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The Role of Atomic Hydrogen in Degradation and Breakdown of SiO₂ Films

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Atomic hydrogen exposure of gate oxides produces a variety of electrically active defects, similar in most respects to the defects produced by high field stress. Many of these effects cannot be explained by any well-known Si/SiO_2 defects, and the dominant electrically active defects have not yet been identified. A model for degradation and breakdown based on hot-electron-induced release of atomic hydrogen and subsequent hydrogen-induced defect generation is described.

1. Introduction

For decades the beneficial effects of hydrogen as a passivant in the MOS system have been recognized, while at the same time¹⁾ the detrimental effects of hydrogen-related defects have been known. While other impurities (e.g. alkali or other metals) may have a more acute effect on oxide performance, hydrogen remains a chronic problem because it is more difficult (and probably undesirable) to eliminate it entirely.

The involvement of hydrogen in hot-electron-induced degradation and dielectric breakdown of SiO_2 films has been suggested by a number of experiments, notably the observation of substrate dopant passivation and hydrogen redistribution during hot electron stress, and the enhanced degradation rate of hydrogen-soaked films.²⁾ The direct observation of radiolytic *atomic* hydrogen (H⁰) in SiO₂, by electron paramagnetic resonance (EPR), led Griscom³⁾ to describe interface state production in terms of the *depassivation* reaction

$$\mathrm{Si-H} + \mathrm{H}^0 \to \mathrm{Si} \bullet + \mathrm{H}_2 \tag{1}$$

This was in part influenced by the prevalent belief that the silicon dangling bond structure (Si•), known from EPR as the P_b center, constitutes nearly all of the electrically active interface states. We have directly verified reaction (1) using EPR with Si/SiO₂ samples exposed to atomic hydrogen from a remote plasma.⁴⁾ At the same time, we found that the P_b center accounts for only a fraction of the interface states, thereby revealing that hydrogen is responsible for a suite of reactions beyond the simple picture of Reaction (1), and highly reminiscent of the phenomena seen during electrical stress. Atomic H exposure may therefore be used to "simulate" the effects of high field stress in order to study the chemical effects involved in SiO₂ degradation independent of carrier injection and heating.⁵⁾

In this report we will review the effects of atomic hydrogen on thermal SiO_2 and the Si/SiO_2 interface, and compare with effects caused by electrical stress. The role of hydrogen in electrical breakdown is described.

2. Experimental Details

The remote plasma system employed for atomic hydrogen exposure has been described in detail elsewhere.⁶⁾ Key features of the apparatus are optical baffles to prevent ultraviolet light from the plasma from reaching the sample, and a bolometric sensor to measure the atomic hydrogen concentration at the sample position.

Thermal oxides were grown on (100) and (111) silicon wafers using standard thermal processing at 850-900°C, with thickness ranging from 3.4-67.5 nm. Both *n* and *p* doping, with various doping levels, were explored. After exposing the bare oxide to the atomic hydrogen for various times, electrical (capacitance-voltage [CV] or current-voltage [IV]) characterization and EPR measurements were performed. Evaporated aluminum gates or a mercury probe were used for electrical measurement, and samples were ungated for EPR. Hydrogen exposure must be performed prior to gate fabrication because atomic hydrogen is unable to penetrate most gate materials.7) Poly-Si gate technology cannot be employed because high temperature processing would perturb the sample. All experiments described here were done at room temperature, and are therefore relevant to normal device operating conditions; elevated temperature experiments, corresponding to typical burn-in or accelerated aging tests, will not be described.

3. Silicon Dangling Bond Chemistry

Under continuous exposure to an atomic hydrogen flux, Reaction (1) competes with the *passivation* reaction

$$Si \bullet + H^0 \to Si-H$$
 (2)

Hence there will be a steady state P_b density, shown in Figure 1, where the P_b densities obtained after H^0 exposure are shown normalized to P_b^{max} , the density obtained after complete depassivation in vacuum.⁴ (Poindexter⁸) has offered a somewhat different interpretation of these data.) The figure shows that the various P_b types at (111) and (100) interfaces exhibit some differences in hydrogen reactivity. Note in particular that the P_{b0} center is fully depassivated by room



Figure 1. Normalized P_b densities after atomic exposure. P_b^{max} denotes the maximum density obtained after complete depassivation in vacuum. Error bars are indicated by the vertical sizes of the boxes. Up arrows indicate data for depassivation (Reaction 1), starting from a fully passivated sample. Down arrows indicate data for the passivation process (Reaction 2), starting from either the vacuum annealed state or using an ultra-dry oxide. The starting condition is important only for P_{b1}¹⁰⁰, suggesting that this defect has some dependence on the thermal history of the sample. The other defects reach a steady-state concentration consistent with the proposed reactions.

temperature hydrogen exposure, whereas P_{b1} is not. This may explain why mostly P_{b0} is seen after irradiation or high-field stress.

4. Comparison of Atomic Hydrogen and Electrical Stress

Electrical measurements show that atomic hydrogen produces fast interface states⁴⁾ and slow interface states (anomalous positive charge).⁹⁾ Figure 2 compares interface state density spectra produced by hot electrons and by H⁰ exposure. The similarity is profound. Likewise, low field leakage currents in the direct tunneling range of ultra thin oxides are generated by H⁰ exposure, very similar to stressinduced leakage currents caused by Fowler-Nordheim tunneling stress.¹⁰⁾ Recently, we have also shown that electrical stress causes *passivation* of P_b centers in vacuum-annealed samples, analogously to the passivation by H⁰ depicted in Figure 1.

5. New Hydrogen-Related Defects

Figure 3 shows the hydrogen-induced build-up of interface states (D_{it} at mid-gap) and positive charge (Q_p), together with data for paramagnetic defects. It can be seen that P_b centers account for only ~5% of the fast interface states induced by hydrogen at the (111) interface. Similarly, for the (100) interface the total P_b density is only $\leq 15\%$ of the hydrogen-induced D_{it} . These results are in marked contrast to previous studies which had found nearly one-to-one correlation between P_b and mid-gap D_{it} in irradiated or as-grown oxides, but are consistent with spin-dependent recombination



Figure 2. Comparison of interface state densities for the (100) Si/SiO₂ interface, caused by hot electrons (left panel, data courtesy of D.A. Buchanan) and by atomic hydrogen (right panel). D_{it} has been measured using the high-low frequency capacitance method.

results in electrically stressed n-MOSFETs.⁴⁾ The identity of the dominant interface defect remains elusive.

Figure 3 also compares the E' density, obtained after extensive hydrogen exposure, with the positive charge measured in similarly exposed samples. The positive charge exhibits a hysteretic behavior⁹⁾ (Figure 4) showing that the defect can be reversibly neutralized and re-ionized by varying the surface potential. The E' center is a paramagnetic hole trapped at an oxygen vacancy, and is responsible for much of the fixed positive charge in irradiated oxides. Here we find that E' centers cannot explain the atomic-hydrogeninduced positive charge. The comparison of EPR and electrical data in this case is somewhat problematic, because the hysteretic electrical behavior means that the charge state in the ungated EPR sample is not known. However, the fast state density is always high enough to pin the surface potential within 200 meV of mid-gap so that it is likely that the defect will remain in the positive state. The small density of E' centers is probably caused by the weak ultraviolet light which escapes the optical baffles of the plasma source.⁶⁾ The microscopic structure of the defect responsible for hydrogeninduced positive charge remains unknown.



Figure 3. Mid-gap interface state density (D_{it}) , positive charge (Q_p) , interface dangling bond density (P_b) and E' density as a function of atomic hydrogen fluence. Q_p is derived from the initial ΔV_{1b} in *n*-type capacitors. All quantities in units of cm⁻², except for D_{it} in units of eV⁻¹cm⁻². The lines are guides to the eye.



Figure 4. Hysteresis of hydrogen-induced positive charge. (After Stahlbush et al.⁹⁾)

Recent spin-dependent measurements¹¹) of stressinduced leakage currents likewise show that the defect which is involved in trap-assisted tunneling is probably neither P_b nor E'. It seems clear, therefore, that more research is needed to uncover the identity of the most important electrically active defect(s) which are created by atomic hydrogen or hot electron stress.

6. Relation to Oxide Degradation and Breakdown

The results described above show that atomic hydrogen alone, in the absence of any oxide field and with no current flowing through the oxide, will cause many of the same defects as are caused by hot electrons. This is compelling evidence that atomic hydrogen release by hot electrons is the basis of hot-electron-induced degradation. Conversely, any process, such as radiation or hot electron injection, which results in the release and redistribution of hydrogenous species will inevitably lead to oxide degradation if the hydrogen is in the form of H^0 or protons.

DiMaria¹²⁾ and others¹³⁾ have shown a correlation between defect generation rates during electrical stress (degradation) and destructive breakdown (charge-to-breakdown, Q_{BD}). Based on this, Cartier and DiMaria have developed a model for oxide breakdown based on the hot-electroninduced release of atomic hydrogen and subsequent defect generation. The physical features of the model are illustrated in Figure 5. Electrons injected into the oxide conduction band (either tunneling through the barrier as shown, or as channel hot electrons injected over the barrier) will be heated as they traverse the oxide. The electron heating can be accurately calculated using a Monte-Carlo method.¹²⁾ When the electron energy at the anode exceeds a threshold²⁾ of about 2 eV, which is the energy required to release hydrogen from Si-H bonds,14) the hydrogen may diffuse through the oxide and react to form defects. The final step has been studied using the atomic hydrogen exposure discussed above. By employing an appropriate Si-H bond breaking cross section and hydrogen profile, this model successfully explains the observed hot electron induced defect generation rates.¹⁵ The model is valid for gate voltages below about 8 V or fields



Figure 5. Five-step hydrogen release mechanism for hot electron induced degradation and breakdown of SiO₂.

below about 6 MV/cm and for oxides thinner than about 20 nm; outside of this range anode hole injection¹⁶⁾ and impact ionization¹³⁾ lead to hole trapping and electron-hole recombination, which provides an additional degradation mechanism.

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