irradiation experiments. The open symbols show the results for the anneal-interrupted experiments: a soft anneal was performed at $D_0 = 7.5$ Mrad and again at $D_0 = 15$ Mrad. As is evident from the figure, the soft anneal completely removes the E' center. Of special importance is the dose dependence of $[E']$ in the interrupted experiments; the concentration rises more steeply with dose in cycles II and II than is the case for experiments on the pristine material, cycle I.

Figure 1(b) shows the corresponding data for the OHC. The room-temperature EPR signals give the total OHC concentration; separate contributions from peroxy radical and nonbridging oxygen are not resolved. The annealing characteristics of the OHC contrast sharply with that of the E' centers. During anneal, the oxygen-hole center concentration *increases* while the E' center concentration *decreases,* as indicated by arrows in Figs. 1(a) and 1(b). The postanneal dose dependence of the oxygen center concentration differs dramatically from the initial behavior; the initial oxygen-hole center concentration *decreases* with increasing dose in cycles II and III.

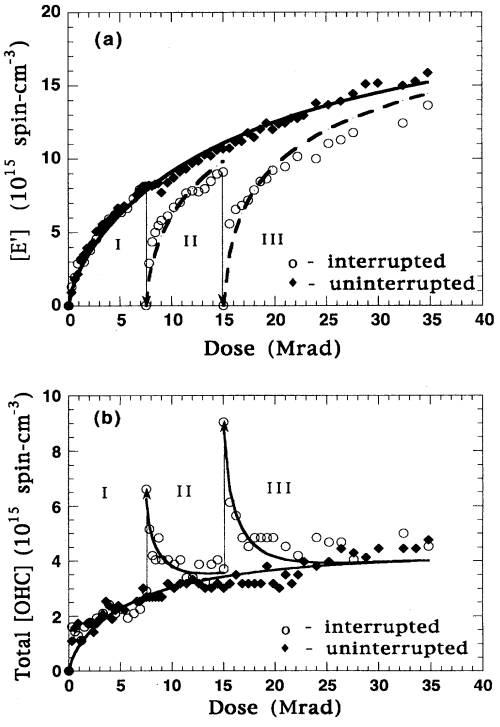

FIG. 1. Radiation-induced defect concentration vs volume-average accumulated dose (Mrad SiO_2) for uninterrupted and anneal-interrupted experiments on a-SiO_2. The lines represent theoretical results calculated using reaction rates $k_1 = 0.1$, $k_2 = 0.7$, and $k_1' = 0.05$ in units of Mrad^{-1}. (a) E' centers, solid line for Eq. (4), dashed lines for Eq. (5); (b) oxygen-hole centers, solid lines for Eq. (3).

The interpretation to be discussed below is based on the coexistence of different forms of oxygen in the material. It has been shown [7,9] that as-manufactured Suprasil W1 behaves like "oxygen-stuffed" material with excess $[O_2]$ in the range of 10^{17} to 10^{18} cm^{-3}. We suppose that, in the pristine material, this excess oxygen occurs as both dissolved and network-bonded O_2. The excess bonded oxygen is generally believed to be in the form of peroxy linkages ($\equiv$Si—O—O—Si$\equiv$) [16]. After irradiation, radiolytically displaced oxygen is also present. Under irradiation, E' centers and OHC are presumably generated by hole trapping at precursors and by the self-trapped exciton mechanism [6,7]. These processes control the kinetics of defect production in the uninterrupted experiments in Figs. 1(a) and 1(b), and also in cycle I of the interrupted experiments.

We have performed preliminary EPR experiments at liquid nitrogen temperature, where it is possible to distinguish the peroxy radical signal from that of the nonbridging oxygen-hole center. These experiments show that, although the room-temperature oxygen-hole center signal contains contributions from both forms of OHC, only the peroxy radicals participate in the interconversions. Thus, to explain the behavior of the defects during cycles II and III, we consider the interconversions of E' centers and peroxy radicals (PR) as described by the following two reactions:

$$E' + O_2^0 \Rightarrow \mathrm{PR} \qquad (1)$$

and

$$\mathrm{PR} + h\nu \Rightarrow E' + O_2^0 . \qquad (2)$$

The first reaction represents the thermal annealing behavior; neutral O_2 molecules are captured at E' centers thereby converting some E' centers into peroxy radicals. This mechanism was proposed by Edwards and Fowler [12], observed by Stapelbroek *et al.* [5], and investigated in detail by Pfeffer [9]. For the reverse conversion, we propose reaction (2), which describes the release of oxygen from the peroxy radical during the postanneal irradiation with the creation of an E' center as a reaction product. The energy $h\nu$ in reaction (2) is due to secondary electrons generated by the incident x-ray photons.

The annealing behavior of E' centers and peroxy radicals shown by the arrows in Figs. 1(a) and 1(b) is in accordance with reaction (1) and in agreement with previous results [5,7,9]. Most important, Figs. 1(a) and 1(b) present the first experimental evidence for reaction (2). This evidence consists of the more rapid rise of $[E']$ with dose in cycles II and III as compared to the pristine material, and the decrease of the peroxy radical concentration during

cycles II and III. These two features are strongly correlated. As Figs. 1(a) and 1(b) show, the two effects occur over the same dose range. Multiple interconversions were observed on other samples for as many as six radiation-anneal cycles with similar results. The enhanced E' center production and the radiation-induced decay of peroxy radicals were strongly correlated in all cases.

Our explanation of the experimental results includes two model assumptions about the kinetics of defect production and thermoanneal. With this model we are able to fit all the data for the OHC as shown in Fig. 1(b), and the data dealing with the *uninterrupted* experiment for E' centers shown as filled diamonds in Fig. 1(a). Most important, using the parameters obtained from fitting the oxygen-hole center data and the uninterrupted E' data, the model predicts the behavior of the postanneal dose dependence of the E' data with no additional fitting parameters.

We assume (Assumption No. 1) the existence of two reaction rates for the radiation-induced production and annealing (relaxation) of the OHC, a slow rate k_1 and a fast rate k_2. The fast rate governs the interconversions of peroxy radicals and E' centers, and the slow rate governs the remaining production of OHC. Recently, Griscom, Gingerich, and Friebele [17] postulated that the radiation response of glass can be described by a universal stretched-exponential response function $\phi(D,k) = \exp[-(kD)^\beta]$ or an analogous function for second-order reaction kinetics, where β is a number between 0 and 1 and k is a radiolytic-reaction rate per unit dose. The corresponding excitation function describing defect production is given by $1 - \phi(D,k)$. For small doses this excitation function gives a defect production proportional to D^β, while it leads to saturation at very high doses. Thus, we fit all our OHC data of Fig. 1(b) by the following equation,

$$N(D) = N_\infty[1 - \phi(D,k_1)] + \Delta N \phi(D - D_0, k_2), \quad (3)$$

where N_∞ is the steady state OHC concentration [OHC] for uninterrupted regime, ΔN is the total increase in [OHC] during thermal annealing processes between irradiation cycles ($\Delta N = 0$ for cycle I), and D_0 is the accumulated dose at the beginning of a particular cycle. The last term in Eq. (3) describes the radiation-induced relaxation of peroxy radicals according to Assumption No. 1. We also fit the E' data for uninterrupted data shown in Fig. 1(a) with an expression similar to the first term in Eq. (3),

$$N'(D) = N'_\infty[1 - \phi(D,k'_1)], \quad (4)$$

where the primes indicate E' populations. The results of the fitting are shown in Fig. 1(a), where Eq. (4) was used to fit the *uninterrupted* data, and in Fig. 1(b), where Eq. (3) was used to fit *all* the data. We found that $\beta = 0.7$ gave a good fit to all the data for both types of defects for both the interrupted and uninterrupted experiments. The reaction rates used in the fitting were $k_1 = 0.1$, $k_2 = 0.7$, and $k'_1 = 0.05$ in units of Mrad^{-1}.

We now describe the fitting of the *interrupted* E' data in cycles II and III with no additional parameters. The stretched-exponential behavior of defect production and thermoanneal is a result of the existence of a probability distribution of corresponding reaction rates in glasses. (The corresponding mathematical connection has been established by Pollard [18].) This initial probability distribution changes not only during irradiation (because the "fast" network sites can be converted into defects with high rate with their resulting elimination from the probability distribution), but also it can change during a thermal anneal (because by itself a thermal anneal is a redistribution of network structural energy during a partial structural equilibrium of the glass network). Consequently, we can assume (Assumption No. 2) that the postanneal statistical distribution of reaction rates which governs the radiation-induced kinetics of E' centers consists of two broad peaks corresponding to two types of precursors for E' centers, i.e., pristine network sites and sites created during the anneal of peroxy radicals. Moreover, the idea of multiple interconversions of defects is viable only if the reaction rates for the increase of $[E']$ and corresponding decrease of [PR], according to reaction (2), and the characteristic differences in their concentrations are the same (i.e., k_2 and ΔN, respectively). The statistical weights of both peaks are experimentally observable quantities and are equal to $N'_\infty - \Delta N$ and ΔN for pristine sites and PR-occupied sites, respectively. Hence, the resulting theoretical expression for anneal-interrupted kinetics for production of E' centers during cycles II and III is as follows:

$$N'(D) = (N'_\infty - \Delta N)[1 - \phi(D - D_0, k'_1)] + \Delta N[1 - \phi(D - D_0, k_2)]. \quad (5)$$

Figure 1(a) shows a plot of Eq. (5) for the interrupted E' data. It can be seen that Eq. (5) gives a good fit to the interrupted E' data *with no additional fitting parameters.* So, Assumption No. 1 about the reaction rates, on the one hand, and Assumption No. 2 about the nature of their statistical distribution, on the other hand, give a good explanation for all the experimental data.

While the data of Figs. 1(a) and 1(b) show a clear correlation between the decrease in $[E']$ and the increase in [OHC] during thermal annealing, the data also show that the changes are not in a 1:1 ratio; in fact, the increase in [OHC] is about one-half the decrease in $[E']$. It is difficult to obtain an accurate value for this ratio because of the difficulty in doing an accurate spin count calibration for the broad OHC line. Nevertheless, we believe that the ratio is clearly different from 1:1. Our interpretation of this result is that there exists a second channel for the annealing of the E' centers which does not involve the creation of PR. This second channel may reconvert the E' center to a precursor state which existed in the pristine material, e.g., by capture of an electron yielding a neutral oxygen vacancy.

In conclusion, we have observed for the first time the multiple interconversions of the two most important coordination defects in a-SiO_2, E' centers and peroxy radicals. We have shown that each of these defects can serve as the precursor of the other under appropriate stimulation, i.e., under thermal anneal an E' center can convert to a peroxy radical due to the capture of an oxygen molecule, and under irradiation the peroxy radical can convert to an E' center due to irradiation-induced release of oxygen. These effects show that the radiation physics of a-SiO_2 differs strongly from that of ionic crystals.

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