Effect of Physical Stress on the Degradation of Thin SiO_2 Films Under Electrical Stress

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***Abstract*—In this work, we demonstrate that for ultrathin MOS gate oxides, the reliability is closely related to the SiO_2/Si interfacial physical stress for constant current gate injection (V_g^-) in the Fowler–Nordheim tunneling regime. A physical stress-enhanced bond-breaking model is proposed to explain this. The oxide breakdown mechanism is very closely related to the Si–Si bond formation from the breakage of Si–O–Si bond, and that is influenced by the physical stress in the film. The interfacial stress is generated due to the volume expansion from Si to SiO_2 during the thermal oxidation, and it is a strong function of growth conditions, such as temperature, growth rate, and growth ambient. Higher temperatures, lower oxidation rates, and higher steam concentrations allow faster stress relaxation through viscous flow. Reduced disorder at the interface results in better reliability. Fourier transform infrared spectroscopy (FTIR) technique has been used to characterize stress in thin oxide films grown by both furnace and rapid thermal process (RTP). In conjunction with the Gibbs free energy theory, this model successfully predicts the trends of time-to-breakdown (t_{bd}) as a function of oxide thickness and growth conditions. The trends of predicted t_{bd} values agree well with the experiment data from the electrical measurement.**

***Index Terms*—Bond breaking, FTIR, oxide breakdown, oxide reliability, physical stress, Q_{bd}, steam concentration, t_{bd}, ultrathin.**

I. Introduction

IT HAS been generally believed in the past that the intrinsic oxide properties, such as, breakdown strength, charge to breakdown (Q_{bd}), etc. improve as the thickness is reduced [1], [2]. The reason was attributed to the fact that for thinner oxides rather than Fowler–Nordheim tunneling, direct tunneling dominates involving less energetic electrons or holes causing lesser damage [1], [3]. Recently, it has been observed that the t_{bd} is lower under gate injection compared to substrate injection [4], [5], and this reduction is stronger for thinner oxides [6]–[10]. Many models have been proposed to explain the degradation and breakdown of thin oxides, for example, E model [11], 1/E model [12], anode hole injection [3], H-release [13], physical bond breaking [1], high field related oxide wearout [14], trap generation, critical electron trap density [15], and interface roughness [4]. These models try to relate electrical stress to dielectric degradation through some phenomenon in it. Most of these studies involve extensive stress conditions and measurements, however, limited attention has been paid to growth conditions which could alter the dielectric properties of the oxides. Therefore, each of these models can explain its own electrical measurement data, but cannot explain the dependence of dielectric degradation to the growth conditions of oxides. In addition, they cannot explain the following two phenomena for gate injection of electrons: 1) the t_{bd} decreases as the oxide thickness is reduced in the Fowler–Nordheim regime; 2) t_{bd} for gate injection is always lower than that of substrate injection.

Han *et al.* have proposed that the physical stress in oxide could be a factor to cause polarity difference of t_{bd} [7]. Miura *et al.* demonstrated that the oxide breakdown failure rate decreases monotonically as internal stress in the MOS gate electrodes is reduced [16]. Eriguchi *et al.*have determined the strained layer near SiO_2/Si interface to be approximately 1 nm [10] and verified that the increased compressive strain decreases t_{bd}.

In this work, we propose that enhanced bond breaking due to physical stress resulting from thermal oxidation of Si plays an important role in the reliability of gate oxides. By investigating the effect of growth conditions on the physical stress and reliability of thin MOS gate oxides, we can explain the thickness and stress polarity dependence. The degradation is always more for those growth conditions, which result in higher physical stress in SiO_2. Higher temperatures and slower oxidation rates allow stress relaxation through viscous flow. Steam oxidation results in lower stress as compared to dry O_2 oxidation. Reduced stress at the interface always results in better reliability.

II. General Background

Most crystalline polymorphs of SiO_2 consist of ordered networks of corner-sharing SiO_4 tetrahedra, with the topology of the network differing from structure to structure. In the amorphous SiO_2, the basic structural unit is the SiO_4 tetrahedron with each Si atom surrounded by four O atoms [17]. The angle of O–Si–O bonds is fixed at 109.5 °. However, the Si–O–Si angle is rather flexible; and being twofold coordinated [18]. Each O atom bridges two neighboring SiO_4 tetrahedrons. The bond is relatively easy to bend, stretch, or rotate. And the Si–O–Si bonds are capable of accommodating large lattice distortion [18]. For this reason, the Si–O–Si bond is of special interest, and it has been used as a basic bonding unit of SiO_2 to characterize its properties [19]. The Si–O–Si bond angle changes with oxide density [20]. At the normal density of 2.2 g/cm^3, the bond angle distribution has a single peak at 144° and the full width at half maximum of this peak is 26°. With an increase in the density, the

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peak in the bond angle distribution broadens and shifts continuously to lower angles: at 2.64 and 2.94 g/cm^3, this peak shifts to 139 and 137°, respectively [20].

The bond strength of the Si–O–Si bonds mentioned in the previous paragraph is severely weakened when the bond angle deviates from the mean value of 144°. Generally, bond angles greater than 180° or less than 120° are rarely observed and an oxygen vacancy also known as E′ centers, tends to occur [21]. It is this molecular defect in intrinsic SiO_2 films that is thought to dominate time-dependent dielectric breakdown [21].

Several models have been developed by different researchers to explain the oxide degradation and breakdown [1], [3], [4], [11]–[15]. The common essence is summarized here. If the electric field is sufficiently high, Fowler–Nordheim tunneling of electrons occurs and electrons are injected into the conduction band of the oxide. They gain energy from the electric field and lose it through lattice scattering. Some of these electrons lose all of the excess energy and get trapped in the oxide if traps are present in it. Many electrons continue to conduct in the conduction band. At the anode, they fall into the conduction band of Si and in the process lose the excess energy. The energy gained by the electrons when they reach the anode can be as high as 3–9 eV [13]. The loss of the excess energy can cause damage through several ways. The high energy imparted by the electron can break bonds between Si and O at the interface. The dangling bonds give rise to traps in the oxide bandgap [1]. The energy released by the electrons can release hydrogen at the interface, which may have been incorporated during the processing. H release leaves a dangling bond giving rise to traps [22]. If the energy released by the electrons is sufficiently high, it can cause impact ionization at the interface generating more hot electrons and hot holes. Hot holes can then be injected in the valance band of SiO_2 via Fowler–Nordheim tunneling. Similar to the case of electrons the holes also cause further damage through trap creation and trapping [3]. Another model states that the high electric field itself may polarize the bonds and ultimately break them under a combination of electrical stress and thermal energy imparted to them [14]. All of these models agree that the damage is caused by bond breaking. If large number of bonds is broken, the damage is excessive and a damage cluster is created in a local region. If several damage clusters are formed and a continuous path is created from anode to cathode oxide breakdown occurs [1], [15].

III. Experiment

LOCOS isolated MOS capacitors made on lightly doped n- and p-type (100)-oriented Si substrates with gate oxides grown either in a furnace or an RTP system were used in this study. N+ poly-Si gates of 250 nm thickness *in situ* doped with phosphorus were deposited by LPCVD. Since the incorporation of hydrogen in oxides plays an important role in oxide breakdown [13], some of the devices went through low temperature forming gas anneal at 400 °C and others didn't. However, there were no significant t_{bd} differences between them. This indicates that there was enough hydrogen incorporated into the oxides during the fabrication passivating the SiO_2/Si interface.

Furnace oxides were grown in dry O_2, whereas RTP oxides were grown in dry as well as wet O_2. For the furnace processing, the oxides of 4–10 nm thickness were grown at 800 °C or 1000 °C in 30% or 70% dry oxygen, diluted with Ar, at a total pressure of 1atm. The difference between 30% and 70% grown oxides is the oxidation time, allowing the determination of the effect of oxidation times on oxide reliability.

For the RTP, the oxides of 4–10 nm thickness were grown at 800–1000 °C in dry, 2% wet or 50% wet oxygen, at a total pressure of 1 atm. In the wet oxidations, both steam and O_2 oxidize at the same time. The percentage of wet oxygen is calculated as the ratio of the partial pressure of steam to the total pressure of steam and O_2 during the oxidation process. The higher the percentage of steam is, the more its contribution to the oxidation is. Such controlled growth of thin SiO_2 films in wet O_2 at higher temperatures would be difficult to perform in a furnace.

The oxidation times and the resulting oxide thickness are shown for different ambients and temperatures for both furnace and RTP oxides in Tables I and II, respectively.

The charge to breakdown, Q_{bd}, was measured under constant current stress on 100 μm × 100 μm capacitors with both positive and negative gate polarities. Time-to-breakdown, t_{bd}, for various oxides was determined from cumulative plots. The t_{bd} data were sampled uniformly all over the wafers. Note that the t_{bd} measurements were done under illumination on n^+ poly-Si gate MOSCAP's with n^- substrates to keep the devices from deep depletion.

To characterize the interfacial stress, FTIR technique was used. From the absorption spectrum, we can get information on interfacial stress from the positions of absorption frequency peaks of Si–O–Si bonds in SiO_2. Higher stress is associated with a denser oxide film, smaller Si–O–Si bond angle and lower peak [17], [23], [24]. For FTIR measurements, a duplicate set of wafers with blanket films of thin oxide was grown concurrently with the gate oxides of LOCOS isolated MOS capacitors.

IV. Time Dependent Dielectric Breakdown (TDDB) Measurement Results

Fig. 1 shows a t_{bd} of furnace grown oxides as a function of their thickness at a gate injection (V_g^-) of 100 mA/cm^2. The t_{bd} values were chosen from 90% value of cumulative plots to obtain the intrinsic properties of oxides. TDDB measurements on 10 μm × 10 μm size devices were also done. The 90% t_{bd} values were very close to those of 100 μm × 100 μm devices although the slopes of the cumulative plots were higher. All the data reported here were collected on devices of the same area of 100 μm × 100 μm. Degraeve *et al.* have shown that Q_{bd} increases as the area decreases, however, the fact that Q_{bd} decreases as the oxide thickness is reduced is still observed for smaller as well as larger devices [15]. From Fig. 1, the following trends can be observed.

1) t_{bd} reduces as the SiO_2 thickness reduces.
2) t_{bd} is higher for oxides grown at the higher oxidation temperature (1000 °C).
3) At the low temperature (800 °C), t_{bd} reduces as the SiO_2 growth rate is increased (or oxidation time is decreased),

TABLE I
OXIDATION CONDITIONS OF FURNACE OXIDES

Dry O2 concentration	800°C time - thickness	1000°C time - thickness
30%	50 min - 39Å	1.1 min - 41Å
30%	155 min - 61Å	5 min - 66Å
30%	350 min - 92Å	11.5 min - 94Å
70%	24 min - 37Å	0.5 min - 41Å
70%	97 min - 68Å	2.7 min - 70Å
70%	180 min - 95Å	5.5 min - 93Å

TABLE II
OXIDATION CONDITONS OF RTP OXIDES

oxidation conditions	time -thickness
800°C, dry	630sec - 43Å
900°C, dry	85 sec - 43Å
1000°C, dry	17 sec - 46Å
800°C, 2% wet	580 sec - 44Å
900°C, 2% wet	68 sec - 42Å
950°C, 2% wet	28 sec - 44Å
1000°C, 2% wet	10 sec - 43Å
1000°C, 2% wet	114 sec -- 106Å
800°C, 50% wet	264 sec - 49Å
1000°C, 50% wet	5 sec - 42Å

as in the case of 70% O_2. However, at 1000 °C, the t_{bd} values are about the same for different growth rates.

Fig. 2 shows t_{bd} of 4 nm dry, 2% wet, and 50% wet oxides grown in an RTP system as a function of oxidation temperature. Following trends can be observed.

1) For both dry and wet oxides, t_{bd} is higher for oxides grown at higher temperatures.
2) At low temperatures (800 °C), t_{bd} increases as the steam concentration is increased, as in the case of 2% and 50% wet oxides. As the temperature is increased the difference becomes less. At 1000 °C, there is no difference. At 50% steam concentration, use of higher temperatures was not feasible as the time of growth was too short to be practical.

Fig. 3 shows t_{bd} as a function of oxide thickness for both gate injection (Vg^-) and substrate injection (Vg^+) for devices from different runs with slight process variations. All the oxides were thermally grown at 800 °C in a furnace. It can be seen that, for gate injection, the t_{bd} increases with the gate oxide thickness. On the other hand, for substrate injections, there are no significant trends. t_{bd} shows only a slight increase for thinner oxides. In general, t_{bd} for substrate injection is higher than that for gate injection.

V. STRESS MEASUREMENT TECHNIQUE AND RESULTS

All the trends of furnace and RTP oxides in the previous section can be explained by examining the role of physical stress at the SiO_2/Si interface. During the thermal growth of SiO_2, there is a 128% volume expansion from Si to SiO_2 [25], and therefore

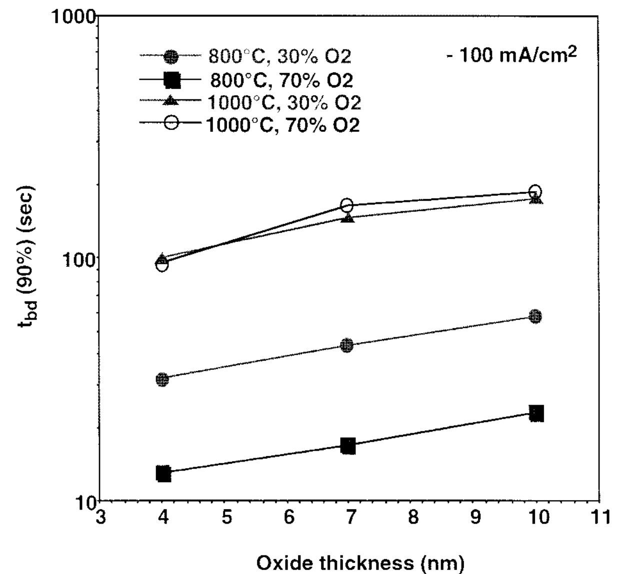


Fig. 1. t_{bd} (90% values from cumulative plots) for various oxides for constant current gate injection (Vg^-) at a current density of 100 mA/cm^2.

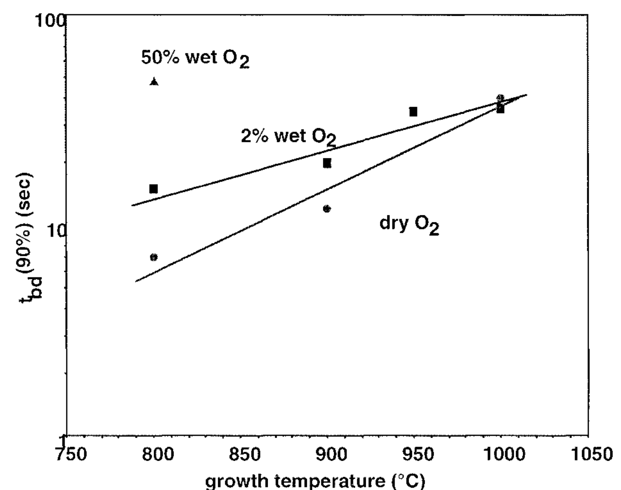


Fig. 2. t_{bd} (90% values from cumulative plots) of 4 nm oxides for gate injection at a current density of 100 mA/cm^2. The RTP oxides were thermally grown in dry, 2% wet and 50% wet O_2 at different temperatures.

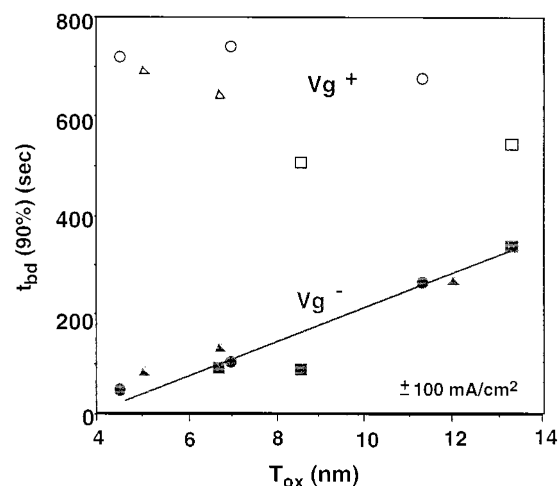


Fig. 3. t_{bd} of 800 °C oxides for constant current gate injection ($Vg-$) and substrate injection ($Vg+$) at a current density of 100 mA/cm^2.

the SiO_2 film is compressed. The newly formed SiO_2 pushes the previously grown SiO_2 upwards. This growth results in a compressive stress in the oxide close to the Si/SiO_2 interface. The interfacial stress decreases as we move farther from the interface. It has been shown that the stress in the SiO_2 thin film at the Si/SiO_2 interface, σ_i (SiO_2), is very large, ≅500 MPa, and there can be very large stress gradients, $\cong 2 \times 10^8$ MPa/cm, in the SiO_2 films in the immediate vicinity of the Si/SiO_2 interface [26]. It has also been demonstrated through XPS measurements that there is a measurable gradient in bond strain in SiO_2 at the SiO_2/Si interface [27]. The strained layer was determined to be about 1 nm for dry, RTP and pyrogenic oxides by XPS [10].

Aside from the intrinsic (growth) stress, σ_i, originating from the molar volume change when converting Si to SiO_2, there is also a thermal expansion stress, σ_{th}, arising from the thermal contraction mismatch which results upon cool-down from oxidation to room temperature. Usually the total residual stress, $\sigma_i + \sigma_{th}$, exists in the film when the electrical and optical measurements are done. However, the difference in the thermal stress is very small for 800 °C and 1000 °C grown oxides, i.e., ≅200 MPa and 230 MPa for 800 °C and 1000 °C oxides, respectively [28]. For the intrinsic stress, the difference can be quite large; for 800 °C grown oxides, the intrinsic stress is about 300 MPa [28], however at 1000 °C oxides are grown in an almost stress-free condition [29].

To prove that oxide film stress varies with processing conditions, FTIR measurements were done on oxides grown under different conditions. From the FTIR absorption spectrum, one can determine the angle of Si–O–Si bonds and therefore the stress in the oxide film [17], [23]. This absorption is associated with the different vibrational energy state transition of Si–O–Si molecular structure [30]. The absorption peak frequency tells us the angle of Si–O–Si bonds and therefore is an indicative of the associated stress. The absorption peak varies when the stress in the oxides is different [23], [24]. When the compressive stress becomes larger, the Si–O–Si bond angle becomes smaller, and therefore the absorption peak frequency is lower.

The measured FTIR results of different furnace oxides grown in dry O_2 are summarized in Fig. 4. The error of the measured absorption peaks was within ± 1 cm^{-1}. An increasing trend of peak stretching frequency as a function of oxide thickness is observed. Lower temperature (800 °C) and faster growth rate give lower peak stretching frequency. The overall trends are similar to those observed earlier in Fig. 1 for t_{bd}. Therefore, there is a strong correlation between the absorption peak and t_{bd}.

Fig. 5 shows the stretching peak frequencies of 4 nm thick RTP oxides grown in dry, 2% wet, and 50% wet oxygen at different temperatures. Although not the same, the overall trends agree well with the t_{bd} trends shown in Fig. 2. The stretching peak frequencies of oxides grown at 800 °C increase as the steam concentration is increased. The frequency increases as the growth temperature increases. However, at 1000 °C, the stretching peak frequency of 2% wet oxide is higher than that of dry oxide but their t_{bd} are about the same. This tells us that the interface stress is a good indicator, but not the only factor in determining oxide reliability.

Higher absorption peak frequency implies lower stress in the oxides. Therefore it implies that the oxide with lower stress has higher t_{bd}. Higher growth temperature and higher steam concentration seem to reduce the stress. Furthermore, the decrease in frequency with the decrease in oxide thickness indicates the existence of stress gradient at the Si–SiO_2 interface as FTIR averages the measurement across the thickness.

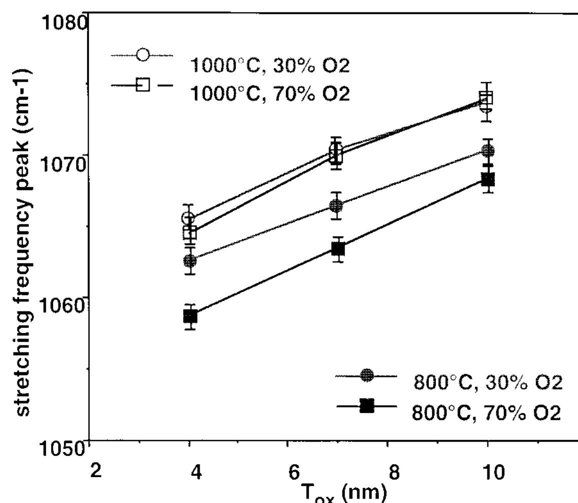


Fig. 4. Absorption peak frequencies as a function of oxide thickness by FTIR measurement. The oxides were grown at different temperatures and dilute concentrations in furnace.

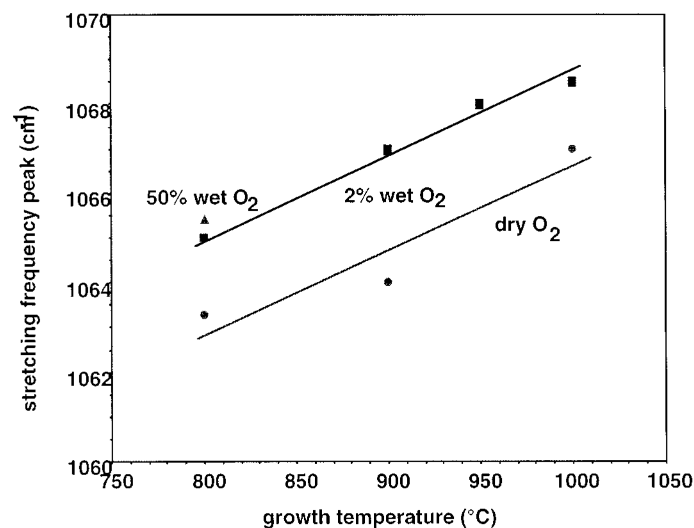


Fig. 5. Stretching peak frequencies of 4 nm dry, 2% wet, and 50% wet oxides grown at different temperatures by RTP.

VI. Physical Stress-Enhanced Bond Breaking Model

We propose a physical stress-enhanced bond-breaking model for thin SiO_2 degradation in the Fowler–Nordheim regime. The oxide breakdown is a two-step process as shown in Fig. 6. McPherson *et al.*have shown the electric field effect on the decomposition of the Si–Si bonds, the second step of the breakdown process [31]. In this work we have focused on the first step. In the discussion below we focus only on the Si–O–Si bonds, however, our methodology can also be applied to other bonds like Si–H. We demonstrate that the first step is strongly dependent on the physical stress in the thin oxide

films. Enhanced stress strains the bonds making it easier to break. As we mentioned in earlier sections, if the stress in oxides is different, the bond angles of Si–O–Si will be different, which is 144 ° at a stress free state. As the stress increases, the bond angle decreases. The bonding energy increases and therefore the bond will be weaker and easier to break by the electrons tunneling due to the electrical stress. Hence, the t_{bd} will be lower.

The free energy approach to time-dependent dielectric breakdown mechanism is used in our model [32]. For any chemical reaction to take place, the reactants (stable state) must overcome a potential difference to form the products (breakdown state). The driving force for this is the free energy difference between the stable state and the bond breakdown state. However, the reaction rate k at which the breakdown progresses depends on the free energy difference ΔG^* which separates the stable state from the activated state that leads to rapid breakdown.

Assuming the time-dependent dielectric breakdown is an activated process obeying standard chemical reaction rate theory [33], [34], the reaction rate constant should hold true by the following equation:

$$k \propto \exp\left(\frac{\Delta G^*}{KT}\right). \tag{1}$$

The total time for this process to take place, t_{bd} in the case, should be inversely proportional to the reaction rate constant as described in the following equation.

$$t_{bd} \propto \frac{1}{k} \propto \exp\left(\frac{\Delta G^*}{KT}\right). \tag{2}$$

The Gibbs free energy difference can be written as

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{3}$$

where ΔH^* is the change in the enthalpy and ΔS^* is the change in the entropy. Usually the entropy S is very small for solids compared to the enthalpy change, so (3) can be simplified to

$$\Delta G^* = \Delta H^*. \tag{4}$$

One can see from (2) and (4) that the t_{bd} value depends on the enthalpy change. Since enthalpy is the formation heat, therefore, t_{bd} is dependent on the bonding energy of the Si–O–Si bonds, which is a function of the bond angles θ.

To determine the bonding energy as a function of θ, the molecular mechanics approach described by Allinger is used [35]. We begin with a potential surface describing a molecule, and approximate this surface near the energy minimum using a Taylor's series expansion. The Taylor's series, if expressed in terms of internal coordinates, leads to an infinite power series, which describes bond bending. Then, we can have the following familiar expression:

$$\begin{aligned} E(\theta) =& E(\theta_0) + \frac{K_\theta}{2}(\theta-\theta_0)^2 \\ &+ \frac{K'_\theta}{3!}(\theta-\theta_0)^3 + \frac{K''_\theta}{4!}(\theta-\theta_0)^4 \cdots \end{aligned} \tag{5}$$

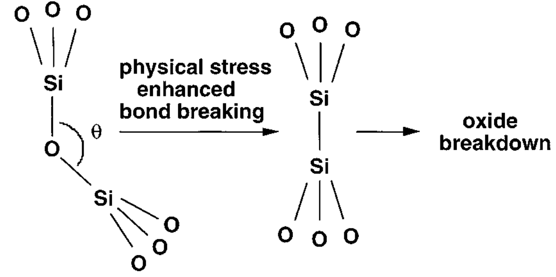


Fig. 6. Proposed physical stress-enhanced bond breaking mechanism. For the oxide breakdown to occur, the Si–O–Si bonds in SiO_2 break and are replaced by the Si–Si bonds, and this process is strongly dependent on the physical stress in the thin oxide films.

where $\theta_0 = 144°$ and K_θ values are the force constants for bending. The linear term is zero because the expansion is at the energy minima.

If the amount of bond bending is not large, we can neglect the higher order terms and (5) can be simplified to

$$E(\theta) = E(\theta_0) + \frac{K_\theta}{2}(\theta-\theta_0)^2. \tag{6}$$

The energy form of (6) is like a harmonic oscillator. Thus, the force constant K_θ can be determined to be 20.5 eV [37] by the measured oscillating frequencies (bending, stretching, and rocking) of thick SiO_2 as shown by Harrison [36]. Therefore, from (2), (4), and (6), for two oxides under the same electric field, the following equation is obtained:

$$\begin{aligned} \frac{t_{bd2}}{t_{bd1}} &= \exp\left(\frac{\Delta G_2^* - \Delta G_1^*}{KT}\right) \\ &= \exp\left(\frac{\frac{K_\theta}{2}(\theta_1-\theta_0)^2 - \frac{K_\theta}{2}(\theta_2-\theta_0)^2}{KT}\right) \end{aligned} \tag{7}$$

where θ_0 is 144°, θ_1 and θ_2 can be calculated from the measured FTIR absorption peaks through the following equation [19]:

$$\nu_p = \nu_0 \sin\frac{\theta}{2} \tag{8}$$

where ν_p is the peak of the absorption frequency and ν_o is 1134 cm^{-1}.

Based on (7) and (8) and the FTIR absorption peak data (Figs. 4 and 5) of various oxides, the relative t_{bd} values can be predicted. For furnace grown oxides, the predicted t_{bd} values are plotted in Fig. 7. Note that all the t_{bd} values have been normalized to the t_{bd} of 800 °C, 70% 4 nm oxide. It can be observed that the t_{bd} trends agree well with the experiment data shown in Fig. 1. Similar results are obtained for the RTP oxides. Figs. 8–10 summarize theoretical t_{bd}, measured t_{bd} and the FTIR absorption peaks for oxides of 4 nm thickness grown in dry and wet O_2 at 800, 900, 950, and 1000 °C. The theoretical t_{bd} value of the 800 °C, 4 nm dry oxide (the one with the lowest t_{bd}) is set to 4.25 s (its experimental value). All the other theoretical t_{bd} values are normalized to this value using (7). It can be observed that the trends of the theoretical t_{bd} agree very well with that of the experimental t_{bd} and the FTIR measurements. The slight t_{bd} difference between the experimental and theoretical values can come from the

following reasons. First, we have assumed in our calculations that the stress in the film is uniform during the bond breaking process that causes the formation of a conducting path from the substrate to the gate electrode. In reality, the stress decreases as one moves away from the substrate interface. Second, only the breakage of the Si–O bonds is considered, not other bonds, for example the Si–H bond, which has been observed to be related to the oxide breakdown [13]. Third, other oxide breakdown mechanisms are not taken into account, e.g., anode hole injection [3] and high field oxide wearout [14].

VII. Discussions

Although constant current stress (CCS) was used throughout the TDDB measurement in this work, the results should be very close to those of constant voltage stress (CVS); Q_{bd} values have been shown to depend on the gate work function [38], the stress polarity in dual-gate CMOSFET's [39], and the testing methodology [40]. In general, they depend on the electric field in oxide E_{ox} and the stressing current density J_{ox}. At a fixed J_{ox}, higher E_{ox} gives lower Q_{bd}, and same E_{ox} gives same Q_{bd} [41]. For a given capacitor, the relation of J_{ox} and E_{ox} is one to one. In our case, J_{ox} is fixed and the tunneling barrier height is the same (3.1 eV for n+ poly-Si gates). Therefore, E_{ox} is the same. Constant current stress in our case is therefore very close to constant voltage stress. The only differences is that under constant current stress, the total voltage drop across the MOS capacitors changes slightly during the measurement due to electron and hole trapping in the oxides, while for the constant voltage stress, the injecting current changes. To the first order, the changes are relatively small compared to the average voltage for constant current stress or the average current for constant voltage stress and therefore they are negligible. Table III shows the initial voltage (V_{init}) drops across the MOS capacitors under constant current stress at a current density of -100 mA/cm^2 for various furnace oxides with information given in Table I. These values are very close to their average voltages before the oxides break down in our measurements (within 5%). In addition, one can observe that the corresponding voltage drops acrossthe capacitors of about the same oxide thickness grown by different conditions are very close. Therefore, results of constant current stress in this work should be very close to constant voltage stress.

Many researchers have shown that there is a strong correlation between the interfacial stress and t_{bd}. Han *et al.* have proposed that the structural transition layer at the SiO_2/Si interface is related to Q_{bd} [7]. Eriguchi *et al.* have determined that the increase of the built-in compressive strain would decrease t_{bd} [10]. Bhat *et al.* have shown the correlation between Q_{bd} and stress in deposited oxides [42], [43]. Lee *et al.* have shown a correlation between stress and oxide soft-breakdown [44]. In this section we discuss how stress affects t_{bd} in more detail.

As we have mentioned earlier, several oxide damage mechanisms have been proposed, and basically, they all agree well with this model as all of them rely on trap creation through some kind of physical damage. The stressed region is more vulnerable to high energy electrons tunneling through the oxide and causing damage at the anode, consistent with anode being the primary damage site [1], [5], [13]. Since the strained layer occupies a larger fraction in a thinner oxide than thicker one, its t_{bd} is lower. This is consistent with the observations that there is a measurable gradient in bond strain at the interface [27] and most of the stress occurs within a 1-nm-thick strained-layer near the SiO_2/Si interface [10]. This can explain the increase in t_{bd} as a function of oxide thickness for gate injection.

During oxide growth, the viscous flow of SiO_2 can occur. If there was no viscous relaxation, we would expect a constant value of stress across the thickness of the films. That is not the case. There is a nonhomogeneous thermal history aspect to all thermally grown SiO_2 films; in a thick oxide film, the topmost increment of oxide was formed first and was being annealed while the underlying oxide was being formed. The increment of oxide nearest the interface has spent very little time at the growth temperature and is therefore expected to show the least amount of relaxation [24]. It is apparent that the stress generated at the growth interface relaxes as we move away from the interface. Therefore, the viscous flow can partially relieve the physical stress in the oxide film. When the temperature is below 950 °C, this process takes place at a very slow rate. However, it is noticeably faster when the temperature is higher than 950 °C [45]. This is because the time required for viscous flow is reduced significantly if the temperature is above 950 °C. Therefore the oxides grown at higher temperatures have lower stress with an accompanying decrease in the oxide density [17], [46]. The stress relaxation time for oxide density can be expressed as in the following equation [47], [48]:

$$\tau(T) = \tau_o \exp(E_a/\mathrm{kT}) \tag{9}$$

where $\tau_o = 2 \times 10^{-20} c$ s and $E_a = 5.1$ eV. The relaxation times at different temperatures based on this equation are summarized in Table IV.

At 1000 °C, the relaxation time of 3 s is so small compared to the oxidation times (see Table I) that no matter whether the oxides were grown in 30% or 70% O_2, the stress was almost all relieved through SiO_2 viscous flow. Hence, no significant t_{bd} differences can be observed for oxides grown at 1000 °C. At 800 °C the relaxation time of 4.76 h is much larger than the oxidation time. Therefore, there is little viscous flow resulting in higher stress. Since the interfacial bonds of 1000 °C oxides have less stress than 800 °C, they are more difficult to break. Therefore, 1000 °C grown oxides have higher t_{bd} as shown in Fig. 1. Similar trend of t_{bd} versus temperature can be seen in Fig. 2 for RTP oxides. Note that in Fig. 2, the t_{bd} of the 2% wet 950 °C oxides is very close to that of the 1000 °C oxides, because for both temperatures the relaxation times are smaller than the oxidation times.

At 800 °C, however, since the viscous flow of SiO_2 is not significant, different growth times will affect t_{bd} results if they are smaller than or comparable to the relaxation time, which is the case for our furnace grown oxides as shown in Table I. As one can see in Fig. 1, longer time growth (30% O_2) gives higher t_{bd}. This is because if the oxidation time is longer, the relaxation of Si–O–Si bonds at the Si/SiO_2 interface through viscous flow will be more. Therefore, it will result in lower stress and higher t_{bd}.

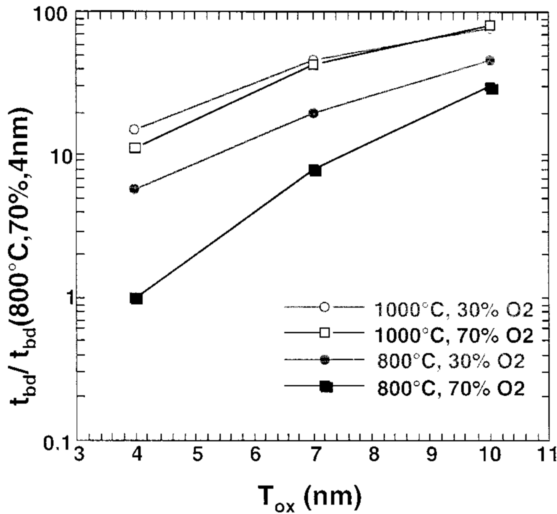


Fig. 7. Theoretical prediction of relative t_{bd} values of furnace dry oxides normalized to 800 °C, 70% O_2, 4 nm oxide. The measured FTIR absorption peaks of various oxides were used in this calculation.

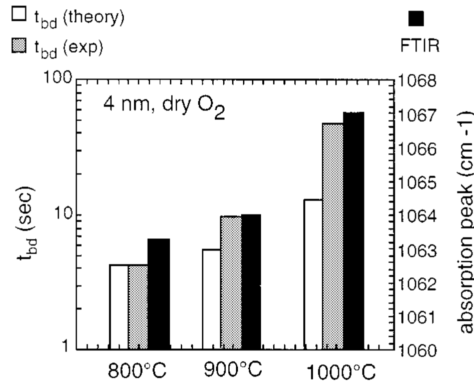


Fig. 8. Theoretical t_{bd}, experimental t_{bd} (90% value) and the FTIR absorption peaks of 4 nm oxides. The RTP oxides were thermally grown in dry O_2 at different temperatures. All the calculated t_{bd} values have been normalized to the t_{bd} of 800 °C, 4 nm dry oxide.

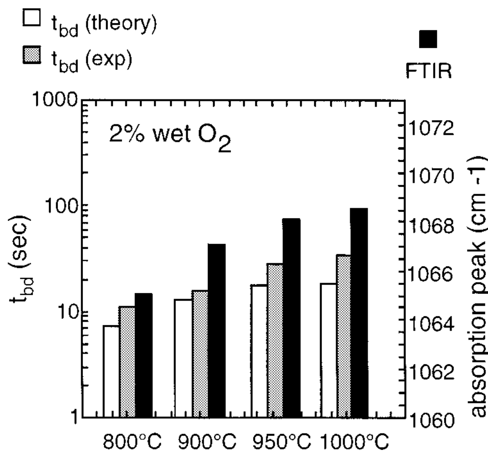


Fig. 9. Theoretical t_{bd}, experimental t_{bd} (90% value) and the FTIR absorption peaks of 4 nm oxides. The RTP oxides were thermally grown in 2% wet O_2 at different temperatures. All the calculated t_{bd} values have been normalized to the t_{bd} of 800 °C, 4 nm dry oxide.

Another interesting result as shown in Fig. 2 is that at 800 °C, more steam during the oxidation gives higher t_{bd}. Eriguchi *et al.* have found similar trend [10]. By investigating the oxide etch rates in dilute HF, they showed that the interface stress in oxides grown in dry O_2 is higher than those grown in pyrogenic steam. We attribute this to the fact that the viscosity of OH-containing SiO_2 is about two orders of magnitude less than that of dry SiO_2 [49]. An oxide with a lower viscosity results in a lower film stress and therefore a higher t_{bd}.

Now let us look at the case of substrate injection. The slightly decreasing trend and the higher t_{bd} for substrate injection in Fig. 3 can be explained using Fig. 11. For gate injection, the primary damage occurs at the substrate/oxide interface [1], [5], [13]. Kao *et al.* showed [45] that the stress is highest at the substrate/oxide interface and reduces continuously as we move away from the interface as shown schematically by

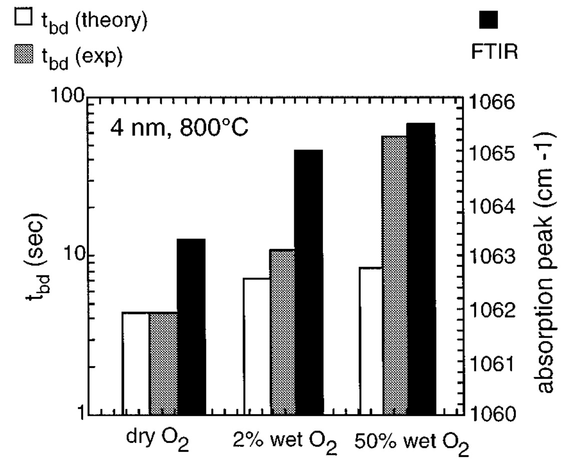


Fig. 10. Theoretical t_{bd}, experimental t_{bd} (90% value) and the FTIR absorption peaks of 4 nm oxides. The RTP oxides were thermally grown at 800 °C at different steam concentrations. All the calculated t_{bd} values have been normalized to the t_{bd} of 800 °C, 4 nm dry oxide.

TABLE III
INITIAL VOLTAGE DROPS ACROSS THE FURNACE GROWN OXIDES UNDER CONSTANT CURRENT STRESS AT A CURRENT DENSITY OF −100 mA/cm2

Dry O2 concentration	800°C Vinit	1000°C Vinit
30%	-4.9 V	-4.9 V
30%	-7 V	-7 V
30%	-12.6 V	-11.5 V
70%	-4.8 V	-4.9 V
70%	-7. 2 V	- 7.4 V
70%	-12.4 V	-11.8 V

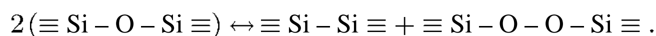
TABLE IV
RELAXATION TIME VERSUS TEMPERATURE

T	τ(T)
800°C	4.76 hours
850°C	25 min
900°C	160 sec
950°C	20 sec
1000°C	3 sec

varying shade in Fig. 11. For substrate injection, stress has much less effect on the primary damage as it occurs at the poly-Si gate/oxide interface. Oxide breakdown occurs when a conducting path forms between the poly-Si gate and the substrate. A conducting path consists of many damage clusters caused by the electrical stress [15]. In a damage cluster there are many traps due to broken bonds, and it becomes conductive due to the traps [1], [15]. The oxide damage initiates primarily at the anode. After a damage cluster is formed the stress voltage drops across the remaining oxide which is now thinner at that spot increasing the electric field in that region. Hence, the generation of the damage clusters in the remaining thickness is accelerated. This concept is similar to the effective oxide thinning proposed by Lee [50]. The total time to breakdown is therefore dominated by the time to initially break the bonds and form a damage cluster in the oxide. From Fig. 11 it is clear that the stress is highest at the SiO_2/substrate interface and therefore for a given electric field it is easier to break bonds at this interface. It will take shorter time to create initial damage for gate injection than for substrate injection. Accordingly the t_{bd} for gate injection is lower than that for substrate injection.

Surface roughness has been shown to influence the t_{bd} of the gate oxides [4]. The surface roughness model can explain the t_{bd} dependence on the injection polarity as well, but it cannot explain the t_{bd} dependence on oxide growth conditions because the rough poly-Si/oxide interface is the same for all growth conditions. Furthermore, it cannot explain why the t_{bd} reduces as the oxide thickness is reduced for constant current gate injection.

In our model, we assumed that the Si–O–Si bond is broken and replaced by the Si–Si bond during an oxide breakdown. This Si–Si bond is very weak and it can be either an electron trap or a hole trap [51]. If it traps an electron, it becomes an electron trap [52], [53]. Degraeve *et al.* have demonstrated that oxide breakdown occurs as soon as a critical density of neutral electron traps in the oxide is reached [15]. If it traps a hole, it becomes an E' center. It is consistent with the observation of E′ centers in oxides during a breakdown process. It has been reported that the Si–Si bond in SiO_2 is the precursor of an E′ center [54]. As to the missing oxygen atom after the formation of the Si–Si bond, the following process was proposed because it is not easy for the oxygen atoms to dissociate out of oxides [54], [55]:



$$2(\equiv \mathrm{Si-O-Si}\equiv) \leftrightarrow \equiv \mathrm{Si-Si} \equiv + \equiv \mathrm{Si-O-O-Si} \equiv .$$

These observations have serious implications for future scaling of MOS devices and fabrication technology, especially for EEPROM's. The fact that Q_{bd} decreases with decreasing oxide thickness will become a more serious problem when EEPROM's are doing erase-operations. The strained layer will play a more important role in oxide reliability and lifetime in the devices of newer generation. Controlling the strained layer and reducing the stress properly will be extremely important for future ultrathin gate oxides in the sub-100 nm ULSI technology. Besides, higher growth temperatures may be needed to improve reliability, which may go against the thermal budget limitations. Rapid thermal processing may become the logical choice to keep thermal budget low.

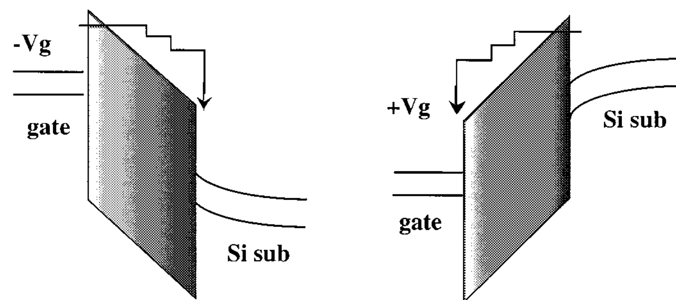


Fig. 11. Energy band diagrams of a MOS capacitor under gate injection (Vg^-) and substrate injection (Vg^+). The darker shade depicts higher stress at the oxide/substrate interface.

VIII. Conclusions

We have demonstrated that in MOS devices the reliability of the thin gate oxides for constant current gate injection (V_g^-) in the Fowler–Nordheim tunneling regime is closely related to the SiO_2/Si interfacial physical stress. This is consistent with anode being the primary damage site. A physical stress-enhanced bond-breaking model is proposed. The oxide breakdown mechanism is very closely related to the Si–Si bond formation from the breakage of Si–O–Si bond, and that depends on the physical stress in the film. The interfacial stress comes from the volume expansion from Si to SiO_2 during the thermal oxidation, and it is a strong function of growth conditions, such as temperature and growth rate. Higher temperatures and slower oxidation rates allow stress relaxation through viscous flow. Reduced disorder at the interface results in better reliability. In addition, the degradation of SiO_2 is enhanced as the thickness is reduced in the Fowler–Nordheim tunneling regime. In conjunction with the Gibbs free energy theory, this model successfully predicts the trends of time-to-breakdown (t_{bd}) as a function of oxide thickness and growth conditions. The trends of predicted t_{bd} values agree well with the electrical t_{bd} and the stress data.

The process techniques, which enable slower growth rate and higher growth temperature, are desirable. These observations have serious implications for future scaling of MOS devices and fabrication technology. Higher growth temperatures may be needed to improve reliability, which may go against the thermal budget limitations. Rapid thermal processing may become the logical choice to keep thermal budget low.

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