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Introduction

It is well known that the interface-state density at the SiO_2 -Si interface in MOS devices increases when these devices are exposed to high energy radiation. In CMOS circuits the buildup of interface states is a contributing factor to the radiation induced threshold voltage shift and to channel mobility degradation, which leads to a deterioration of CMOS switching time and a greater susceptibility to noise. In surface channel CCD's, the increase in interface states decreases the transfer efficiency. At this time the physical mechanisms responsible for the increase in interface-state density are unknown.

Several mechanisms have been reported to account for the buildup of interface states in metal- SiO_2 -Si capacitors subjected to ionizing radiation. These mechanisms include structural modifications (e.g., broken bonds) of the SiO_2 layer (by the radiation) that in turn cause bonds at the SiO_2 -Si interface to break,¹⁻³ direct interaction of the radiation at the interface to break strained bonds,^{3,4} and the buildup of an inhomogeneous charge distribution trapped in the oxide close to the interface leading to fluctuations in surface potential and a dispersion of the experimental C-V curves interpreted as an increase in the density of interface states.⁵⁻⁸ Many workers maintain⁶⁻⁸ that the fluctuations in surface potential caused by the inhomogeneous charge distribution at the interface merely give rise to an "apparent" increase in interface-state density (case of lateral inhomogeneities); other workers⁹⁻¹¹ suggest that an inhomogeneous charge distribution trapped close to the interface may create localized states, known as band-tail states, capable of trapping electrons and holes.

In a prior publication,¹¹ Winokur and Sokoloski reported that the nature and magnitude of the buildup of interface states in MOS capacitors under positive bias was the same for both penetrating Co^{60} γ and non-penetrating 10.2 eV uv radiation. They suggested that the buildup of interface states in MOS capacitors subjected to highly ionizing radiation was not due to the direct interaction of radiation at the interface or to a structural modification of the SiO_2 layer, but resulted from the production of electron-hole pairs in the insulator and the subsequent transport of holes to the interface. In the work reported on in this paper we have repeated the uv- Co^{60} study (adding negative bias) on another set of thermally grown oxides and have monitored the interface-state density as a function of time from 40 ms to 400 s following a 4- μ s electron pulse using a fast C-V technique.¹² From the results of the latter experiment we report that in addition to hole transport to the interface, some slow (relative to the hole transport time) interaction of the holes in the interface region appears to be responsible for the buildup of interface states. In addition, in both the uv- Co^{60} study and the interface-state density with time study, we have separated the effects of lateral inhomogeneities from interface states by measuring the frequency dependence of the C-V traces and by measuring

the Gray-Brown shift¹³ between room temperature and liquid nitrogen temperature. It is shown that all three irradiations, uv, Co^{60} , and e-beam, produce interface states.

Sample Preparation and Experimental Procedures

The MOS capacitors used in all experiments were from the same wafer. The oxide was 714 Å dry thermally grown SiO_2 (at 1000 °C) on 7-10 Ω cm n-type Si. In order to be able to perform uv experiments 40-mil-diam 145-Å-thick semitransparent Au electrodes were deposited on all samples. In addition to 10.2 eV uv exposures, Co^{60} and 13 MeV e-beam irradiations were performed.

The 10.2 eV uv irradiations were performed at the National Bureau of Standards (NBS) using a Seya monochromator attached to a hydrogen discharge source. An absolute light intensity incident on the sample of 2.3×10^{11} photons/(cm²s) was measured by a calibrated Stanford window photodiode.¹⁴ The dose delivered to a sample was calculated from the measured uv beam intensity and the transmission properties of the semitransparent Au electrode. Co^{60} irradiations were performed using a 12 kCi (~ 2 Mrad(C)/h) source at NBS. The dose delivered to the samples was measured by using thin film chlorostyrene dosimeters.¹⁵ All irradiations were performed with bias applied to the gate electrode; the bias was kept on for 2000 s following all uv and Co^{60} steady-state irradiations to insure that hole transport was in its final stages.¹² High frequency 1-MHz and quasistatic C-V curves were measured before and after irradiation, and from these curves the density of interface states as a function of energy in the Si band gap was calculated by the Terman,¹⁶ Berglund,^{17,18} and Castagne¹⁹ techniques. In order to address the question of lateral nonuniformities the following measurements were made: (1) C-V traces were recorded as a function of frequency from 10 Hz to 100 kHz by using a lock-in amplifier, and (2) the Gray-Brown shift was measured between room temperature and liquid nitrogen temperature.

The electron beam irradiations were performed at the Armed Forces Radiobiology Research Institute (AFRRI) electron linear accelerator (LINAC). The LINAC produced a nominal 13 MeV 1-A electron beam with a pulse width of 4 μ s. Sample dose per pulse was controlled by varying the LINAC-to-sample distance. Multiple pulses could be delivered to the sample at a rate of 60/s. A thin foil Cu calorimeter was used for pulse-to-pulse electron beam dosimetry. Teflon:CaF₂ thin disc thermoluminescent dosimeters were employed for absolute dose measurements. During the pulsed electron irradiations high-frequency capacitance-voltage curves were recorded by using a fast technique.¹² This apparatus recorded the C-V characteristics of the sample at logarithmically spaced times from 4 ms to 2000 s after a radiation pulse. Sample capacitance was measured during a 2 ms-duration voltage ramp by using an oscillator and phase-sensitive detector at 1 MHz.

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In this experiment MOS capacitors were exposed to both penetrating Co⁶⁰ γ radiation ($\gamma = 1.17, 1.33$ MeV) and nonpenetrating Lyman-Alpha uv radiation ($h\nu = 10.2$ eV). The uv radiation (Fig. 1) is rapidly absorbed (producing electron-hole pairs) in the first few hundred angstroms of the oxide, with virtually no light reaching the oxide-semiconductor interface.^{20,21} The electrons produced by the uv radiation are quickly swept to (under a bias of +20 V) and collected at the gate electrode, while the holes undergo a stochastic transport to the SiO₂-Si interface.¹² When the holes arrive at the interface a certain percentage²² is trapped in localized states in the oxide that do not communicate via charge transfer with the semiconductor. The Co⁶⁰ radiation (Fig. 1) generates electron-hole pairs uniformly throughout the oxide and penetrates to the interface. Once again, the electrons are swept to and collected at the gate electrode, while holes transport under the applied field to the SiO₂-Si interface, where a certain percentage is trapped. Co⁶⁰ and uv exposure times were adjusted to produce the same number of holes in the oxide.

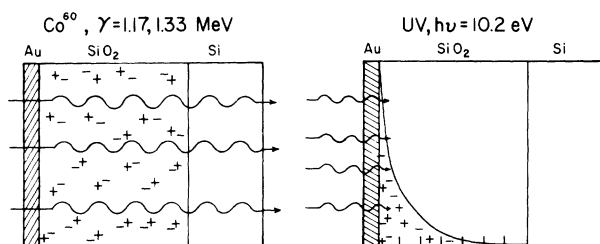


Figure 1. Profile of electron-hole pairs produced in Au-SiO₂-Si capacitors exposed to penetrating Co⁶⁰- γ radiation (left, $\gamma = 1.17, 1.33$ MeV) and nonpenetrating Lyman-Alpha uv radiation (right, $h\nu = 10.2$ eV).

High-frequency 1-MHz and quasistatic C-V curves were measured before and after irradiation, and from these curves the density of interface states as a function of energy in the Si band gap was calculated by several techniques. Figure 2 shows the preirradiation interface-state distribution calculated by the Berglund technique, as well as the interface-state distributions calculated by using the Berglund, Terman, and Castagne techniques following a 500 krad(SiO₂) Co⁶⁰ exposure with +20 V applied to the gate electrode. The interface-state distribution calculated by the Terman technique is in fairly good agreement with the interface-state distributions calculated by using the Berglund and Castagne techniques, the latter two techniques yielding identical results. (The Castagne technique yields information only from the inversion threshold to a surface potential where the surface state time constant has become equal to the ac signal frequency.) The preirradiation interface-state density was calculated from the Berglund technique (which analyzes the quasistatic curve) since this technique yields the best results for low interface-state densities. The interface state density is seen to rise sharply toward the valence and conduction bands (the positions of the valence and conduction bands, E_v and E_c , are noted on the figure); this characteristic U-shaped interface profile may represent

localized Si band-tail states resulting from the highly disordered SiO₂-Si interface.^{10,11} The sharp drop or decrease in the interface-state density observed near the conduction band is due to the breakdown of the analysis techniques in this region.

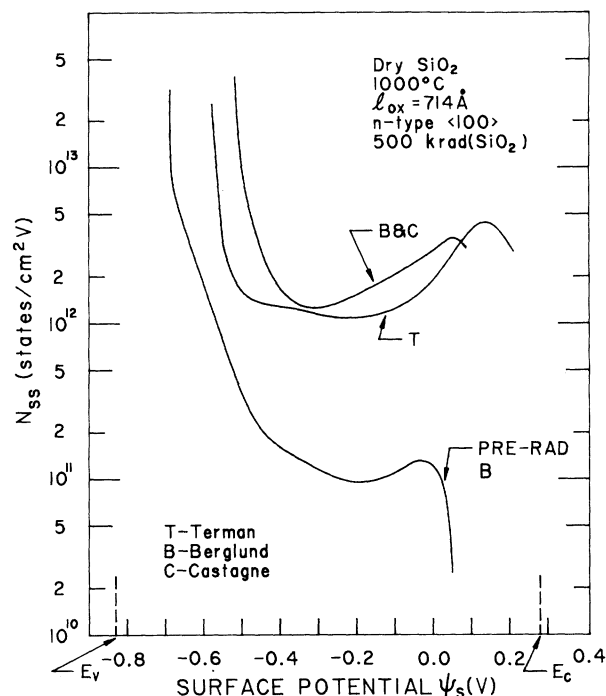


Figure 2. Interface-state density as a function of surface potential calculated by using the Terman, Berglund, and Castagne techniques for MOS capacitors following a 500 krad(SiO₂) Co⁶⁰ irradiation with +20 V applied to the gate electrode.

Figure 3 shows the density of interface states, N_{ss} , (calculated by the Terman technique) versus surface potential, ψ_s , for MOS capacitors before and after 1 Mrad(SiO₂) or equivalent of Co⁶⁰, uv, and LINAC irradiation with +20 V applied to the gate electrode. (A 1 Mrad(SiO₂) equivalent uv irradiation is defined as an irradiation in which the number of electron-hole pairs generated equals the number produced by a 1 Mrad(SiO₂) Co⁶⁰ or LINAC irradiation.) The interface-state density for the Co⁶⁰ and LINAC irradiations showed close agreement, while the interface-state density resulting from the uv exposure was approximately twice as large. Uncertainties in absolute dosimetry may be partly responsible for the factor of two difference in uv versus Co⁶⁰-LINAC buildup. An equivalent uv irradiation of 1 Mrad(SiO₂) with -20 V applied to the gate electrode (dashed line, Fig. 3), where holes are swept to the gate electrode, resulted in an interface-state distribution an order of magnitude below that shown in Fig. 3 for the case of +20 V applied to the gate electrode. The comparable buildup of interface states resulting from both penetrating and nonpenetrating radiation with the gate electrode at positive bias, together with the considerably reduced buildup of interface states resulting from nonpenetrating radiation with the gate electrode at negative bias, imply that the buildup is directly related to the transport of holes to the interface and is not caused by direct interaction of radiation in the oxide or at the interface.

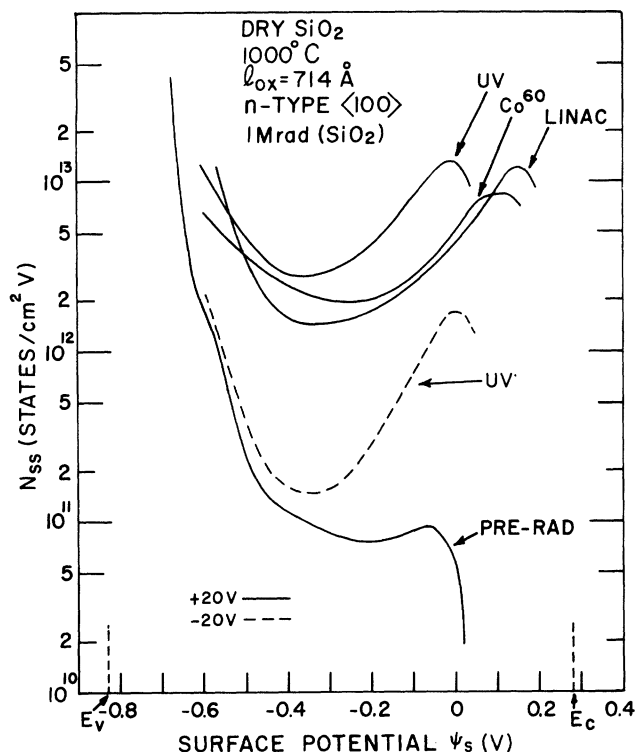


Figure 3. Interface-state density versus surface potential (calculated by using the Terman technique) in MOS capacitors following 1 Mrad(SiO₂) or equivalent of 10.2 eV uv, Co⁶⁰-γ, and 13 MeV e-beam irradiation with + 20 V applied (solid curves), and a 1 Mrad(SiO₂) equivalent 10.2 eV uv irradiation with -20 V gate bias (dashed curve).

Measurements were performed on the MOS capacitors following uv and Co⁶⁰ irradiations to determine if the distortions in the experimental C-V traces were caused by lateral inhomogeneities or interface states. Figure 4 shows C-V traces as a function of frequency following a 1 Mrad(SiO₂) equivalent uv irradiation. C-V traces were taken at 10⁶, 10⁵, 10³, 10 Hz, and dc (quasistatically). The increasing capacitance at a given applied bias (surface potential) as the measurement frequency is lowered is due to the increasing contribution of the interface-state capacitance in parallel with the silicon space charge capacitance. This is because at a given ac signal measurement frequency, only those interface states with time constants greater than or equal to the measurement frequency can respond; as the measurement frequency is lowered, more interface states respond, resulting in an increasing interface-state capacitance. The Castagne technique uses the difference in capacitance between the quasi-static and 1-MHz C-V traces to calculate the number of fast surface states with time constants less than 1 μs. Using this technique, an interface-state density of 5.7×10^{12} states/(cm²V) was calculated at midgap ($\psi_s \sim -0.28$ V) from the curves in Fig. 4. The midgap interface-state density in Fig. 3 calculated by the Terman technique was 3.0×10^{12} states/(cm²V). Also seen in Fig. 4 is the Gray-Brown shift between 1-MHz C-V traces at room temperature and liquid nitrogen. The Gray-Brown shift yielded a value of 8.7×10^{11} states/cm². If an extrapolation of the interface-state distribution in Fig. 3 is made in the 0.00 to 0.25 V

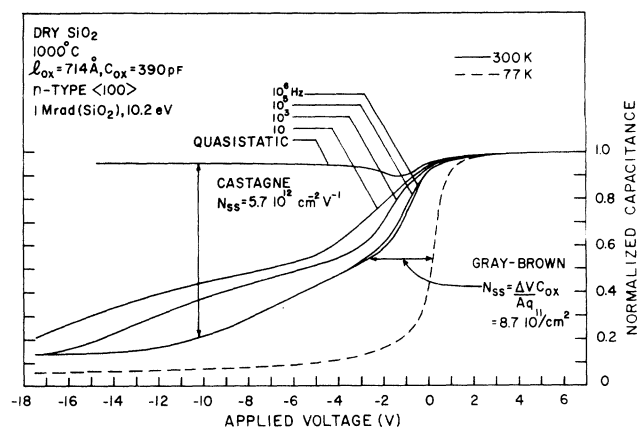


Figure 4. Gray-Brown shift and frequency dependence of C-V traces following a 1 Mrad(SiO₂) equivalent uv irradiation with + 20 V gate bias during irradiation. C_{ox} is the oxide capacitance. From the 1-MHz and quasistatic C-V curves the interface-state density at midgap has been calculated by using the Castagne technique.

surface potential range sampled by the Gray-Brown shift, one obtains a Gray-Brown shift of 11.3×10^{11} states/cm². It is important to note that the 1-MHz liquid nitrogen C-V trace is very close in shape to a preirradiation C-V trace. This indicates that there are very few lateral inhomogeneities. Figure 5 shows measurement of the Gray-Brown shift before and after high field bias stressing at room temperature for an MOS capacitor with an unstable thermal oxide. (The MOS capacitor was not from the same lot as the capacitors used in our interface-state measurements.) The Gray-Brown shift is seen to be constant, while the distortion of the liquid nitrogen C-V trace tracks the room temperature curve. This is clearly a case where there is a buildup of lateral nonuniformities, with negligible interface-state production. The C-V traces as a function of frequency, which show a time constant dependence of the capacitance, together with the Gray-Brown shift, indicate that we are measuring primarily interface states.²³ We obtained similar results when we measured C-V traces as a function of frequency and Gray-Brown shifts following a 1 Mrad(SiO₂) Co⁶⁰ irradiation.

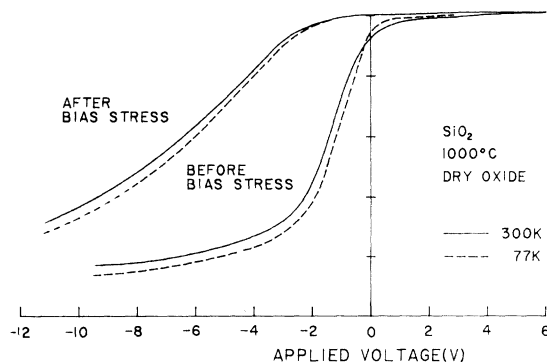


Figure 5. Gray-Brown measurement on an unstable MOS capacitor exhibiting lateral nonuniformities after high field bias stressing at room temperature for several hours.

Interface-State Distribution as a Function of Time

In our studies on the transport properties of SiO_2 , it was noted that in some samples, even at low doses, the C-V traces become gradually more distorted as a function of time.¹² This effect was especially noticeable below room temperature where the hole transport was slowed down. In this experiment measurements were made at room temperature in order to compare the final response to the response of the capacitors exposed to uv and Co^{60} irradiation at room temperature.

Figure 6 shows the C-V curves from 40 ms to 400 s following a single electron beam pulsed irradiation of an MOS capacitor. The largest dose that could be delivered in a single pulse was 200 krad(SiO_2). As described earlier, these curves were obtained using a fast C-V technique at 1 MHz in which a 2 ms voltage ramp was applied to the sample. From the figure, we see that the trace at 0.04 s is only slightly more distorted than the preirradiation curve. However, as time increases (with the +20 V applied continuously) the curves become increasingly more distorted. The corresponding interface-state distributions calculated by the Terman technique for the C-V traces in Fig. 6 are shown in Fig. 7. From this figure, we see that the interface-state densities as a function of energy in the Si band gap are increasing with time following the electron beam pulse. At 400 s, which is much longer than the characteristic time necessary for holes to transport across the oxide, we are still observing interface-state buildup. This point is dramatically made in Fig. 8, which shows the midgap interface-state density as well as the fraction of holes which have reached the SiO_2 -Si interface²⁴ as a function of time. Comparing the plots, we see that at 1 s approximately 90% of the holes have reached the interface but the interface-state buildup has just begun. This important observation implies that the arrival and trapping of holes at the interface alone is not sufficient for interface-state production.

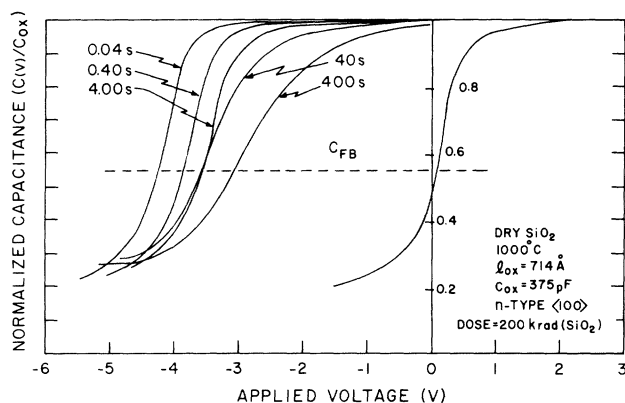


Figure 6. High-frequency 1-MHz C-V curves from 40 ms to 400 s following an electron beam pulsed irradiation of an MOS capacitor with +20 V applied to the gate electrode. The trace at the extreme right is the preirradiation C-V trace.

A similar test was performed on a capacitor which received five LINAC pulses for a total dose of 1 Mrad(SiO_2). The results of this irradiation are shown in Fig. 9, where we have plotted the midgap interface-state density as a function of time. For this sample, the measurements were continued for a time long enough to observe saturation of the buildup. In this case

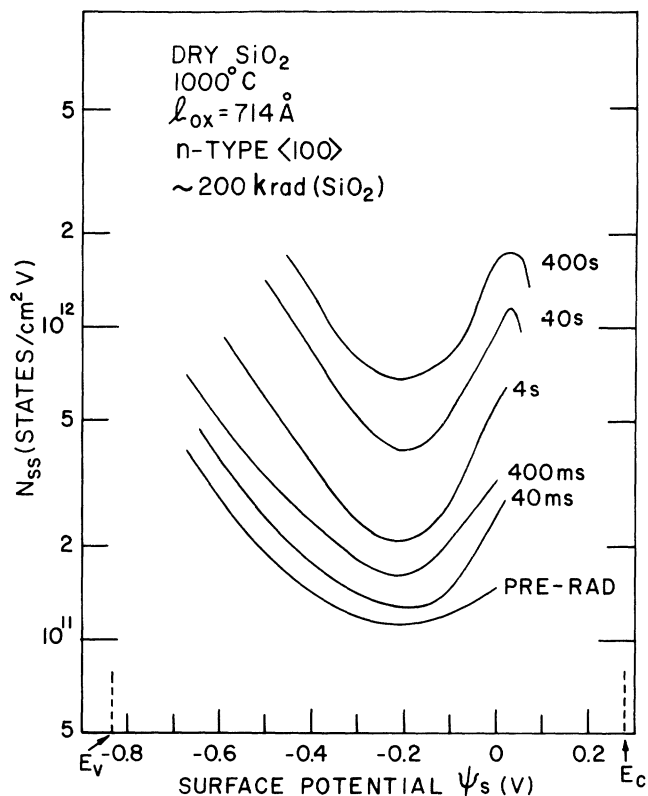


Figure 7. Interface-state distributions calculated by using the Terman technique on the C-V traces in Fig. 6.

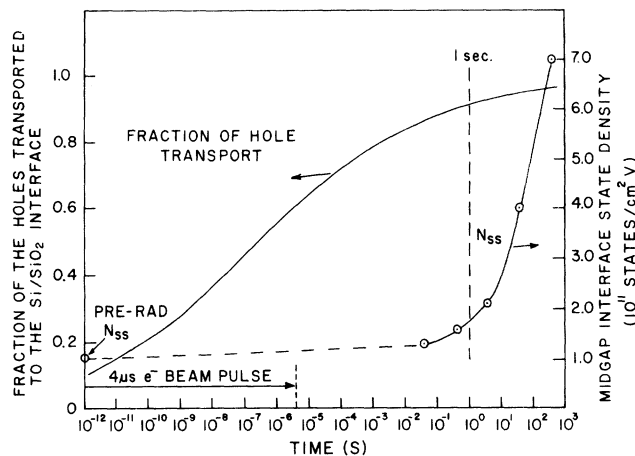


Figure 8. Midgap interface-state density and fraction of holes transported to the SiO_2 -Si interface as a function of time following a 4- μs LINAC pulse.

+10 V had been applied during the irradiation, and in Fig. 9 we show that there was no effect of bias stressing the sample at room temperature for a similar period of time. In addition, a Gray-Brown measurement was performed after saturation was reached; the +2.5 V flatband voltage shift between 1-MHz C-V traces taken at room temperature and liquid nitrogen (77 K) yielded a calculated total interface-state density of 7.5×10^{11} states/cm². Comparing the pre- and postirradiation 77 K C-V traces we observed some distortion in the weak inversion region due to lateral nonuniformities (<10% of the Gray-Brown shift).

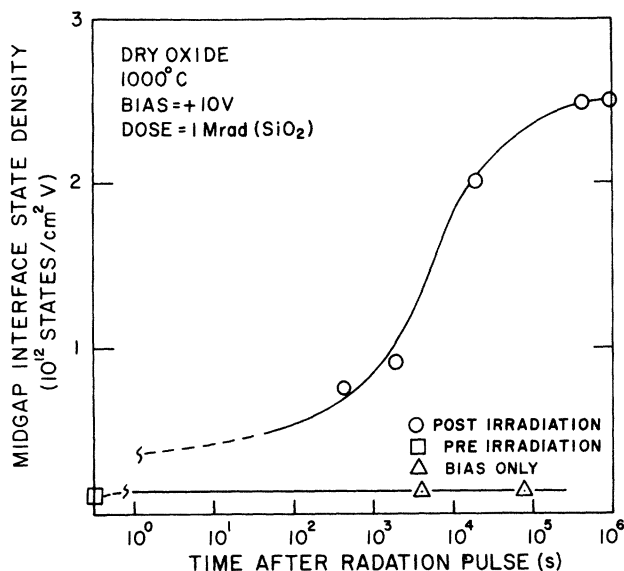


Figure 9. Midgap interface-state density versus time following a 4- μ s LINAC pulse with +10 V gate bias applied during irradiation. Also shown is the midgap interface-state density versus time for a sample bias-stressed out to 10^5 s.

Discussion

The results of the two experiments show (1) that direct interaction of radiation at the SiO_2 -Si interface is not needed to produce interface states,¹¹ (2) that the interface-state buildup is dependent on the transport of holes to the SiO_2 -Si interface,^{11,12} and (3) that the major part of the interface-state buildup begins after the holes have had time to reach the interface (~ 1 s), continues for long times ($\sim 10^5$ s), and saturates ($\sim 10^6$ s).

As seen in Figs. 2, 3, and 7, the interface-state density as a function of surface potential has a minimum near midgap and rises sharply toward the band edges. As pointed out in the discussion of Fig. 2, the characteristic U-shaped interface distribution for preirradiation curves with low interface-state densities may represent localized Si band-tail states resulting from the highly disordered SiO_2 -Si interface. Since the postirradiation interface distribution maintains this characteristic shape (Fig. 7), a plausible mechanism for interface-state buildup should account for such a distribution. In the past, attention has been focused on the relation between the inhomogeneous charge distribution trapped in the oxide close to the interface and the buildup of interface states. (Any interaction at the interface that leads to a defect with a localized state must be ruled out since a defect of this nature would lead to a peak in the interface-state distribution. Such a peak was not observed.)

Goetzberger⁹ suggested a correlation between trapped oxide charge and interface-state production. He argued that charge trapped within 30 Å of the interface could produce fluctuations in surface potential capable of trapping electrons and holes. Localized states close to the valence and conduction band were caused by single charge centers capable only of shallow trapping. States whose energies were deeper in the Si band gap were induced by clusters of two or more charges. In support of this idea, Brews⁷ calcu-

lated that charge clusters constituted the lowest energy configuration for a charge distribution at the interface. Using a laser-photoemission technique to scan the SiO_2 -Si interface, charge clusters have been

observed^{25,26} for the case of mobile ions transporting to the interface. The ion clusters were ~ 10 μ wide, or 100 times the oxide thickness (~ 1000 Å) for the MOS capacitors used in these experiments.

If we assume in our experiments that the holes at the SiO_2 -Si interface are forming similar clusters, then depending on their size and spacing, the time to form a cluster could be hundreds to thousands of times longer than the transit time for holes to reach the interface. According to the model of Goetzberger,⁹ the clustering of holes in the plane of the interface would result in interface states which are deeper in the Si band gap than those induced by single charge centers. Therefore, hole clustering with its resultant interface-state buildup appears to be a plausible mechanism to explain our experimental results.

Independent of the particular mechanism involved in creating interface states, the results on the buildup can explain some anomalous radiation response data on CMOS devices. Srour et al.²⁷ have examined dose rate effects in commercial CMOS devices. In this investigation they compared the total dose response of the RCA CD4007AD out to 10^5 rad at two dose rates, 23 rad/s and 0.23 rad/s. They observed a 0.8 V negative threshold voltage shift at 10^5 rad for the 23 rad/s irradiation. For the exposure at 0.23 rad/s the shift was 0.4 V positive. It was found, however, that if the first sample was kept under bias for a period of time (140 h) equal to that required for the irradiation at 0.23 rad/s, then it eventually showed a net positive shift equal to the samples irradiated at the lower rate. At that time they attributed this effect to annealing of the positive charge trapped at the interface. Based on the results reported in this paper, Srour et al.²⁸ now suggest that long term interface-state buildup can explain their results.

In addition, we have observed an increasing distortion of the C-V traces as a function of time in pulse-irradiated hard wet oxides. Detailed interface-state distributions have not yet been determined, but the Gray-Brown shift indicates the radiation induced interface-state buildup is only about 25 percent of the buildup for the samples reported on in this paper. The interface-state buildup in a hard dry oxide was only 10 percent of that reported in this paper, and it showed very little change with time. In addition to completing the analysis of interface-state buildup in hard wet and dry oxides, further experiments are needed to identify the mechanisms which relate the arrival of holes in the interface region to the eventual buildup of interface states.

Acknowledgments

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