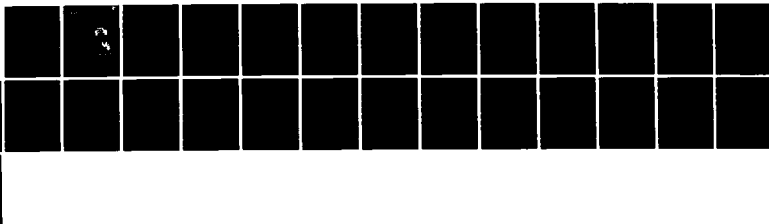AD-A167 280   PHYSICAL PROCESSES ASSOCIATED WITH RADIATION-INDUCED   1/1
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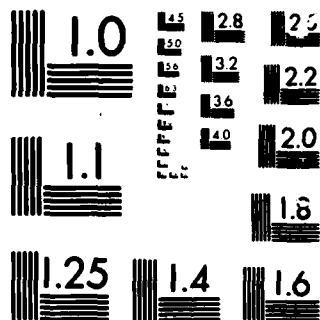   P S WINOKUR ET AL. APR 86 HDL-TR-2081

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April 1986

Physical Processes Associated with Radiation-Induced Interface States

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AD-A167 280

U.S. Army Laboratory Command
Harry Diamond Laboratories
Adelphi, MD 20783-1197

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER HDL-TR-2081	2. GOVT ACCESSION NO. *AD-A167280*	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Physical Processes Associated with Radiation-Induced Interface States		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Peter S. Winokur* F. Barry McLean H. Edwin Boesch, Jr.		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Harry Diamond Laboratories 2800 Powder Mill Road Adelphi, MD 20783-1197		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Program Ele: 6.11.02.A DA Project: 1L161102AH44
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Laboratory Command 2800 Powder Mill Road Adelphi, MD 20783-1145		12. REPORT DATE April 1986
		13. NUMBER OF PAGES 27
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Metal oxide semiconductor
MOS
Interface states
Radiation effects

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The buildup of interface states in Al-SiO$_2$-Si metal-oxide-semiconductor capacitors following exposure to pulsed electron-beam irradiation has been previously shown to be a two-stage process. In the present work, we further examined the buildup by varying the polarity and magnitude of the field across the oxide during the two stages of the buildup. Specifically, both early (10^{-6} to 1 s) and late (1 to 10^4 s) time regimes are explored. An empirical model of radiation-induced interface states at the SiO$_2$/Si interface is presented. The formulation, which explicitly addresses the time-dependent two-stage nature of the buildup process, gives the mathematical dependencies of the experimentally observed buildup on time,

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20. Abstract (cont'd)

field, temperature, and dose. Along with the results of the field-switching experiments, the implications of the empirical model for the microscopic mechanisms involved in the buildup are discussed. In particular, the first stage is attributed to positive ion release in the bulk of the oxide via interactions with radiation-generated holes. The second stage is then associated with the transport of the liberated ions to the SiO_2/Si interface (for positive gate bias) where a subsequent interaction results in the appearance of electrically observable interface states. The experimental results and model are compared to and interpreted in light of recent related work in the literature.

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1. INTRODUCTION

The generation of radiation-induced interface states has been reported for many years in the literature.[1-4] Our group has previously reported work[1] in which we observed a time-dependent buildup of interface states, taking place over several thousand seconds, in metal-oxide-semiconductor (MOS) capacitors under positive bias following pulsed electron-beam irradiation. We initially examined the buildup in several key experiments by varying the magnitude of the field across the oxide at critical times during the period of interface-state generation.[2] The results of these experiments indicated that two separate stages were required to describe the buildup of interface states in these structures.[5,*] The first stage, which occurs on the time scale of the transport of radiation-generated holes through the oxide or to the SiO_2/Si interface, determines the final or saturation value of interface states and was found to be field dependent and temperature independent. The second stage, which begins after the hole transport and continues for several thousand seconds, determines the time scale for the buildup and was found to be dependent on both field and temperature.

In this report, we further examine the buildup in several experiments by varying both the polarity and magnitude of the field across the oxide during the two stages of the buildup. Both early (10^{-6} to 1 s) and late (1 to 10^4 s) time regimes are explored, and the results are interpreted in terms of their implications for physical processes occurring during the two stages of the buildup. In particular, the first stage is identified as the interaction of radiation-generated holes in the bulk of the oxide that leads to the release of positive ions (possibly H^+). The second stage is then associated with the transport of the liberated ions to the SiO_2/Si interface, where a subsequent interaction results in the appearance of electrically observable interface states.

2. SAMPLES AND MEASUREMENT TECHNIQUES

The MOS capacitors used in these experiments were supplied by Hughes Aircraft Corporation and consisted of 96.5-nm wet-grown SiO_2 on nominal 3 to 5 Ω-cm <100> n-type Si. The wet oxide was grown at 950 C in pyrogenic H_2O and annealed in N_2 for 20 min; Al electrodes were vapor-deposited from a carbon

[1]P. S. Winokur, J. M. McGarrity, and H. E. Boesch, Jr., IEEE Trans. Nucl. Sci. NS-23 (1976), 1580.

[2]P. S. Winokur, H. E. Boesch, Jr., J. M. McGarrity, and F. B. McLean, J. Appl. Phys. 50 (1979), 3492.

[3]T. P. Ma, G. Scoggan, and R. Leone, Appl. Phys. Lett. 27 (1975), 61.

[4]C. T. Sah, IEEE Trans. Nucl. Sci. NS-23 (1976), 1563.

[5]H. E. Boesch, Jr., IEEE Trans. Nucl. Sci. NS-29 (1982), 1446.

*The work reported in the present paper was observed for MOS capacitors that employed a thin (<100 nm) SiO_2 layer with reduced hole trapping, i.e., radiation "hardened." Interface-state buildup resulting from apparently different processes has been observed in MOS capacitors employing thicker (>100 nm) SiO_2 layers; see reference 5.

crucible. An initial interface-state density at midgap of ~6 × 10^{10} $cm^{-2}V^{-1}$ was calculated from quasistatic capacitance-voltage (C-V) curves by the Berglund technique.[6] Bias-temperature stressing the capacitors at 200 C and 20 V for 5 min resulted in a flatband voltage shift of 70 mV. Voltage stressing at room temperature and fields from 1 to 6 MV/cm under positive and negative bias for 1 hr resulted in a flatband voltage shift of less than 100 mV and negligible interface-state production. For these capacitors, we concluded that lateral charge nonuniformities at the SiO_2/Si interface were small, because C-V traces taken at 77 K before and after irradiation had essentially the same distortion.[7]

The buildup of interface states following irradiation was monitored through several measurement techniques. In a very fast field-switching experiment, we measured C-V curves at 295 and 77 K using a C-V apparatus that applied a 50-ms voltage ramp and monitored sample capacitance with a phase-sensitive detector operating at 1 MHz. The difference in the flatband voltage between these curves (i.e., the Gray-Brown shift,[8] V_{GB}) yields an integrated value of interface states over ~0.25 eV of the Si band gap defined by the Fermi levels at 295 and 77 K. In other field-switching experiments, we measured C-V traces using a system employing a 1-MHz capacitance meter and a 10-s duration voltage ramp. These C-V traces were analyzed by the Terman technique[9] to obtain a distribution of interface states over the Si band gap. The resulting distribution of interface states was integrated from midgap to flatband to provide single values, N_{it} (cm^{-2}), of interface states in the samples.

3. EXPERIMENTAL RESULTS

In one experiment, MOS capacitors were irradiated to ~60 krad(SiO_2) with a single 4-μs 13-MeV electron pulse from an electron linear accelerator (LINAC). During the radiation pulse, the sample was maintained under positive bias corresponding to a 1-MV/cm electric field across the oxide layer. At a predetermined time following the radiation pulse, t_{sw}, the field was switched to 5 MV/cm. (A switch takes less than 1 μs.) The field was then maintained for ~2000 s, at which time a Gray-Brown measurement was performed to determine the increase in radiation-induced interface states. This field switching is shown schematically in figure 1a.

The measured increase in the Gray-Brown shift from its preirradiation value, ΔV_{GB}, is plotted in figure 1b for switching times of 1 μs, 160 μs, 10 ms, and 1 s. The upper and lower horizontal lines in the figure correspond to measured increases in the Gray-Brown shift for cases in which the oxide field was held constant (not switched during and after the radiation pulse) at 5 and 1 MV/cm, respectively. As reported previously, the final or saturation value of interface states is strongly field dependent and increases with increasing

[6] C. N. Berglund, IEEE Trans. Electron Devices ED-13 (1966), 701.

[7] C. C. Chang and W. C. Johnson, IEEE Trans. Electron Devices ED-24 (1977), 1249.

[8] P. V. Gray and D. M. Brown, Appl. Phys. Lett. 8 (1966), 31.

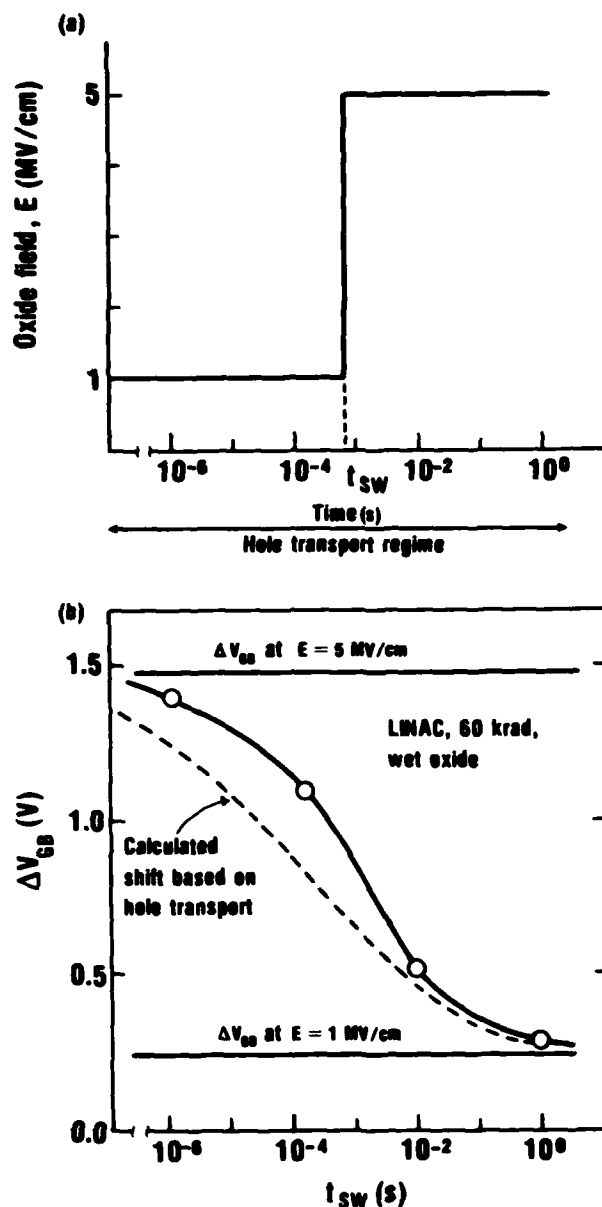[9] L. M. Terman, Sol. St. Electron. 5 (1962), 285.

Figure 1. Oxide field switching experiment: (a) oxide field as a function of time following a 4-μs LINAC irradiation. At a predetermined time, t_{sw}, oxide field is switched from 1 to 5 MV/cm. Hole transport regime is shown to cover times out to 1 s. (b) Measured increase in Gray-Brown shift, ΔV_{GB}, plotted for switching times of 1 μs, 160 μs, 10 ms, and 1 s (circles). Upper and lower horizontal lines correspond to measured increases in ΔV_{GB}, where oxide field is held constant (not switched) at 5 and 1 MV/cm, respectively. Dashed line is a calculation of expected increase in ΔV_{GB} based on details of hole transport.

field.[10] It is evident that the value of the measured increases in the Gray-Brown shift decreases uniformly from its constant 5-MV/cm value (~1.5 V) to its constant 1-MV/cm value (~0.25 V) as t_{sw} is increased. This corresponds to a decrease in the production of radiation-induced interface states as t_{sw} is increased.

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[10]P. S. Winokur, H. E. Boesch, Jr., J. M. McGarrity, and F. B. McLean, IEEE Trans. Nucl. Sci. NS-24 (1977), 2113.

Several conclusions can be drawn from this experiment. First, the magnitude of the applied field during the radiation pulse has essentially no effect on the final number of interface states. Clearly, the ΔV_{GB} produced for a switch from 1 to 5 MV/cm at 1 µs after the radiation pulse is approximately the same as that for the case of a constant 5 MV/cm maintained both during and after the radiation pulse. The small (5-percent) difference in the final number of states can be easily explained by the slightly lower yield of electron-hole pairs for a 1-MV/cm compared to 5-MV/cm irradiation.[11] Second, radiation-generated electrons are not responsible for the buildup of the interface states. Electrons are swept out of the oxide during the radiation pulse (in picoseconds) and are not affected by postirradiation bias switches. Since these bias switches have been shown to determine the magnitude of the final interface-state buildup, electrons cannot play a major role. On the other hand, because of their relatively slow transport in SiO_2,[12] most of the radiation-generated holes are present in the oxide at 1 µs after the radiation pulse, and their transport will be affected by postirradiation bias switches. This correlation is strengthened by a calculation of the final ΔV_{GB} based on the details of the hole transport; the result of this calculation is shown as the dashed line in figure 1b. In this calculation, ΔV_{GB} is determined by weighting the Gray-Brown shifts for constant 1- and 5-MV/cm irradiations (given by the horizontal lines) with the fraction of the hole transport at those fields as predicted by the continuous time random walk (CTRW) model for hole transport in SiO_2.[12-15] The agreement between calculated and measured values of ΔV_{GB} is seen to be good.

We performed another series of experiments to examine whether the interaction of holes which produces the interface states occurs at the SiO_2/Si interface or in the SiO_2 bulk. In these experiments, we programmed the fast C-V system to change the polarity of the applied bias at selected times after a series of 5 to 7 LINAC pulses, delivered at the rate of 60/s, to obtain a total dose of 600 to 800 krad(SiO_2) while avoiding problems of space charge and heating.

In figure 2, we examine the effect of gate-bias polarity on the interface-state buildup. Curve A shows the buildup of interface states, N_{it}, under a constant positive field of 4 MV/cm following a 600-krad(SiO_2) LINAC irradiation. The buildup is seen to take place over several thousand seconds, which is on a time scale considerably longer than the time it takes radiation-generated holes to transport to the SiO_2/Si interface (milliseconds at 4 MV/cm).[15] The final or saturation value of interface states is ~3 × 10^{11} cm^{-2}. For curve B, the holes were transported under negative bias to the Al/SiO_2 interface, and the bias was then switched positive at 0.8 s. For this

[11] H. E. Boesch, Jr., and J. M. McGarrity, IEEE Trans. Nucl. Sci. NS-23 (1976), 1520.

[12] F. B. McLean, H. E. Boesch, Jr., and J. M. McGarrity, IEEE Trans. Nucl. Sci. NS-23 (1976), 1506.

[13] F. B. McLean and G. A. Ausman, Jr., Phys. Rev. B 15 (1977), 1052.

[14] F. B. McLean, G. A. Ausman, Jr., H. E. Boesch, Jr., and J. M. McGarrity, J. Appl. Phys. 47 (1976), 1529.

[15] F. B. McLean, H. E. Boesch, Jr., and J. M. McGarrity, Proc. Intl. Conf. Physics of SiO_2 and Its Interfaces, Pergamon Press, New York (1978), p 19.
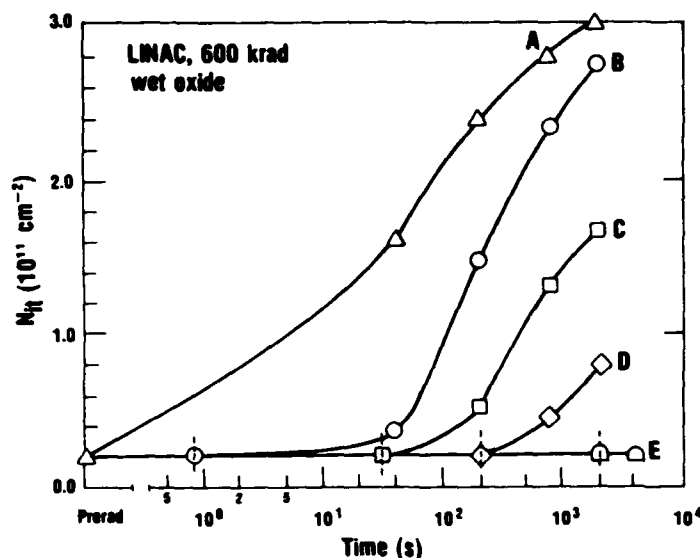
Figure 2. Effect of switching gate-bias polarity on interface states, N_{it}, as a function of time for wet-oxide MOS capacitors following a 600-krad(SiO_2) LINAC irradiation. Curve A: oxide field is a constant (not switched) +4 MV/cm. Curve B: oxide field switched from -4 to +4 MV/cm at 0.8 s. Curve C: oxide field switched from -4 to +4 MV/cm at 29 s. Curve D: oxide field switched from -4 to +4 MV/cm at 200 s. Curve E: oxide field switched from -4 to +4 MV/cm at 2000 s.

case, an interface-state buildup at late times was observed with a magnitude comparable to that observed for a constant 4-MV/cm irradiation, i.e., curve A. For curves C through E, the holes were once again transported to the gate, but the field was maintained negative for 29, 200, and 2000 s, respectively, before being switched back positive. Here one can see the inhibiting effect of maintaining negative bias on the eventual interface-state buildup. The longer the bias is maintained negative following the hole transport, the smaller the final or saturation value of interface states that is observed. If the bias is maintained negative for ~2000 s, then no measurable buildup of interface states is observed.

Curves A and B in figure 2 clearly indicate that the interaction of holes that produces interface states is in the bulk of the oxide, since the same final value of interface states is observed whether the radiation-generated holes transport to the Al/SiO_2 or to the Si/SiO_2 interface. Table 1 summarizes the results of several field-switching experiments in which the interface-state buildup was monitored following irradiation for all combinations of first- and second-stage gate-bias polarity. It is clear that a necessary condition to observe an N_{it} buildup is that the field be maintained positive during the second stage (after the hole transport is complete).

TABLE 1. EFFECT OF GATE-BIAS POLARITY ON BUILDUP OF INTERFACE STATES, N_{it}

First stage (10^{-6} to 1 s)	Second stage (1 to 10^4 s)	N_{it} (cm^{-2}) buildup
+	+	yes
-	-	no
+	-	no
-	+	yes

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In figure 3 we examine the effect of switching both gate-bias polarity and magnitude during the first and second stages of the buildup. Curve A represents a constant 4-MV/cm irradiation with a buildup of radiation-induced interface states similar to that shown in figure 2. In curve B, the field was -4 MV/cm during the radiation pulses and hole transport stage, and then switched to a positive value of 2 MV/cm. Here we observe a buildup which is approaching the same saturation value as for curve A, but at a reduced rate. This result is in agreement with work we have previously published[2] that concludes that the field during the first stage determines the final value of interface states, while the field during the second stage determines the time scale for the buildup. More specifically, as the field during the second stage is reduced, the rate of buildup is reduced. In curve C, the field was -2 MV/cm during the radiation pulses and hole transport, and then switched to a positive value of 4 MV/cm. For this case, we observe a lower final value of interface states at late times, but a buildup to saturation at the same rate as curve A, i.e., a 4-MV/cm irradiation. Once again this agrees with earlier work[2] showing that the magnitude of the field during the hole transport or first stage determines the final value of interface states, while the field during the second stage sets the rate of buildup.
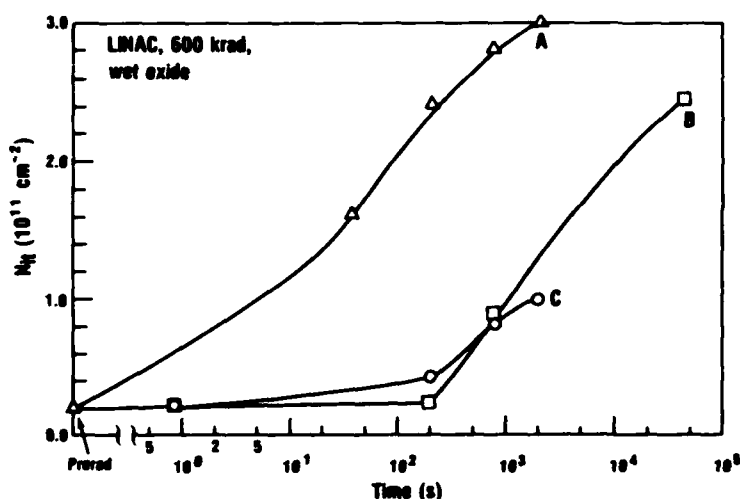

Figure 3. Effect of switching gate-bias polarity and magnitude on interface states, N_{it}, as a function of time in wet-oxide MOS capacitors following a 600-krad(SiO_2) LINAC irradiation. Curve A: oxide field is a constant (not switched) +4 MV/cm. Curve B: oxide field switched from -4 to +2 MV/cm at 0.8 s. Curve C: oxide field switched from -2 to +4 MV/cm at 0.8 s.

4. DISCUSSION

Recently one of us (McLean) presented an empirical model of radiation-induced interface states in SiO_2 MOS capacitors.[16] The formulation explicitly addressed the time-dependent two-stage nature of the buildup process, and it gave the mathematical dependencies of the previously observed experimental buildup on time, field, temperature, and dose. Here we first briefly review

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[2]P. S. Winokur, H. E. Boesch, Jr., J. M. McGarrity, and F. B. McLean, J. Appl. Phys. 50 (1979), 3492.

[16]F. B. McLean, IEEE Trans. Nucl. Sci. NS-27 (1980), 1651.

the empirical model. Then, using the model as well as the results of the present field-switching experiments, we discuss the implications for the physical mechanisms involved in the two stages of interface-state buildup.

4.1 Review of Empirical Model

The two-stage character of the buildup process can be expressed mathematically as the product of two functions, each corresponding to a single stage of the buildup. In particular, the change in interface-state density, $\Delta N_{it}(t)$, is written as

$$\Delta N_{it}(t) = N_{it}^{\infty}(E_1, D) f(t/\tau) \quad , \tag{1}$$

where N_{it}^{∞} is the saturated value of $\Delta N_{it}(t)$ at long times and $f(t/\tau)$ is a time-dependent function which approaches unity at late times. The saturation value, N_{it}^{∞}, is determined solely by the first-stage process as the holes transport through the oxide film; it is a function of dose D and of the field E_1 applied during the first stage, but is independent of temperature.[2] The time dependence of the buildup is contained in the "second-stage" function $f(t/\tau)$, where the time scale $\tau(T, E_2)$ depends on temperature T and the field, E_2, applied during the long-term buildup stage, but not on the field or temperature during the first stage.

The explicit dose and field dependence of the "first-stage" function N_{it}^{∞} is given by

$$N_{it}^{\infty}(E_1, D) = AD^{2/3} \exp\left(\beta E_1^{1/2}\right) \quad . \tag{2}$$

The functional dependencies given in equation (2) were found to be the same in both wet and dry oxides, although the numerical constants vary between oxides.[16,17] For the wet oxides under investigation, $A = 4.6 \times 10^{10}$ $cm^{-2}Mrad^{-2/3}$ and $\beta = 1.32 \ (MV/cm)^{-1/2}$. Our group has observed[10,17] that the rather unexpected 2/3 power law dependence on dose applies to a number of different oxides (wet and dry, hard and soft) over almost three orders of magnitude in dose with no apparent saturation with dose; this dependence has also been reported by other investigators.[18,19] Details of the analysis used to obtain equation (2) and values of the constants A and β for several different oxides are given elsewhere.[16]

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[2] P. S. Winokur, H. E. Boesch, Jr., J. M. McGarrity, and F. B. McLean, J. Appl. Phys. 50 (1979), 3492.

[10] P. S. Winokur, H. E. Boesch, Jr., J. M. McGarrity, and F. B. McLean, IEEE Trans. Nucl. Sci. NS-24 (1977), 2113.

[16] F. B. McLean, IEEE Trans. Nucl. Sci. NS-27 (1980), 1651.

[17] P. S. Winokur and H. E. Boesch, Jr., IEEE Trans. Nucl. Sci. NS-27 (1980), 1647.

[18] K. Naroke, M. Yoshida, and K. Maejuchi, IEEE Trans. Nucl. Sci. NS-30 (1983), 4054.

[19] C. M. Dozier and D. B. Brown, IEEE Trans. Nucl. Sci. NS-30 (1983), 4382.

Although for a fixed dose N_{it}^{∞} is determined by the field during the first stage, $\Delta N_{it}(t)$ does not achieve the saturation value until long times after the radiation pulse. At room temperature and for positive bias, the interface states begin to be manifested typically from 0.1 to 1.0 s after the pulse and continue increasing in approximately logarithmic fashion until saturation occurs at thousands to tens of thousands of seconds. Hence, for positive gate bias, V_g, the second-stage time-dependent function can be expressed approximately as

$$f(t/\tau) \cong b \ln(1 + t/\tau) \quad , \quad V_g > 0 \quad , \tag{3a}$$

for t less than the time at which saturation occurs, t_{sat}. The factor b is chosen so that $f(t/\tau) \to 1$ as $t \to t_{sat}$, i.e., $b = 1/\ln(1 + t_{sat}/\tau)$. For negative bias

$$f(t/\tau) = 0 \quad , \quad V_g < 0 \quad . \tag{3b}$$

The important quantity of interest associated with the second stage is the time scale τ for the buildup; τ was found to be both temperature and field activated, i.e.,

$$\tau = \tau_0 \exp\left(\Delta/kT - \alpha E_2\right) \quad , \tag{4}$$

where Δ is an activation energy, k is the Boltzmann constant, E_2 is the applied electric field during the second stage, and τ_0 and α are constants. From an analysis of the time-dependent data for the wet oxides as a function of temperature and field, $\Delta = 0.82$ eV, $\alpha = 0.51$ (MV/cm)$^{-1}$, and the preexponential factor $\tau_0 \cong 2 \times 10^{-13}$ s.

4.2 Implications for Physical Mechanisms

From the results of the field-switching experiments reported in this paper, it is clear that the first stage of the radiation-induced interface-state buildup is associated with an interaction of the holes throughout the bulk of the oxide layer. To gain insight into the nature of the interaction, consider the field dependence of the first stage, i.e., of the saturated interface-state density (see eq (2)). The exponential dependence on the square root of the field is a classic signature of charge ejection over a field-reduced Coulomb-like (1/r potential) barrier, i.e., the Schottky effect. This would suggest as a possibility for the first-stage process an interaction of the holes in which some charged species is released. The fact that the first stage is temperature independent indicates that thermal energy is insignificant in the process; that is, essentially all the energy for bond breaking and charge release is derived from the transporting holes.

One envisions a process in which a hole makes a transition to a localized trap site next to or involving a weakly bonded ion impurity, where

the initial overall charge state of the impurity complex is neutral. In the light of what is known about hole transport in SiO_2,[12-15,20,21] a broad distribution of energies with an average in the range from 0.5 to 1.0 eV is expected to be deposited locally whenever a hole undergoes either a polaron hopping transition or a trapping event. (In a small fraction of transitions, such as for a long hop at high fields, the amount of energy transfer can be significantly higher than the average.) The ion is then liberated by the sudden localized energy excitation. If the released ion has positive charge (see below), then the interaction probably involves a charge-transfer process in which the hole is annihilated by an electron initially involved in bonding the ion, and the positive charge is then carried by the ion. The defect site remains in a neutral charge state.

With the first-stage process apparently being that of ion release in the bulk, the interpretation of the long-term buildup stage becomes evident. It is simply that of a field-assisted ionic transport to the interface with a subsequent interaction of the ions at the interface which produces the observed interface states. From table 1, the important polarity condition for N_{it} buildup is positive gate bias during the second, long-term buildup stage. This then argues for a positively charged ion species, which would drift toward the Si interface under positive bias.

Based on electrical measurements alone, we cannot identify the positive ionic species or complex involved in the buildup process. Previously,[16] we have argued that the most likely candidate for the positive ion is H^+ because (1) hydrogen is present to some degree in all oxides, (2) the major difference in the interface-state buildup in wet-grown versus dry-grown oxides is simply one of magnitude, with the buildup being considerably larger for wet-oxide capacitors,[17] (3) hydrogen is expected to be relatively mobile in SiO_2 at room temperature, and (4) H^+ is known to be highly reactive at the SiO_2/Si interface. However, other positive ions such as Na^+ or even ionic complexes (e.g., a mobile ion-defect complex) cannot be ruled out.

If the time scale is indeed related to a field-assisted thermally activated ionic transport process, then we argue that it should be possible to express equation (4) as

$$\tau = \tau_0 \exp\left[(\Delta_0 - eaE/2)/kT\right] , \tag{5}$$

[12] F. B. McLean, H. E. Boesch, Jr., and J. M. McGarrity, IEEE Trans. Nucl. Sci. NS-23 (1976), 1506.

[13] F. B. McLean and G. A. Ausman, Jr., Phys. Rev. B 15 (1977), 1052.

[14] F. B. McLean, G. A. Ausman, Jr., H. E. Boesch, Jr., and J. M. McGarrity, J. Appl. Phys. 47 1976), 1529

[15] F. B. McLean, H. E. Boesch, Jr., and J. M. McGarrity, Proc. Intl. Conf. Physics of SiO_2 and Its Interfaces, Pergamon Press, New York (1978), p 19.

[16] F. B. McLean, IEEE Trans. Nucl. Sci. NS-27 (1980), 1651.

[17] P. S. Winokur and H. E. Boesch, Jr., IEEE Trans. Nucl. Sci. NS-27 (1980), 1647.

[20] R. C. Hughes, Phys. Rev. B 15 (1977), 2012.

[21] O. L. Curtis, Jr., and J. R. Srour, J. Appl. Phys. 48 (1977), 3819.

where Δ_0 is the zero field activation energy for diffusion, a is an average hopping distance in the field direction, and a high field regime is assumed, i.e., $eaE/kT > 1$. From the analysis of the field- and temperature-dependent data,[16] we find an average hopping distance of 0.26 nm and zero field activation energy of 0.87 eV. An average hopping distance of 0.26 nm is very reasonable. Indeed, this is precisely the average distance between nearest-neighbor oxygen atoms in amorphous SiO_2. One may well expect that H^+ ions would tend to temporarily bond to the lone-pair, nonbonding p orbitals on the O atoms between hops and hence transport by hopping between nearby O atoms. We may also note that the preexponential factor that was determined for equation (4), $\tau_0 \stackrel{\sim}{=} 2 \times 10^{-13}$ s, is reasonable for ionic transport; it is about a factor of 10 larger than the period associated with the optical phonon vibration in SiO_2.

The approximate logarithmic buildup of N_{it} with time follows simply from the dispersive nature of diffusive ionic transport, with the ions being released throughout the SiO_2 bulk. The buildup is generally observed to occur over about three decades in time (see curves A of fig. 2 and 3). This spread in time is directly correlated with the number of hops required for an ion to transit the entire film (~400), which corresponds to the saturation time for the buildup, whereas the buildup begins at times comparable to a single hop time for those ions released near the interface.

Because no tendency toward saturation with dose up to 20 Mrad(SiO_2) was discernible in either hard wet or dry oxides,[17] we are unable to estimate the initial concentration of hydrogen in our SiO_2 films. Lower bounds on the concentrations necessary to explain the experimental observations over the dose range studied were ~1 × 10^{19} and ~2 × 10^{18} cm^{-3} in the wet and dry oxides, respectively. But these are lower bounds only; the actual concentrations may be significantly higher.[22]

We may summarize at this point with the statement that much of the empirical information obtained from the electrical measurements of radiation-induced N_{it} can be understood simply on the basis of a positive ion release in the bulk by hole transport and the subsequent field-induced drift of the ions to the interface. In this light, the interpretation of the data in figures 2 and 3 is rather straightforward. For curves A and B of figure 2, positive ions are released uniformly in the bulk during hole transport to either the SiO_2/Si or the Al/SiO_2 interface. Immediately following the hole transport, ions move under the applied positive field to the SiO_2/Si interface where they react to form interface states. In curves C through E, where the field is kept negative for increasingly long periods of time following the hole transport, a certain fraction of the released positive ions will be trapped or

[16] F. B. McLean, IEEE Trans. Nucl. Sci. NS-27 (1980), 1651.

[17] P. S. Winokur and H. E. Boesch, Jr., IEEE Trans. Nucl. Sci. NS-27 (1980), 1647.

[22] A. G. Revesz, IEEE Trans. Nucl. Sci. NS-24 (1977), 2102.

removed at the gate and cannot contribute to the eventual N_{it} buildup when the field is returned positive. We therefore observe a lower final value of N_{it} the longer the field is maintained negative. Finally, if the field is maintained negative for the time required for all the positive ions to transport to the gate (~2000 s, curve E), then no further N_{it} generation is observed when the field is returned positive. A similar interpretation applies to the curves of figure 3, with the additional points that (1) the final or saturated value of N_{it} is determined by the field during the ion release process, i.e., during the first-stage hole transport regime, and that (2) the field during the ion drift (second-stage) regime only affects the average drift velocity of the ions and therefore the time scale of the buildup.

When the ions reach the SiO_2/Si interface, they undergo a further interaction which results in the electrically observable interface states. Based on purely electrical measurements one cannot say anything specific about the nature of the interaction at the interface. However, it would appear that this reaction occurs immediately. The time scale for the second stage as well as the results of the bias-switching experiments can be entirely understood on the basis of field-assisted ion diffusion, and there is no evidence of any significant time delay after the ions reach the interface before the appearance of N_{it}. This is further indirect evidence that the positive ions involved are H^+, as they are expected to be highly reactive, whereas the results of bias-stress measurements on samples deliberately contaminated with alkali ions (Na^+, K^+) indicate that these ions can be moved freely back and forth across the oxide layer by reversing the bias polarity.

4.3 Relation to Other Work

The role of a water-related species or defect in radiation-induced interface-state generation has been discussed by several authors. Sah[4] in 1976 proposed that the holes under positive gate bias interacted in the interface region to break weak Si-OH bonds, freeing OH^- radicals to drift toward the gate, leaving behind dangling Si bonds which resulted in interface states. More recently Sah et al[23] postulated that the Si dangling bonds are generated by holes breaking weak Si-H bonds in the interface region. However, the two-stage character of the buildup cannot be understood with these processes, especially the long-term generation process which continues long after the hole transport is complete. In 1978, Svensson,[24] in work based on previous work of Revesz,[22] postulated the essence of a possible two-stage process, namely, that transporting holes broke Si-H bonds in the bulk of the oxide film, leading to positively charged trivalent Si centers in the bulk and neutral interstitial hydrogen atoms which were free to diffuse away. Svensson

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[4]C. T. Sah, IEEE Trans. Nucl. Sci. NS-23 (1976), 1563.

[22]A. G. Revesz, IEEE Trans. Nucl. Sci. NS-24 (1977), 2102.

[23]C. T. Sah, J. Y. C. Sun, and J. J. T. Tzou, J. Appl. Phys. 54 (1983), 2547.

[24]C. M. Svensson, Proc. Intl. Conf. Physics of SiO_2 and Its Interfaces, Pergamon Press, New York (1978), p 328.

then suggested that the atomic hydrogen which diffused to the interface reacted with Si-H bonds in the interface region to produce molecular hydrogen, H_2, and dangling Si bonds, which, as in the Sah model, resulted in the creation of interface states.

Although this model does involve a two-stage process for the generation of interface states, it fails to explain the field and polarity dependencies of the second stage. However, with the simple modification that H^+ ions replace atomic hydrogen, the Svensson-Revesz model becomes entirely consistent with the results of the present field-switching experiments. Further, the generation of Si dangling bonds upon irradiation and the correlation of these dangling bond states with radiation-induced interface states have been inferred from recent electron spin resonance measurements.[25]

Recently, Grunthaner et al[26] have also suggested a two-stage process for radiation-generated interface states. Based on analysis of their x-ray photoelectron spectroscopy (XPS) data, they postulate that the generation of electron-hole pairs in a strained region within about 3 nm of the SiO_2/Si interface leads to rupture of strained Si-O bonds. In their model, the dangling Si bonds remain immobile and can act as hole traps. However, the nonbridging oxygen defects resulting from the bond rupture migrate toward the interface because of the bond-strain gradient in the strained region. This migration is enhanced by the presence of OH groups. When the migration of the defects is terminated at the SiO_2/Si interface, dangling Si bonds are formed, resulting in interface states.

Although similar to our model in some respects, the Grunthaner model is not consistent with our results on several accounts: (1) The migrating defect would have to be positively charged to account for the observed field dependencies of the interface-state buildup. (2) The first-stage process in which holes release the positive-charge species is not restricted to the interface region, but occurs throughout the bulk of the oxide film. (This is supported by the data presented in fig. 1b, which clearly show that the interface-state buildup is related to the transport of holes and not to the electron-hole pair-creation process itself. If the critical interaction of the holes occurred within a narrow region near the interface, then there should be a large difference in the magnitudes of the final saturated values of interface states between curves A and B in both fig. 2 and 3.) (3) Earlier work on interface-state generation due to penetrating versus nonpenetrating radiation showed that it is not necessary for the ionizing radiation to penetrate to the interface for interface states to be produced.[27]

The presence of a strain region localized in the interface region of thermally grown oxides, as inferred from the XPS studies, may be an important factor, however, in the interaction at the interface resulting in the observable interface states. In particular, the possible interactions may very well

[25]P. M. Lenahan and P. V. Dressendorfer, J. Appl. Phys. 54 (1983), 1457.

[26]F. J. Grunthaner, P. J. Grunthaner, and J. Maserjian, IEEE Trans. Nucl. Sci. NS-29 (1982), 1462.

[27]P. S. Winokur and M. M. Sokoloski, Appl. Phys. Lett. 28 (1976), 627.

result in an increase in the localized strain fields at the interface. One indication that this may be the case is that a significant component of the radiation-induced interface-state distributions (in energy across the Si band-gap) is almost always observed to be U-shaped, with a relatively flat minimum near midgap and a sharp rise toward the conduction and valence band edges. Recent density-of-state calculations for the SiO_2/Si system[28] indicate that a specific defect in the interface region (such as a dangling Si bond) results in a peaked structure in the density-of-state distribution function, which sharply contrasts with the universally observed U-shaped distributions. The calculations show, however, that fluctuations in bond angles and lengths in the interface region can result in U-shaped distributions via band tailing from both the Si conduction and valence bands.

The most probable origin of such fluctuations is localized microscopic strain fields. In general, a certain amount of local reconstruction occurs with the formation of any defect in SiO_2, or even with a change in the charge state of a defect due to the large lattice coupling with charge centers in SiO_2 (the polaron effect). As one example, there is well-documented electron paramagnetic resonance (EPR) evidence[29] of a local reconstruction associated with the formation of E' centers in vitreous SiO_2. Another possible explanation involves a class of defects, the so-called valence-alternation pairs, which are under increasingly active discussion[30-32] in the theory of amorphous semiconductors, particularly the chalcogenide glasses, and have been discussed recently in connection with the nature of intrinsic defects in vitreous SiO_2.[33-35] They provide a possible link between dangling Si bonds, appearing perhaps via interactions with H^+ ions, as discussed above, and large localized strain fields. In any case, the possible role that strain plays in interface-state generation deserves attention in future work.

The H^+ ion release/drift model for N_{it} generation proposed in this work is very similar to the process suggested by Feigl et al[36] to account for their observations of oxide trapped charge and interface-state buildup upon electron injection into thermal SiO_2 films.* They, too, envision a two-stage process, in which the first "fast" stage is attributed to an electron-induced release of a mobile impurity species from an H/OH structural defect grown into

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[28] R. B. Laughlin, J. D. Joannopoulos, and D. J. Chadi, Proc. Intl. Conf. Physics of SiO_2 and Its Interfaces, Pergamon Press, New York (1978), p 321.

[29] D. L. Griscom, Phys. Rev. B 22 (1980), 4192.

[30] P. W. Anderson, Phys. Rev. Lett. 34 (1975), 953.

[31] R. A. Street and N. F. Mott, Phys. Rev. Lett. 35 (1975), 1293.

[32] M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. 37 (1976), 1504.

[33] G. Lucovsky, Phil. Mag. B 39 (1979), 513; see also G. Lucovsky and D. J. Chadi, Proc. Intl. Conf. Physics of MOS Insulators, Raleigh, Pergamon Press, New York (1980), p 301.

[34] M. Pepper, IEEE Trans. Nucl. Sci. NS-25 (1978), 1283.

[35] C. T. White and K. L. Ngai, Proc. 6th Annual Conf. Physics of Compound Semiconductor Interfaces, American Institute of Physics, New York (1979), p 1412.

[36] F. J. Feigl, D. R. Young, D. J. DiMaria, S. Lai, and J. Calise, J. Appl. Phys. 52 (1981), 5665.

*The introduction rate of damage resulting from a hole flux is several orders of magnitude greater than that from an equivalent avalanche-induced electron flux.

17

the SiO_2 network. They suggest neutral H as the most likely possibility for the mobile impurity species. The second "slow" stage results from the transport of this species to the interface. They note that the detailed reactions at the interface are not known. Except for the charge state of the mobile species, this is the same scenario that is indicated by our data. It is conceivable that the charge state of the mobile species could be different in the two cases because of the charge difference of the initiating carrier (electrons as opposed to holes). This charge difference remains an open question.

In related work,[37] S. K. Lai suggests a two-step process for the generation of interface states. In the first step, he simulates the effect of radiation damage by the avalanche injection of holes from the Si into the SiO_2, where a certain percentage of holes are trapped in the SiO_2/Si interface region. The second step involves the injection of electrons and their capture by the trapped holes, and results in the generation of an interface-state distribution with a peak in the Si band gap. The relationship between this work and our results is not clear at this time.

Finally, we note that the H^+ ion release/drift model for N_{it} generation is also compatible with results on interface-state generation under high-field stressing of MOS capacitors recently reported by Hu and Johnson.[38] Upon positive bias stressing at 90 K with fields of 7.1 to 7.5 MV/cm, they found a buildup of positive charge in the oxide layer, but they observe no buildup of interface states. Upon warming the samples to room temperature, however, they observed a time-dependent buildup of N_{it}, the number of which was correlated with the amount of positive charge initially present at 90 K after bias stressing. These results can be explained on the basis of H^+ ions being released in the bulk during the high-field stressing, either by field-injected hot electrons or by holes generated as a result of impact ionization by the hot electrons moving under the high fields. But at 90 K the H^+ ions are essentially immobile and remain near their points of origin. However, when the samples are warmed to room temperature the H^+ become mobile, and those which reach the SiO_2/Si interface result in a time-dependent N_{it} buildup. This is completely analogous to the manner in which the time-dependent buildup of radiation-induced N_{it} at room temperature was studied in the hard dry oxide[17] after irradiation at liquid nitrogen temperature.

[17]P. S. Winokur and H. E. Boesch, Jr., IEEE Trans. Nucl. Sci. NS-27 (1980), 1647.

[37]S. K. Lai, Appl. Phys. Lett. 39 (1981), 58.

[38]G. Hu and W. C. Johnson, Appl. Phys. Lett. 36 (1980), 590.

5. CONCLUSIONS

In summary, it would appear that a large number of experimental observations on the generation of interface states due to various stresses (holes from ionizing irradiation, injected electrons, high electric fields) can be *explained by a two-stage process.* The first stage is the bulk release of a mobile species due to the interaction of the stressing agent (holes, electrons, high fields). The second "long-term" buildup stage is then associated with the drift of the released mobile species to the interface, where a subsequent reaction results in the observable interface states. It appears likely that the mobile species is a water-related ion or defect. We have argued that it is H^+ for the case of ionizing radiation.

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