SESSION A:
BASIC MECHANISMS OF RADIATION EFFECTS
IN
STRUCTURES AND MATERIALS

THE TIME DEPENDENCE OF INTERFACE STATE PRODUCTION*

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Abstract

A model for the reaction kinetics of interface state generation is developed. The reaction kinetics lie between third and first order for high and low concentrations of radiolytic molecular hydrogen, respectively. The application of these equations to the treatments of post irradiation effects is discussed.

Introduction

In using radiation hard parts in military and space systems it is necessary to extrapolate from the hardness measured in hardness testing (typically 10^1 s after irradiation) to the hardness to be expected at short times ($<10^1$ s after a radiation pulse) or at very long times (e.g. 10^8 s). These extrapolations are made difficult by the time dependent production and removal of radiation induced charged defects. It is tentatively suggested that in MOS devices there are four key processes whose time dependence must be considered. They are (1) the transport of holes to the vicinity of the Si-SiO₂ interface and subsequent trapping as E' centers, (2) the generation of interface states, (3) the "annealing" of trapped holes, and (4) the annealing of interface states. These four processes have significantly different time scales. An estimate of the characteristic time scales of each process, based on published experimental data, is summarized in Table I. Note that knowledge of the time dependence of processes 1 and 2 may be

TABLE I

#	Process	Time for 50% Completion at Room Temperature	Notes	Ref.
1	hole transp. & trapping	10^{-4} s	field = 1 MV/cm	[1]
2	int. state generation	20 s	field = 1 MV/cm	[2]
3	hole annealing	5×10^5 s	field = 1 MV/cm	[3]
4	int. state annealing	10^9 s**		[4]

** This value is an extrapolation of the data of Ref. 4 to room temperature

necessary to extrapolate back to the device behavior to be expected at very short times. Similarly, knowledge of processes 3 and 4 may be necessary to extrapolate to results to be expected at long times.

Some work exists in the literature giving models for the time dependence of these processes.

The time dependence of the first process has been treated by McLean et al. using a hopping model for hole transport [1]. The third process has been treated by Neamen using an electron tunneling model [5]. The fourth process has been treated by Brown et al. assuming the diffusion of H₂O to be the rate limiting step [4]. The present paper will present a treatment of the second process using a microscopic model of the process of interface state generation.

Background

D. L. Griscom has recently presented a model giving chemical reaction equations and chemical kinetics equations for interface state production at SiO₂-Si interfaces in devices [6,7]. In his model radiolytic molecular hydrogen is produced in the oxide bulk. The diffusion of this hydrogen then determines the time dependence of post-irradiation interface state buildup. The potential importance of radiolytic hydrogen to the production of electrically active defects had been discussed at an earlier date by, for example, Revez [8] and Hughes [9]. This paper will first briefly review selected portions of the Griscom model and then extend the model with emphasis on the time dependence of interface state buildup.

Review of the Model

This section will briefly state those portions of the Griscom model [6,7] which will serve as foundation for the developments of the present paper. For a more detailed treatment, and for a detailed justification of the model, the reader is referred to the original paper [7]. In the model, the interaction of ionizing radiation with hydrogen combined in the SiO₂ in the form of O₃=Si·H or as O₃=Si·OH results in the production of molecular hydrogen. This hydrogen then reacts with defects in the oxide bulk and at the Si-SiO₂ interface. The key reaction at the interface is

Note that the hydrogen, which diffuses as H₂, is presumed to decompose to form a short lived intermediate, H^o. This reacts at the interface with the interface state precursor Si₃=Si-H to form a P_b center, which is assumed to be the interface state. Note also that this reaction requires an electron which is supplied from the Si under positive gate bias. This fact provides the electric field dependence of the model. The reader is referred to Griscom [7] for further discussion of the field dependence.

The key kinetic equations presented by Griscom are

$$\frac{d[H_2]}{dt} = -2k_1[H_2]^2 \quad (\text{bulk}) \quad (2)$$

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and

$$-\frac{d[\text{Si}_s\text{H}]}{dt} = k_1 [\text{H}_2] [\text{Si}_s\text{H}] \quad (\text{surface}). \quad (3)$$

These are Griscom's Eqs. 19 and 22 [7].

Equation 2 treats the kinetics of consumption of H_2 within the bulk of the oxide by reaction with nonbridging oxygen hole centers, $\text{O}_3 \rightleftharpoons \text{Si}-\text{O}^\bullet$. The parameter k_1 is the reaction rate constant for that reaction. The square bracket notation, $[\dots]$, refers to the molecular concentration (molecules/ cm^3). Equation 3 treats the consumption of H° and the production of interface states at the interface, where the interface state precursor is abbreviated as Si_sH . Thus, Eq. 3 is the kinetic equation corresponding to Eq. 1. The reactions represented by Eqs. 2 and 3 are both assumed to be limited by the diffusion of hydrogen. Thus, the reaction rate constant k_1 is equal to $4\pi r^*D$ where r^* , the capture radius, is a constant and D is the diffusivity of H_2 in silica. It should be noted that Griscom states that a characteristic distance for diffusion, $\sqrt{4Dt}$, corresponds to 2.5×10^3 nm for the diffusion of H_2 for 1000s in SiO_2 at room temperature [7]. This corresponds to 350 nm in 20s, a value which should be compared with the characteristic time for interface state generation given in Table I.

Finally, Griscom considered the possibility of fitting a set of data published by McGarrity et al. [2] giving the time dependence of interface state buildup. He observed that he could obtain an excellent fit to one set of data if he replaced the coupled Eqs. (2) and (3) with a classic third order kinetics equation, i.e.

$$[\text{Si}_s\text{H}] = [\text{Si}_s\text{H}]_0 (1 + (n-1)D(4\pi r^*)^{(3n-5)} \times [\text{Si}_s\text{H}]_0^{(n-1)} t)^{-1/(n-1)} \quad (4)$$

where n is set to 3. The notation $[\dots]_0$ implies the concentration at $t=0$. It was emphasized that the good fit was obtained using only physically reasonable parameters and no fitting factors (other than the choice of n). The reason for this good fit will be one of the themes of this paper.

Theory

Griscom's observation of a third order reaction is quite striking in that it was for a case for which the coupled Eqs. 2 and 3 should represent the kinetics. It will be shown that Eqs. 2 and 3 (and related equations) lead directly to a prediction of the order of reaction in two limiting cases. It will be seen that the form of the reaction kinetics flows from the competition between the consumption of H_2 in the oxide bulk and at the interface.

The first case is one where the value of $[\text{H}_2]$ in the bulk is sufficiently great, in comparison to the value of $[\text{Si}_s\text{H}]$ at the interface, that the interface reaction has no appreciable effect on the value of $[\text{H}_2]$. As a result, the value of $[\text{H}_2]$ is given by Eq. 2 alone. A solution scheme then becomes: (a) solve Eq. 2, (b) substitute the

results into Eq. 3, (c) solve Eq. 3, and (d) differentiate the solution of Eq. 3. Applying this scheme it is found that

$$\frac{d}{dt} \frac{[\text{Si}_s\text{H}]}{[\text{Si}_s\text{H}]_0} = -k_1 [\text{H}_2] \left\{ \frac{[\text{Si}_s\text{H}]}{[\text{Si}_s\text{H}]_0} \right\}^3, \quad (5)$$

which is clearly a reaction of third order.

The second case is the inverse one where $[\text{H}_2]$ in the bulk is sufficiently small, in comparison to the value of $[\text{Si}_s\text{H}]$ at the interface, that the value of $[\text{Si}_s\text{H}]$ is only negligibly reduced by interface state production. On the other hand, the value of $[\text{Si}_s\text{H}]$ is sufficiently large to result in significant H_2 consumption. In order to solve this case it is necessary to use the following kinetic equations:

$$\begin{aligned} \frac{d[\text{H}_2]}{dt} &= -k_1 [\text{H}_2] [\text{SiO}^\bullet] \\ &\quad + k_3 \frac{x_d}{x_{\text{ox}}} [\text{H}^\circ] [\text{Si}_s\text{H}] \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{d[\text{H}^\circ]}{dt} &= k_1 [\text{H}_2] [\text{SiO}^\bullet] - k_2 [\text{H}^\circ] [\text{SiO}^\bullet] \\ &\quad - k_3 \frac{x_d}{x_{\text{ox}}} [\text{H}^\circ] [\text{Si}_s\text{H}] \end{aligned} \quad (7)$$

$$\frac{d[\text{Si}_s\text{H}]}{dt} = k_3 [\text{H}^\circ] [\text{Si}_s\text{H}] \quad (8)$$

$$\begin{aligned} \frac{d[\text{SiO}^\bullet]}{dt} &= -k_1 [\text{H}_2] [\text{SiO}^\bullet] \\ &\quad - k_2 [\text{H}^\circ] [\text{SiO}^\bullet] \end{aligned} \quad (9)$$

These four equations correspond to Griscom's Eqs. 15-18 [7] with three modifications. First, a second term has been added in Eq. 6, to account for H_2 generation at the interface. Second, the factor x_d/x_{ox} has been introduced in Eqs. 6 and 7 to account for the fact that $[\text{Si}_s\text{H}]$ represents a concentration which exists within a layer x_d thick near the interface, while all the other concentrations represent defects spread evenly over the oxide thickness, x_{ox} . This change is necessary to obtain conservation of material. Third, Eq. 9 was implied, but not explicitly stated in reference 7.

Following Griscom [7] the stationary-state hypothesis is applied to Eq. 7, i.e. $d[\text{H}^\circ]/dt$ is assumed equal to zero. The resulting equation can be solved for $[\text{H}^\circ]$ and this result can be substituted into Eqs. 6, 8 and 9. The result is:

$$\begin{aligned} \frac{d[\text{H}_2]}{dt} &= -k_1 [\text{H}_2] [\text{SiO}^\bullet] \\ &\quad + k_1 [\text{H}_2] [\text{Si}_s\text{H}] \frac{x_d}{x_{\text{ox}}} F \end{aligned} \quad (10)$$

$$\frac{d[\text{Si}_s\text{H}]}{dt} = -k_1 [\text{H}_2] [\text{Si}_s\text{H}] F \quad (11)$$

$$\frac{d[\text{SiO}^*]}{dt} = -k_1 [\text{H}_2] [\text{SiO}^*] (1 + F) \quad (12)$$

$$F = \frac{1}{1 + \frac{x_d}{x_{\text{ox}}} \frac{[\text{SiH}]_s}{[\text{SiO}^*]_s}} \quad (13)$$

In the above equations we have used, also following Griscom [7], the assumption that $k_1 \approx k_2$ since they are both based on the diffusion of H^0 .

It is now appropriate to apply the limiting case assumption $x_d [\text{SiH}]_s \gg x_{\text{ox}} [\text{H}_2]_s$. Since $[\text{SiO}^*]_s = 2[\text{H}_2]_s$ (see reference 7), this corresponds to

$$F = \frac{x_{\text{ox}}}{x_d} \frac{[\text{SiO}^*]_s}{[\text{SiH}]_s} \quad (14)$$

Substitution of Eq. 14 into Eq. 10 results in $d[\text{H}_2]/dt = 0$. This fact permits the solution of Eq. 12, the result of which permits the solution of Eq. 11. The final result is, then,

$$\frac{dR}{dt} = -k_1 [\text{H}_2] R \quad (15a)$$

where

$$R = \frac{([\text{SiH}]_s - [\text{SiH}]_{s,\text{min}}) - ([\text{SiH}]_s - [\text{SiH}]_s)}{([\text{SiH}]_s - [\text{SiH}]_{s,\text{min}})} \quad (15b)$$

and

$$([\text{SiH}]_s - [\text{SiH}]_{s,\text{min}}) = 2.0 [\text{H}_2]_s (x_{\text{ox}}/x_d), \quad (15c)$$

where $[\text{SiH}]_{s,\text{min}}$ is the value of $[\text{SiH}]_s$ at the completion of the reactions, i.e. at long times. The parameter R is the number of interface state precursors remaining to be consumed, normalized by the total number which will be consumed in the reaction. Note that Eq. 15 is clearly of first order. It seems clear that in the general case the order of reaction can vary between three and one, depending on the relative concentrations $[\text{H}_2]_s$ and $[\text{SiH}]_s$.

Figure 1. Time dependence of post-irradiation interface state buildup. Figure reproduced from Ref. [2].

The experimental data of McGarrity et al. [2], previously used by Griscom [6,7], is an unusually good vehicle for testing the material of the previ-

ous paragraph. Curve A of Fig. 1 represents a case where the interface state generation was followed while a positive bias was maintained. For curves B, C, and D, the bias polarity was reversed at 0.8 s, and then returned to positive bias at 20, 200 and 2000 s, respectively. On the basis of Griscom's model it is to be expected that during the negative bias period the H_2 concentration should continue to drop (due to reaction with nonbridging oxygen hole centers, Eqn. 2) while the interface state concentration should remain constant (because that reaction requires electrons supplied from the silicon). It follows from the present reasoning that one may expect to see a progressive reduction of reaction order as we consider curves A, B, etc. In order to test this hypothesis, the data of Fig. 1 are have been used to prepare Fig. 2, where the rate of the interface state reaction is displayed. The data plotted in Fig. 2 are the measured slopes of curves A, B, and C of Fig. 1. If it is hypothesized that the data should represent an n th order chemical reaction (see Eq. 4) then it follows that the data of Fig. 2 should lie on straight lines whose slope is the reaction order, n .

It will be observed in Fig. 2 that Curve A (corresponding to curve A of Fig. 1) gives a slope (and thus a reaction order) of about 2.9. This curve is based on the data which Griscom was able to fit using Eq. 4 with n set to 3. Curves B and C show slopes (reaction orders) of about 1.6 and 1.2, respectively. Thus, the maximum reaction order corresponds to the case which is expected to have the maximum $[\text{H}_2]_s$ while the minimum reaction order corresponds to the minimum expected $[\text{H}_2]_s$. In

Figure 2. The reaction rate deduced from the data of Fig. 1. N_{ss}^{∞} is the maximum interface state production.

TABLE II

Case	Initial $\frac{d}{dt} (N_{ss}^{\infty} - N_{ss})$
A	.38 ($10^{11} \text{ cm}^{-2} \text{ s}^{-1}$)
B	.012
C	.005

addition, the initial values of the reaction rate can be seen in Fig. 2 and in Table II. Note that those results are consistent with the predictions of Eqn. 3 that larger initial values of $[H_2]$ lead to larger values for the initial reaction rate. Thus, to summarize, these data support:

- the understanding of the interface state generation provided by the Griscom model, and
- the conclusion that the reaction order must lie between 3 and 1.

It should be emphasized, however, that the data of Fig. 1 were determined using capacitors with wet-process oxides and metal gates. It remains to be shown that similar results are obtained with other processes.

The results of a numerical solution of the coupled Eqs. 10-13 are presented in Fig. 3. The dashed and solid lines in Fig. 3 show the reduction of hydrogen and the increase of interface states as a function of a reduced time. The notation for this plot is:

$$A = [H_2] \quad (16a)$$

$$B = [Si\ H] \quad (16b)$$

$$R = \frac{x_d}{x_{ox}} \frac{B}{A} \quad (16c)$$

$$s = k_1 A_0 t \quad (16d)$$

Figure 3. The time dependence of hydrogen consumption and interface state production. The dashed and solid lines are the results of a numerical solution of Eqs. 10-13. Note that $A = [H_2]$, $B = [Si\ H]$, $R = (x_d/x_{ox})(B/A)$, and $s = k_1 A_0 t$. The dashed lines show the hydrogen consumption on the left ordinate. The solid lines show the interface state production on the right ordinate. The x's represent the predictions of $(B_0 - B)/B_0$ obtained from Eqs. 19a and 19b.

where, again, the subscript zero (e.g. A_0) implies a value at time equals zero. An important result of Fig. 3 is the fact that at long times (large s) the values of $(B_0 - B)/B_0$, a term which is proportional to interface state production, go to a well defined limiting value, i.e.

$$\frac{B_0 - B}{B_0} = \frac{1}{0.5 R_0 + 1} \quad (17)$$

This fact can be used to produce a version of an nth order kinetics equation (e.g. Eq. 4) where n is specified in terms of the initial concentrations. The starting point is

$$\frac{dB}{dt} = - \frac{1}{\tau} \left[\frac{B - B_\infty}{B_0 - B_\infty} \right]^n \quad (18)$$

where τ is a characteristic time for the process. Note that Eq. 18 is supported by the data of Fig. 2 inasmuch as $N_{ss} - N_{ss}^\infty \equiv B - B_\infty$. It is then required that (a) the first derivative of Eq. 18 at $t=0$ must yield the same result as do Eqs. 10-13, and (b) the result of Eq. 17 must hold. With these conditions it is found that

$$\frac{d}{ds} \left[\frac{B_0 - B}{B_0} \right] = \left[\frac{1}{0.5 R_0 + 1} \right] \left\{ 1 - [0.5 R_0 + 1] \left[\frac{B_0 - B}{B_0} \right] \right\}^n \quad (19a)$$

$$n = \frac{0.5 R_0 + 3}{0.5 R_0 + 1} \quad (19b)$$

The results of this equation are also plotted in Fig. 3 for $R_0 = 1$. Note that this approximate equation agrees with the numerical solution of Eqs. 10-13 with an error of less than 10%. Note also that it has been demonstrated that an nth order reaction equation such as Eq. 19 must be exact for small values of R_0 (where $n=3$) and for large values of R_0 (where $n=1$).

Extrapolation of P.I.E. Data

It has been suggested frequently [10,11] that the time dependence of post irradiation effects can be fit by an equation of the form

$$\frac{N}{N_0} = b \ln(1 + t/\tau). \quad (20)$$

The use of such an equation is usually based on entirely empirical grounds. The model under discussion here lends no support to the use of such an equation. For the processes discussed here, at least, it has no physical basis. Thus its use to extrapolate to long times introduces an undesirable (though perhaps sometimes unavoidable) uncertainty. An alternative to the use of Eq. 20 is the following:

$$\ln \left[1 - \frac{N_{ss}}{N_{ss}^{\max}} \right] = - \frac{1}{n-1} \ln \left[1 + (n-1) \frac{t}{\tau} \right]. \quad (21)$$

This equation is simply derived from Eq. 4 by (a) replacing several constants by a reaction time τ , (b) stating the equation in terms of interface states rather than interface state precursors, and (c) some algebraic manipulation to achieve a useful form.

It should be recalled that Eq. 4 is in general an approximate (rather than exact) solution to Eqs. 10-13. Its use is justified on the grounds that

- (a) it is an exact solution for the limiting cases $n=1$ and $n=3$,
- (b) Fig. 2 suggests that Eq. 4 provides a rather good fit to the experimental data, and
- (c) The calculations displayed in Fig. 3 demonstrate that Eq. 4 is quite a good fit to the presumably more accurate Eqs. 10-13.

Equation 21 has the property that a log-log plot yields straight lines at long times. Further, this straight line has the slope $-1/(n-1)$, where n is the reaction order. This is shown in Fig. 4 where curve A of Fig. 1 (data of McGarrity et al.) has been replotted in this form. Note that the meas-

Figure 4. Replot of the data of McGarrity et al. showing the utility of Eq. 13 as a model for data plotting.

ured slope at long times is consistent with the reaction order, n , of 2.9 determined in Fig. 2.

Dose Dependence

Finally, the model developed in this paper has implications for the dose dependence of interface state production. It follows from Eq. 17 for the first limiting case ($n = 1$, $[H_2]$ very small, and thus R_0 very large) that the final interface state production is linearly dependent on $[H_2]_0$. Similarly, it follows for the second limiting case ($n = 3$, $[H_2]$ very large, and thus R_0 very small) that the final interface state production is independent of small changes in the initial hydrogen concentration, $[H_2]_0$. If we can assume that the generation of hydrogen is linearly dependent on radiation dose then it follows that the first case corresponds to a D^1 dependence while the second corresponds to a D^0 dependence, i.e. saturation. Reports of experimentally determined values of the exponent [10,12,13] give 0.66 and 0.8-0.9 (i.e. values intermediate

between 0 and 1). Of particular interest is the work of Winokur and Boesch [13] who show data supporting a $D^{2/3}$ dose dependence over more than two orders of magnitude in dose. A plot of $(B_0 - B)/B_0$ vs. $1/R_0$ (see Eq. 17) suggests that such a dose dependence should be approximately obeyed over only a bit more than one order of magnitude in dose. It is not clear how the present model can lead to the dose dependence observed by these authors. Moreover, data presented at the 1985 IEEE Nuclear and Space Radiation Effects Conference show a more complex dose dependence [14,15].

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