Hydrogen-Release Mechanisms in the Breakdown of Thin SiO_2 Films

J. Suñé[1] and E. Y. Wu[2]

[1]*Departament d'Enginyeria Electrònica, Universitat Autónoma de Barcelona, 08193-Bellaterra, Spain*
[2]*Microelectronics Division, IBM, 1000 River Road, Essex Junction, Vermont 05452, USA*

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The mechanism of hydrogen release from the anode Si/SiO_2 interface that triggers defect generation and finally the dielectric breakdown of the oxide in metal-oxide-semiconductor structures is investigated. Extensive experimental charge-to-breakdown statistics are used to derive the defect generation efficiency as a function of gate voltage and oxide thickness in wide ranges. The presented results provide strong support to single-electron assisted Si-H bond breakage and discard multiple electron induced incoherent vibrational heating mechanisms.

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Silicon dioxide is still the gate dielectric of choice for complementary metal-oxide-semiconductor integrated circuits. The dielectric breakdown (BD) of the required ~1 nm insulator films is a serious concern [1,2]. It is now understood that the BD is related to defect generation caused by electron fluence [3], and the relation between defect generation and BD is well understood within the percolation models of BD [4,5]. Previous work suggests a two-step defect generation mechanism: (i) tunneling electrons release some species from the Si/SiO_2 anodic interface and (ii) the released species react with some precursors (probably oxygen vacancies) to generate electrically active defects [6–8]. Both the interface release process and the bulk reaction depend on the temperature; however, there is evidence that the dependence on the stress voltage (V_G) is fully determined by the release process [9]. There is still debate as to whether the released species are holes [6] or hydrogen [7,8], although recent results raise serious doubts about the role of holes [10]. Hydrogen is present at the Si/SiO_2 interface because forming gas anneal is used to reduce the density of interface states. Hydrogen also forms a variety of defects in the silica network and one of them, the hydrogen bridge, has been recently identified as the trap responsible for stress-induced leakage current, a forerunner of the BD [8]. In this Letter, we investigate the physics of H release from the Si/SiO_2 anode interface by means of an extensive database of charge to BD statistics and comparison with H desorption from Si surfaces by the scanning tunneling microscope (STM) [11–14].

Although we are interested in the mechanism of hydrogen release from the Si/SiO_2 interface, it is not possible to directly probe this process. Information on the generation of defects is usually based on indirect measurements such as charge trapping, stress-induced leakage current, etc. In this work we use an alternative approach and extract the defect generation efficiency ζ (defined as the number of generated defects per injected carrier) from the analysis of statistical BD data in the framework of the BD percolation model [4,5]. This procedure is also indirect, but at least it ensures that the measured defects are those that trigger oxide BD.

Standard N-type field effect transistors (FETs) with different oxide areas (A_{ox}), and oxide thickness (T_{ox}) ranging from 1.0 to 5.0 nm (as measured by transmission electron microscopy and from the capacitance-voltage characteristic), were stressed to BD under constant voltage stress (CVS) conditions at 140 °C. The range of V_G was selected to fit a time to the breakdown (T_{BD}) window of ~ 10 to 10^5 s for wafer-level stress experiments. This imposes a practical V_G range of a few tenths of a volt for A_{ox} and T_{ox} fixed, because T_{BD} strongly depends on V_G. To relax this limitation, two strategies have been combined [15]: (i) stress bonded devices during very long times up to 10^7 s and (ii) stress structures of different A_{ox} because the effects of area are well known for a weakest link phenomenon as BD [4,5,15]. For each sample, the stress current is integrated until T_{BD} so as to calculate the total charge injected to the BD, which is the statistical variable of choice. The BD distribution fits well into a Weibull model [4,5] with Weibull slope β, and characteristic charge to the breakdown Q_{BD}. Both β and Q_{BD} are given by the percolation model [4,5] in terms of the linear size (a_0) of the defects involved in the BD. Every reported Q_{BD} data point was obtained from a distribution of at least 40 samples, and in some cases with as many as hundreds of samples depending on T_{ox}, so as to ensure the accuracy of the results and to make the error bar associated with each data point comparable to the size of the symbols plotted in the figures. Following the cell-based version of the BD percolation model [5], the area-independent ζ is related to the Q_{BD} measured in structures of area A_{ox}:

$$\zeta = \frac{eT_{ox}}{a_0^3 Q_{BD}} \exp\left\{-\frac{1}{\beta}\ln\left(\frac{A_{ox}}{a_0^2}\right)\right\}, \tag{1}$$

with e being the electron charge. The single parameter, a_0, is independently determined from the experimental dependence of β on T_{ox} [5]. In the framework of the two-step model of the BD, it is known that ζ is given by the

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product of the H release rate and a temperature dependent factor related to the bulk reaction process [6]. The voltage, current, and thickness dependences of ζ are directly related to the mechanism of H release from the Si/SiO$_2$ interface. Figure 1(a) shows ζ as a function of stress current density for $T_{\rm ox}$ ranging from 1.4 to 5 nm. Given the $T_{\rm BD}$ window (roughly the same for all $T_{\rm ox}$), J increases (about 5 orders of magnitude) and ζ decreases (more than 10 orders of magnitude) when $T_{\rm ox}$ is decreased from 5 to 1.4 nm. A power law is shown to reasonably fit each set of results, and the exponent is found to increase linearly when $T_{\rm ox}$ is reduced below 3 nm. These results apparently support the recent proposal of McMahon *et al.* [16], who suggested that, similar to what has been demonstrated for interface state generation under FET hot carrier (HC) stress [17,18], a transition from single to multiple electron generation mechanisms might occur at low voltages and high currents, i.e., when $T_{\rm ox}$ is scaled down. McMahon *et al.* have suggested that multiple electron assisted incoherent heating of the Si-H bond [19] might explain H desorption when the available electrons have less energy than required to overcome the Si-H desorption barrier, $\Phi_{\rm B}$. They proposed that the degradation rate should be described by the sum of a series of terms, each involving a different number of electrons (n) for the Si-H bond breakage. At high voltages and low currents, the term with $n = 1$ should dominate and a transition towards the maximum value of n, $n_{\rm max} = \Phi_B/\hbar w_0$, should occur at low voltages/high currents, ω_0 being the frequency of the local vibration mode (LVM) being heated. According to their model, the H desorption efficiency and, consequently, ζ should depend on both the stress current and the stress voltage. Moreover, the nth term of the series gives a power law current dependence $\zeta \sim J^n$ dependence and also a power law voltage dependence $\zeta \sim V^{-4n}$ (the factor of 4 in the exponent coming from the empirical fitting of the inelastic tunneling fraction in the STM hydrogen desorption experiments of Shen *et al.* [11]). Considering a desorption barrier of about 2.5–3 eV, and $\hbar\omega_0 \sim 0.25$ eV for the stretching Si-H bond mode, the maximum current power law exponent should be around 10–12 and the $V_{\rm G}$ power law exponent around 40–48. A power law $T_{\rm BD} \sim V_{\rm G}^{-44}$ had already been previously reported by Wu *et al.* [15]. The results of Fig. 1 seem to support the McMahon *et al.* proposal in several respects: (i) a power law dependence reasonably fits the experimental current dependence, (ii) the exponent increases with the current density, and (iii) the values of the exponent quantitatively fit into this picture as well. In spite of these results, we argue that this is just a coincidence. In Fig. 2, we show ζ versus the maximum energy of the injected electrons at the anode interface, $E_{\rm max}$. This energy is quantitatively defined in [9] and allows one to cancel the polarity dependence of $Q_{\rm BD}$. Only in the ballistic regime ($T_{\rm ox} < 3$ nm) and when a FET is biased in accumulation, $E_{\rm max}$ is precisely equal to $V_{\rm G}$. This figure shows a very strong dependence of ζ on $E_{\rm max}$ and the existence of an energy threshold of about 5–6 eV (inset). This threshold is fully compatible with that found in the experiments of H desorption from a (100) silicon surface by STM [11], which was attributed to direct electronic excitation of the Si-H bond [12]. Moreover, the data points fall onto a single $\zeta(E_{\rm max})$ curve for all the different values of $T_{\rm ox}$. This demonstrates that the current

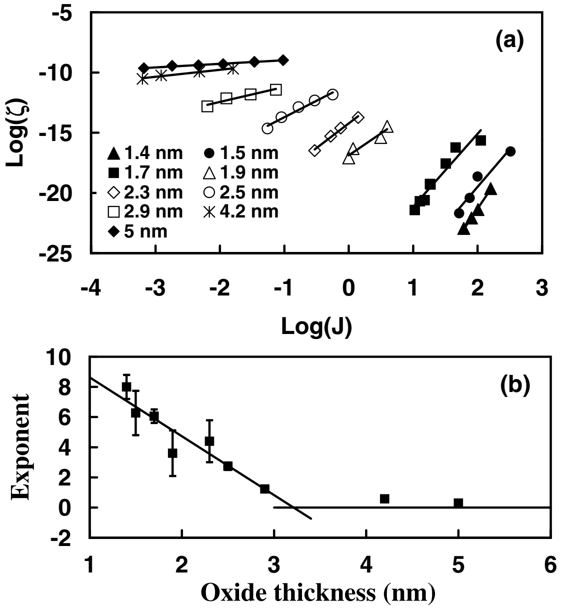

FIG. 1. (a) Defect generation efficiency as a function of stress current density (in A/cm^2) for oxides with thickness ranging from 1.4 to 5 nm. Symbols are experimental results and lines are power law fits. (b) The exponent of the power law fits of (a) as a function of oxide thickness. For some points, the error bar is smaller than the size of the symbol.

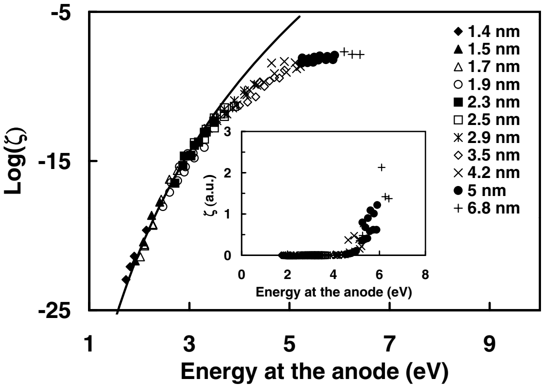

FIG. 2. Defect generation efficiency as a function of maximum electron energy at the Si/SiO$_2$ interface. The data points are directly calculated from experimental $Q_{\rm BD}$ data using Eq. (1). $T_{\rm ox}$ ranges from 1.4 to 5 nm and includes all the data points of Fig. 1(a). The solid line is a power law fit (exponent equal to 38) in the low energy region. The inset shows the same data in a linear scale.

dependence analyzed in Fig. 1 is only a consequence of the dependence of ζ on $E_{\max}$. It is worth noting that in CVS experiments the current density is fully determined by V_G (which is closely related to $E_{\max}$) and T_{ox}; i.e., current density and V_G are not independent as in STM atom manipulation experiments [11–13,20]. Figure 2 demonstrates that if the dependence on $E_{\max}$ is taken into account, ζ does not depend on the current. This discards the multiple electron H desorption mechanism proposed by McMahon *et al.* [16] at least in the voltage/thickness range considered in this Letter (i.e., down to 1.9 V and $T_{ox} = 1.4$ nm). This conclusion is confirmed in Fig. 3 which shows that ζ is almost independent of T_{ox} at fixed stress voltage. The slight T_{ox} dependence at 2.3 V is mostly due to the inclusion of two data points corresponding to 1.1 and 1.25 nm oxides, respectively. In our opinion, this second order effect has to do with process differences (higher nitrogen concentrations are required for such ultrathin oxides) and/or with the failure of the percolation model in the ultrathin oxide limit. In any case, a power law dependence of ζ on the current ($\zeta \propto J^n$) would give a very strong dependence of ζ on T_{ox} (because J depends exponentially on T_{ox} in the direct tunneling regime); this is completely inconsistent with the thickness independent results of Fig. 3. On the other hand, these results cannot be due to a cancellation of current and thickness dependencies because both the increase of J and the reduction of the BD defect density [effect considered in Eq. (1)] would cause a decrease of Q_{BD} (raw data used to calculate ζ) for decreasing T_{ox}. The results of Fig. 3 reject the possibility of thermal heating of the Si-H bonds as the mechanism controlling the H desorption in the bias conditions of our BD stress experiments. This does not mean that the interaction of electrons with LVMs does not play a role; this only discards any H-release mechanism assisted by multiple electrons.

At least three different mechanisms have been suggested in the literature to explain the desorption of H from Si-H bonds by inelastic tunneling of electrons. The direct electronic excitation explains the energy independent desorption yield above the 5–6 eV threshold [11,12]. On the other hand, resonance enhanced interaction of electrons and LVMs has been considered to explain the strongly energy dependent subthreshold regime [11,13,14]. Electrons resonantly tunnel to a peak of the Si-H bond density of states [14] and couple to the LVMs. At least two different models have been proposed to explain this coupling and both consider the representation of the bond vibrational degrees of freedom by a truncated harmonic oscillator potential with m energy levels. Each single resonant electron has a certain probability to induce a $i \rightarrow i + N$ transition between vibrational states. Usually, the transitions involving $N = 1$ are the most probable [14]. However, bond breakage can take place by different mechanisms depending on the ratio of electron current and LVM relaxation rate γ [11,21]. If the current is high and γ is small, incoherent multiple excitation of the bond by m electrons that cause one-level transitions between the bond vibrational states is the most likely mechanism for bond breakage. This is the so-called incoherent thermal heating mechanism [19], which has been invoked to explain the STM desorption results [11] and also the interface state generation under HC stress conditions [17,18]. However, when the electron current is low, the direct excitation of the LVM to the mth level can be more probable than the staircase of incoherent transitions. This is the so-called coherent inelastic tunneling model and requires only one electron for bond disruption [22]. The McMahon *et al.* proposal is a combination of both types of mechanisms similar to what was suggested by Stipe *et al.* [20] to explain the dissociation of O_2 molecules. It has been argued that the coherent mechanism should dominate below the characteristic current $I^* = eC_m\gamma$, where C_m is a constant of the order of 10 related to the number of levels in the LVM potential well [22]. The lifetime of the Si-H can be very long ($\gamma \sim 10^8$ s^{-1} [21]); hence the incoherent mechanism is a reasonable explanation for the subthreshold H desorption in STM experiments [11,13] and HC results [17,18]. Moreover, this mechanism can explain the experimental giant isotope effects in terms of the different lifetimes of the Si-H and Si-D bonds [13,17,18]. However, the gate current in BD stress experiments is orders of magnitude smaller, and the coherent electron-LVM interaction mechanism proposed by Salam *et al.* [22] is a more likely explanation for the H release from the anode interface in BD stress experiments. This mechanism is current independent and gives a strongly nonlinear voltage dependence, similar to a power law in a limited range well below the resonance threshold (about 4.6 eV above the Si conduction band for the Si-H $6\sigma^*$ resonance [14]). Hence, this mechanism might also explain the power law voltage dependence of ζ at low gate voltages (Fig. 2). On the other hand, since this mechanism does not depend on the LVM lifetime, it can also explain why BD results show much reduced isotope effects [23], as compared with HC damage. A more quantitative analysis of the range of validity of this model is difficult because we are dealing with Si-H bonds at the Si/SiO$_2$; this introduces a lot of unknowns (H might be

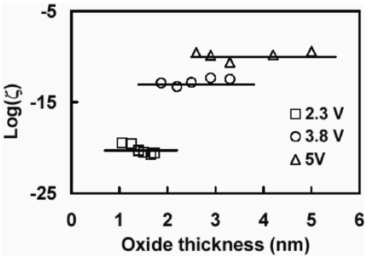

FIG. 3. Dependence of the defect generation efficiency on T_{ox} for three fixed stress voltages. Symbols are derived from experiments using Eq. (1). Solid lines are guides to the eye.

released from suboxide bonds with much reduced desorption barrier [24], the relaxation rate is strongly dependent on the local structure and cannot be probed at the Si/SiO_2 interface [21], etc.). It has been argued that the transition to a local energy minimum near a suboxide Si-H bond requires only about 1 eV [24]. Thus, the coherent mechanism of Salam *et al.* [22] can be dominant down to $V_G = 1$ V as required for the end-of-the-road SiO_2 based gate dielectrics.

Recently, others have also considered the incoherent thermal heating model to explain BD results [25,26]. The results of Lin *et al.* [25] completely lack statistical relevance. The results of Ribes *et al.* [26] are based on substrate HC injection, which allow one to vary current and voltage independently. These authors have found a power law current dependence compatible with the incoherent heating mechanism. In our opinion, the conditions of their experiments are closer to a HC stress experiment, with a lot of carriers impinging from the substrate to the Si/SiO_2 interface (cathode) so that we speculate that the degradation mechanism might be related to H desorption from the cathode interface.

In conclusion, our analysis of BD data indicates that multiple-electron-induced incoherent heating of Si-H bonds is not the H release mechanism involved in oxide BD. Single-electron coherent inelastic tunneling is suggested as an alternative explanation for the desorption of H from the Si/SiO_2 interface in BD stress experiments.

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