Fundamental Role of Creation and Activation in Radiation-Induced Defect Production in High-Purity Amorphous SiO_2

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A model for the radiation-induced production of defects in amorphous insulators is proposed. It is shown that an *irreversible* creation of defects from network sites follows power law kinetics, and a *reversible* activation of precursor sites follows Kohlrausch kinetics. Electron spin resonance was used to measure the concentration of x-ray induced E' centers in high-purity amorphous SiO_2 over an extremely wide dose range with high precision. The agreement between theoretical and experimental defect densities, over more than 4 orders of magnitude in dose, is unprecedented.

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Paramagnetic point defects are produced in wide-gap materials such as ionic crystals, quartz and oxide glasses, optical fibers, and dielectric thin films by energetic photons (x rays, γ rays, intense ultraviolet laser light) and particles (electrons, neutrons, etc.). In high-purity amorphous silicon dioxide (a-SiO_2) the most important radiation-induced defects are the E' center (an unpaired spin on a three-coordinated silicon atom, $\equiv$Si·) and oxygen hole centers (an unpaired spin on a nonbridging oxygen atom, $\equiv$Si—O·, or a peroxy radical, $\equiv$Si—O—O·) [1–6]. Among the effects studied has been the dependence of defect concentration on radiation dose [7–15]. Not only is the dose dependence of obvious technological importance, but it is related to the defect formation mechanisms and the physics of amorphous materials. Defect concentration generally depends nonlinearly on dose. Galeener and Mikkelsen [7] interpreted the nonlinear dose dependence in terms of two general processes: the creation of new defects from the network by rupture of bonds, and the spin activation of precursors by charge transfer. The creation mechanism was assumed to depend linearly on dose for any experimentally achievable dose while the activation mechanism was assumed to saturate with dose. While the phenomenological creation and activation model has been very useful in interpreting experimental results, it is not clear that it can explain the power law dependence on dose often observed [12,14]. Also, the model does not account for the interconversion of defects (a specific type of activation) which is known to be important in many cases [15].

The problem of defect production is closely related to the old problem of the origin of fractional exponents in amorphous networks [16–18]. Since Kohlrausch [19], much work has been done to interpret fractional exponents in terms of a distribution of relaxation rates [20,21], distribution of waiting times for random walks [22], hierarchically constrained dynamics [23], fractal structure and anomalous diffusion [24], etc. In addition to Kohlrausch relaxation, studies of defect production in amorphous materials have revealed clear experimental evidence for the importance of power law kinetics [12,14,25].

We propose a general model of radiation-induced defect production in amorphous insulators which enables us to get the Kohlrausch law and the fractional power law simultaneously on an equal footing, and to separate reversible and irreversible contributions to the entire process. We assume that both laws with a single fractional exponent are a result of a unique relaxation process occuring in amorphous materials during irradiation. We tentatively associate this relaxation with the radiation-induced compaction which is known to occur in amorphous silica [26,27], and should occur in every loosely packed, covalently bonded amorphous network. This relaxation can be interpreted in terms of the radiation-driven anomalous diffusion of excess free volume from the bulk to the surface. Because disorder and excess free volume are intrinsic properties of amorphous materials, they affect all physical properties, including defect production probabilities which become slowly decreasing functions of time or dose.

We propose that the radiation creates paramagnetic defects d from the network n with a relative probability k_c per unit time or dose. This process is assumed to be *irreversible* at normal temperatures and for experimentally achievable dose, i.e., there is no thermal or radiation-induced annealing back to the network configuration during the production process. Defects are also produced from a set of precursor sites. The interaction with the precursor sites is assumed to be *reversible,* and is described by relative probabilities k_d and k_a with the interconversion of precursors and defects being dominated by radiation-induced processes. To corroborate theoretical expressions which may reliably predict the radiation response of amorphous insulators at high doses, it is necessary to have high-quality experimental data over a wide dose range. We describe below such experiments on high-purity a-SiO_2 which cover more than 4 decades in dose. Our model gives an excellent description of the experimental results.

The set of defect processes described above is indicated by the following diagram:

$$n \xrightarrow{k_c} d \underset{k_a}{\overset{k_d}{\leftrightarrows}} p\,. \tag{1}$$

If the rate constants k in Eq. (1) are independent of time, or dose, the differential equations which govern populations of paramagnetic defects N and precursor sites N_p are

$$dN/dt = k_c q N_0 + k_a q N_p - k_d q N \tag{2}$$

and

$$dN_p/dt = k_d q N - k_a q N_p\,, \tag{3}$$

where q is the dose rate. N_0 represents an effective concentration of network sites for the irreversible creation of defects; we assume that this concentration is sufficiently high so as to remain essentially constant for any experimentally achievable radiation dose $D = qt$. More generally, when the rate constants depend on time, or dose, we assume the existence of a single fractional exponent b to describe the statistical distributions involved in defect production as discussed above. In analogy with the general theory of relaxation [28], consider ϕ as a relaxation function. Kohlrausch relaxation can be obtained from simple exponential kinetics $(d\phi/dt = -w_0\phi)$ by using the change of dimensionless variable $w_0 t \rightarrow (w_0 t)^b$, $0 \le b \le 1$ [28]. The rate equation is $d\phi/d(w_0 t)^b = -\phi$, which has the solution $\phi = \exp[-(w_0 t)^b]$. The rate equation can also be written as $d\phi/dt = -(b w_0^b/t^{1-b})\phi = -w(t)\phi$, where $w(t)$ is understood to be a time-dependent relaxation rate $0 < w(t) < \infty$. Acting in the same manner, we construct a formulation of our model applicable to the description of fractional kinetics by using the following change of variables:

$$kqt \rightarrow (kqt)^b = \xi, \quad 0 \le b \le 1, \quad k = k_a + k_d\,. \tag{4}$$

In this case we start with a new system of rate equations relative to the new dimensionless variable ξ to replace Eqs. (2) and (3):

$$dN/d\xi = cN_0 + \alpha_a N_p - \alpha_d N \tag{5}$$

and

$$dN_p/d\xi = \alpha_d N - \alpha_a N_p\,. \tag{6}$$

It is necessary to determine the relationship between the two sets of parameters $(c, \alpha_d, \alpha_a, k)$ and (k_c, k_d, k_a). Considering the case $b = 1$, when Eqs. (5) and (6) must reduce to (2) and (3), gives $\alpha_d = k_d/k$ and $\alpha_a = k_a/k$ with $\alpha_d + \alpha_a = 1$. A scaling representation for the parameter c is dictated by a dimensional analysis of limiting behavior of N vs D at $k \rightarrow 0$ $(k_d, k_a \rightarrow 0, k_d/k_a = \text{const})$: $N(D) = N_0 k_c D (b = 1)$ and $N(D) = cN_0(kD)^b (b \ne 1)$. Thus, comparing the two expressions for $N(D)$ we conclude that the product ck^b is finite as $k \rightarrow 0$, giving $c = (k_c/k)^b$.

The solution of Eqs. (5) and (6) is facilitated by adding the two equations to obtain $dN/d\xi + dN_p/d\xi = cN_0$ with the solution $N + N_p = cN_0\xi + N_p(0)$. Here we take $N(0) = 0$ corresponding to the pristine material. Using these relations enables us to separate the unknown functions N and N_p:

$$dN/d\xi = cN_0 + \alpha_a N_p(0) + cN_0\alpha_a\xi - N \tag{7}$$

and

$$dN_p/d\xi = \alpha_d N_p(0) + cN_0\alpha_d\xi - N_p\,. \tag{8}$$

The solutions for defect densities are expressed in terms of the total dose D:

$$N(D) = N_c(kD)^b + N_a\{1 - \exp[-(kD)^b]\} \tag{9}$$

and

$$N_p(D) = N_p(0)\exp[-(kD)^b] + N_{pc}(kD)^b + N_{pa}\{1 - \exp[-(kD)^b]\} \tag{10}$$

with creation and activation factors defined as $N_c = cN_0\alpha_a$, $N_a = cN_0\alpha_d + \alpha_a N_p(0) > 0$, and $N_{pc} = cN_0\alpha_d$, $N_{pa} = \alpha_d[N_p(0) - cN_0]$. This is a generalization of Galeener's phenomenological model. We recover the "two-slope" Galeener formula when $b = 1$ and $\alpha_d = k_d/k = 0$. Equation (9) predicts a universal power law dependence in the very low, and very high, dose ranges where the behavior is described by the fractional exponent b. For $(kD)^b \ll 1$ and $\gg 1$ we have, respectively, $N(D) = (N_c + N_a)(kD)^b$ and $N(D) = N_a + N_c(kD)^b$. In between these two extremes there is a transition region, which can be rather broad depending on the magnitude of N_a. Typical radiation experiments at low q cover only a small fraction of the dose range needed to observe the fractional two-slope behavior predicted by the theory; thus it is easy to understand how experiments which cover only the transition region can be fitted with a power law characterized by a smaller exponent than the true fractional exponent b.

To test the predictions of Eq. (9), measurements over a very wide dose range were performed on a well-known, high-purity silica material—Suprasil W1 [29]. The radiation response of silicas is known to depend on OH content and oxygen content. Suprasil W1 has less than 3 ppm of OH [30]. It has been shown [5,31] 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}. Silica samples of approximate dimensions 8.5 mm × 3.4 mm × 0.9 mm were cut from the bulk material. x irradiations employed either a Mo or W target tube operated at 50 kV peak voltage. The x rays impinged normally on the 8.5 mm × 3.4 mm face. Dose measurements were performed with an ionization chamber calibrated to yield dose in SiO_2 with a precision of 20%. All irradiations were performed at room temperature. The E' center concentration was measured vs accumulated x-ray dose using electron spin resonance (ESR). The X band ESR measurements were performed on a Bruker spectrometer at a temperature of 77 K. Absolute spin counts were calibrated under nonsaturating conditions against the concentration of a known standard. The

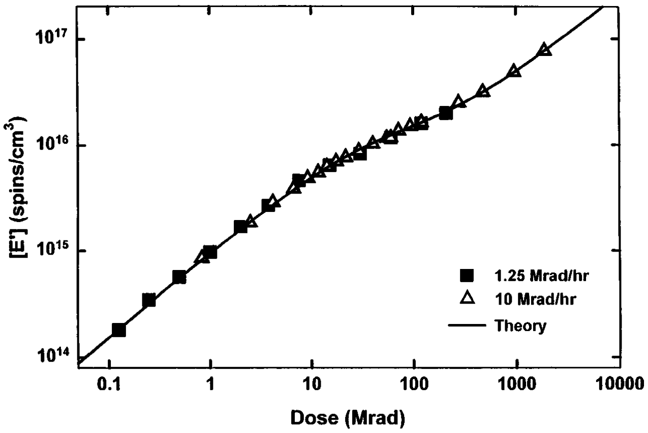

FIG. 1. E' concentration vs dose. The filled squares and open triangles represent data on Suprasil W1 taken at dose rates of 1.25 and 10 Mrad/h, respectively. The solid line represents a fit of Eq. (9) to the data.

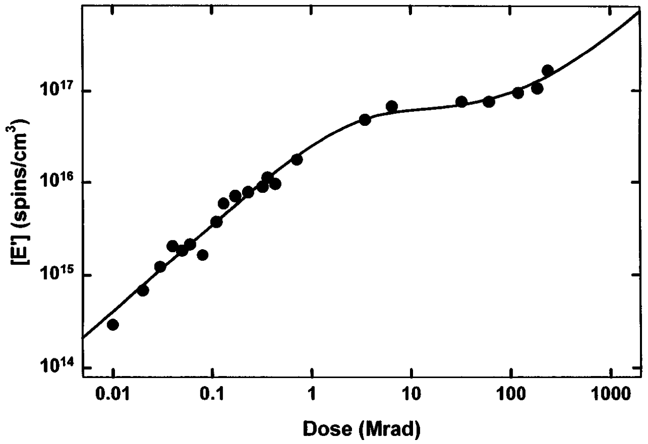

FIG. 2. The filled circles represent data on S2 from Ref. [13]. The solid line represents a fit of Eq. (9) to the data.

samples were stored in liquid nitrogen at all times following the x irradiation.

The E' concentration vs x-ray dose for Suprasil W1 is shown in Fig. 1. For the dose range of 0.1 to 200 Mrad, twelve different samples were used. Each sample was irradiated continuously to the indicated dose at a volume average dose rate of 1.25 Mrad/h using the Mo target tube. Following the irradiation, the ESR measurements were made. These data are presented as filled squares. For the dose range of 1 to 2000 Mrad, a single sample was used. This sample was irradiated at a volume-average dose rate of 10 Mrad/h using the W target tube. After irradiation to a particular dose, the ESR measurements were performed and then the irradiation continued. As can be seen from Fig. 1, there is no measurable difference between the two sets of data. In separate experiments we have shown that, for Suprasil W1, there is no effect of dose rate on the final defect concentration, only the total accumulated dose matters. The solid line of Fig. 1 is a fit of Eq. (9) to the data. The fitting parameters are given in Table I. Figure 1 shows that, for more than 4 orders of magnitude in dose, the agreement between theory and experiment is excellent for the dry, *oxygen-excess* silica.

It is important to determine the validity of Eq. (9) for other types of silicas. Imai and Hirashima [13] have presented data for a large number of silicas. We replot in Fig. 2 data for their sample S2 (see Fig. 8 of Ref. [13]) which is a dry, *oxygen-deficient* material containing 10^{18} cm^{-3} Si-Si bonds and 3×10^{18} cm^{-3} chlorine atoms. The fitting parameters are given in Table I. Figure 2 shows that, for more than 4 orders of magnitude in dose, the agreement between theory and experiment is excellent for the dry, *oxygen-deficient* silica.

It is instructive to compare the fitting parameters of the two types of materials. N_c represents an effective concentration associated with the creation process. It depends on the creation of defects from the network through N_0 and c, which are expected to be roughly the same for the two materials, and on the activation of defects from the precursors through α_a, which may differ for the two materials. However, α_a represents the normalized probability of activation of a defect as compared to the radiation-induced decay of the defect back to the precursor. There is no reason to expect α_a to differ strongly for the two materials. Thus, it seems reasonable that N_c differs only by a factor of 2 for the two materials (Table I). In contrast to the behavior of N_c, N_a is approximately 6 times larger for the oxygen-deficient material. This larger N_a is most likely due to the large number of Si-Si bonds in this material which give a large value of $N_p(0)$. The rate constant k, characterizing the interconversion of precursors and paramagnetic defects, is an order of magnitude greater in the oxygen-deficient material. We conclude that the radiation-induced interconversion of precursors and paramagnetic defects in the oxygen-deficient material, associated presumably with the Si-Si bonds, is more efficient than the interconversion in the oxygen-excess material. This conclusion is consistent with the observation that the E' center can be converted very rapidly into the B_2 center (neutral oxygen vacancy)

TABLE I. Fitting parameters for Figs. 1 and 2.

Sample	N_c (cm^{-3})	N_a (cm^{-3})	k (Mrad^{-1})	b
Suprasil W1	1.76×10^{15}	8.9×10^{15}	0.05	0.80
S2 (Ref. [13])	0.86×10^{15}	56.8×10^{15}	0.54	0.95

near SiO_2/Si interfaces [32]. According to our previous results [15], we expect that the interconversion in the oxygen-excess material is associated with peroxy radicals.

To clarify further the physical meaning of the model, we represent the accumulation of defects by

$$N(t) = \int_0^t dt' \left[w(t')N_c + e^{-\int_{t'}^{t} dt_1\, w(t_1)} w(t')N_a \right], \quad (11)$$

where N_c and N_a are effective concentrations for creation and activation as in Eq. (9), and the *time-dependent* probability $w(t)$ resulting from the radiation-driven relaxation is given by $b(kq)^b t^{b-1}$ [compare with Eqs. (4)–(6) where $d\xi = w(t)\,dt$]. Equation (11) describing creation and activation as affected by the radiation-driven relaxation leads to Eqs. (7) and (9), respectively, on differentiation or explicit integration. Thus, Eqs. (7), (9), and (11) give the most general description of the creation plus activation phenomena in defect production.

The present theory may be applicable to the laser, x-ray, and γ-ray induction of defects in a wide range of amorphous materials. For example, defects are produced in germanium-doped optical fibers by a one-photon process which is believed to be dominated by the activation of precursors [33]. The defect production was found to follow a power law dependence on dose with a fractional exponent ranging from 0.26 to 0.32; the results could not be explained with a simple exponential depletion of precursors. However, the present model shows that pure activation can be described by a power law dependence in the low dose range.

In conclusion, a model of the production of defects in amorphous insulators by ionizing radiation has been presented. The fractional power law and the Kohlrausch behavior arise naturally as creation and activation processes, respectively. ESR was used to measure the concentration of E' centers in high-purity, *oxygen-excess* amorphous SiO_2 over more than 4 orders of magnitude in absorbed x-ray dose. The theoretical prediction for the dose dependence of defect concentration was in excellent agreement with the experimental results. Published data for *oxygen-deficient* amorphous silicon dioxide, covering a broad dose range, were also found to be well described by the theory. The excellent agreement between the theory and experimental data for doses less than 0.1 up to 2000 Mrad, including regimes dominated in turn by activation and creation, gives confidence that the presented physical model can provide a quantitative prediction of the radiation response of a variety of amorphous materials.

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