A physically based predictive model of Si/SiO_2 interface trap generation resulting from the presence of holes in the SiO_2

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A physically based model is developed which explains apparently unrelated aspects of the Si/SiO_2 interface trap generation process; the predictions of the model are in at least semiquantitative agreement with observations previously reported in the literature. The model involves interactions between molecular hydrogen and trivalent silicon dangling bond defects in the oxide (E' centers) and at the Si/SiO_2 interface (P_b centers). Our model is primarily directed at interface trap generation caused by ionizing radiation and by hot hole injection phenomena observed in short channel transistors. © *1997 American Institute of Physics.* [S0003-6951(97)03747-9]

Although the Si/SiO_2 interface trap generation phenomenon has been intensively investigated for over 30 years,[1–8] a fundamental physical understanding of the process has yet to emerge. However, some aspects of the phenomena can be described with considerable assurance. Interface trap defects are created when charge carriers are introduced to the amorphous SiO_2 film above the silicon.[1–8] (Holes are many orders of magnitude more effective in this process than are electrons; however electrons may also have a role under some circumstances.[4]) Many studies indicate that a hydrogen species is involved[5–12] and that some interaction of a hole in the oxide and a hydrogen species triggers the interface trap generation process.

Electron spin resonance (ESR) measurements by several independent groups have shown that the generation of silicon ''dangling bond'' defects called P_b centers accompanies the interface trap formation process[13–18] and that there is an approximate one-to-one correspondence between the density of P_b centers and the density of interface traps created during the process.[13,15,17] Since the P_b centers defects are clearly interface trap defects with two broad levels in the silicon band gap,[14,15,19,20] one may reasonably conclude that they dominate interface trap generation.

Recently, Conley *et al.*[11,12] demonstrated a link between the interface trap generation and a second silicon dangling bond defect, this one in the oxide. The oxide defects are called E' centers and involve an unpaired electron residing on a dangling bond of a silicon back-bonded to three oxygens. The dangling bond orbital ''points'' toward a positively charged silicon. The defect is thus a hole trapped at an oxygen vacancy. ESR studies by at least four independent groups indicate that the E' center dominates oxide hole trapping in quite a wide variety of oxides.[15,17,18,21–23]

Conley *et al.*[11,12] showed that E' centers in oxide films on silicon react rapidly at room temperature with molecular hydrogen, H_2. In their study, about 25% of the E' centers disappeared as about an equal number of hydrogen complexed E' centers (which we term $E'H$) appeared; the loss in E' density was accompanied by an approximately equivalent gain in interface trap density. No increase in interface trap density occurred with H_2 exposure if the positively charged E' centers were absent. It is interesting to note that Mrstik and Rendell[10] have reported electrical measurements showing that an increase in interface trap density was accompanied by a roughly equivalent 25% decrease in oxide trapped holes when previously irradiated SiO_2 films were exposed to H_2 at room temperature. These observations are significant because when SiO_2 is subjected to ionizing radiation, atomic hydrogen is created; above 110 °K it very rapidly dimerizes leaving behind H_2 in the oxide.[24]

It is well established that silicon dangling bond sites at the Si/SiO_2 interface (P_b centers) are passivated by hydrogen.[25,26] We assume, as have many others, that the interface trap creation process involves the breaking of silicon-hydrogen bonds at P_b center precursor sites at the Si/SiO_2 interface; the precursor site will be termed P_bH.

The linkage between E' centers, P_b centers, and H_2 is key to understanding the interface trap generation process.

We propose a reaction of the following form:

$$H_2 + P_bH + E' \rightleftarrows H_2 + P_b + E'H. \tag{1}$$

In this reaction, H_2 plays the formal role of a catalyst. When a hole drifting to an E' precursor site is captured, a positively charged silicon dangling bond site (E' center) is created, which, as Conley *et al.*[11,12] have shown, can react with radiolytic H_2 to form a complex which we term $E'H$. After irradiation, the H_2 is eventually dissipated, but for a short time the system will *approach* equilibrium. Elementary statistical mechanics tells us that, if the system were to reach equilibrium, one could write[27]

$$\frac{[P_b][E'H]}{[P_bH][E']} = K, \tag{2}$$

$$\text{where } K = \exp\left(\frac{-\Delta G}{kT}\right). \tag{3}$$

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Here ΔG is the difference in Gibbs free energy of the reactants and products. Since expression (1) involves the transfer of a hydrogen atom from a silicon at the interface (P_b) to a silicon in the oxide (E'), one would reasonably conclude that ΔG is small. Thus, $K \cong 1$, at least within about an order of magnitude.

In order to solve Eq. (2) for ΔP_b, the concentration of P_b centers eventually generated after the interface trap formation process is complete, we define the initial (prestress) P_b concentration to be $P_{\rm bi}$, the initial (prestress) P_bH concentration to be $(P_b{\rm H})_i$, and the density of E' trapped holes present immediately after irradiation (and immediately after all the holes which were not trapped are swept from the oxide) to be E_i'.

With these definitions, Eq. (2) becomes

$$\frac{[P_{\rm bi}+\Delta P_b][\Delta P_b]}{[(P_b{\rm H})_i-\Delta P_b][E_i'-\Delta P_b]}=K. \tag{4}$$

In Eq. (4), we take the number of E'H complex sites created to be equal to the number of P_b sites created.[12] Assuming it captures the essential physics of the process, Eq. (4) should allow us to predict the interface trap generation behavior in a wide range of oxides.

Suppose we first consider the technologically important situation in which we initially have an excellent Si/SiO_2 interface with a very low interface trap density and thus a very low P_b density. In this case $P_{\rm bi} \cong 0$. At low dose $[\Delta P_b \ll (P_b{\rm H})_i]$, Eq. (4) becomes

$$\frac{[\Delta P_b][\Delta P_b]}{(P_b{\rm H})_i(E_i'-\Delta P_b)} \cong K. \tag{5}$$

This expression yields

$$\Delta P_b \cong \frac{K}{2}\,(P_b{\rm H})_i\{(1+4E_i/[K(P_bH)_i])^{1/2}-1\}. \tag{6}$$

For a low level of initial E_i' generation ΔP_b will be almost equal (always slightly less than) the initial E_i' density. Thus, if we were to flood a very good oxide with a small number of holes, suppress the interface trap generation process, measure the initial trapped hole concentration, and then allow interface trap generation to proceed, we would expect that the eventual interface trap density (each P_b has two levels) would be roughly equal to the initial trapped hole density.

The generation of interface traps *can* be suppressed for hours by lowering the temperature of the system;[28] warming to room temperature allows the process to proceed. Many years ago, Hu and Johnson[28] subjected good oxide/silicon devices to relatively low levels of hole flooding at temperatures low enough to temporarily suppress interface trap generation. Initial oxide hole densities were evaluated, then interface traps allowed to generate, and those interface trap densities were also evaluated. As Eq. (6) predicts, Hu and Johnson found that the initial oxide hole density was approximately equal to the eventual interface trap density.

There are other semiquantitative aspects of this model which are in agreement with results in the literature.[5–10,12,18,21,29]

(1) Expression (6) shows that ΔP_b should be sublinear in E_i'. Since E_i' generation should itself be sublinear in dose,[30] our model predicts a sublinear buildup of interface sites with dose. Such behavior is widely reported.[29]

(2) The model predicts that in devices with low initial interface trap density, the hole trapping and interface trap generation, P_b generation and E' generation would approximately scale together. This behavior (both cases) has been observed.[21]

(3) Since the model involves interaction of a trapped hole site with molecular hydrogen triggering a reaction at a Si/SiO_2 interface P_bH site, one would expect that the time involved in interface trap generation would be significantly increased by reversing the irradiation bias from positive gate voltage to negative gate voltage. This behavior is consistently observed.[5–8]

(4) Since the E' center precursors (oxygen vacancies) are intrinsic defects, one would expect that their number would be an exponential function of processing temperature. Thus one would expect a strong increase in interface trap generation with increasing temperature of gate oxide processing. This behavior is observed.[21]

(5) Radiolytic, molecular hydrogen will be rapidly dissipated from the oxide; in some cases this will not allow equilibrium densities of P_b interface traps to be achieved. One would thus expect that post irradiation exposure to a molecular hydrogen ambient generally increases interface trap density. This behavior is observed.[9,10,12]

(6) Consider a metal-oxide-semiconductor device in which the oxide has been flooded with holes for a brief period. If a positive voltage was applied to the gate electrode. E' precursors near the Si/SiO_2 boundary would be populated with holes: if a negative voltage was applied. E' precursors near the gate (usually polycrystalline Si)/SiO_2 boundary would be similarly populated. Our model, at least to zero order, predicts a similar radiation response, in that the eventual number of P_b centers created would be the same with either sign of gate bias during irradiation. (This assumes equal E' precursor density at both interfaces.) Experimental work indeed shows this to be the case ''electrically'' for brief bursts of irradiation *provided* that the oxide bias is positive *after* the irradiation.[8] (That is, the eventual interface state densities generated are approximately equal for both cases.)

(7) Briefly consider the technologically irrelevant case of a very high initial interface trap density and a very high initial P_b density. In such a case we would expect a reaction of the following form:

$$H_2+P_b+E' \rightleftarrows E'{\rm H}+P_b{\rm H}. \tag{7}$$

Thus, the model would clearly predict an initial post irradiation *decrease* in P_b density for Si/SiO_2 structures with quite high initial P_b density. This behavior has been reported.[18]

A particularly useful aspect of the model is its prediction of a quantitative relationship between P_b and E' generation. Recently Lenahan and Conley developed a model which allows a quantitative prediction of E' densities based on processing parameters.[30]

By combining the Conley/Lenahan E' model with Eq. (6) one should, on the basis of processing parameters, be able to predict *both* radiation induced interface trap densities and radiation induced oxide charging.

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