Impact of O-Si-O bond angle fluctuations on the Si-O bond-breakage rate

Stanislav Tyaginov[(1)], Viktor Sverdlov[(2)], Wolfgang Gös[(1)], Tibor Grasser[(1)]

[(1)]Christian Doppler Laboratory for TCAD at the [(2)]Institute for Microelectronics,
Technische Universität Wien, Gußhausstraße 25-29, A-1040 Vienna, Austria
e-mail: tyaginov@iue.tuwien.ac.at fax: +43-1-58801-36099
submission preference: oral presentation

Abstract: We extend the McPherson model for silicon-oxygen bond-breakage in a way to capture the impact of the O-Si-O angle fluctuations on the breakage rate. It is shown that the mean rate is more than 5 times higher and its standard deviation is comparable to the nominal rate corresponding to the fixed angle (typical for α-quartz). The mean rate has appeared to grow exponentially with the electric field supporting the thermo-chemical model for time-dependent-dielectric-breakdown.

1. Introduction

The Si-O bond-breakage has been suggested to be a crucial contributor to hot-carrier-injection (HCI) damage and to time-dependent-dielectric-breakdown (TDDB) [1,2]. A model recently proposed by McPherson [3,4] considers Si-O bond rupture as a transition of the Si ion from the 4-fold equilibrium position (the primary minimum) in the center of the SiO_4 tetrahedron to the 3-fold position (the ledge) beyond the O_3 plane (Fig. 1a), resulting in the formation of a Si-Si bridge. This transition is considered as a superposition of the Si tunneling through the barrier between the primary and the secondary minima and its thermionic excitation. The potential profile is formed by 4 contributions due to interactions of the Si with the surrounding O ions situated in the vertices of the SiO_4 tetrahedron. To describe Si-O interactions the Mie-Grüneisen pair-wise potential is used [3,4].

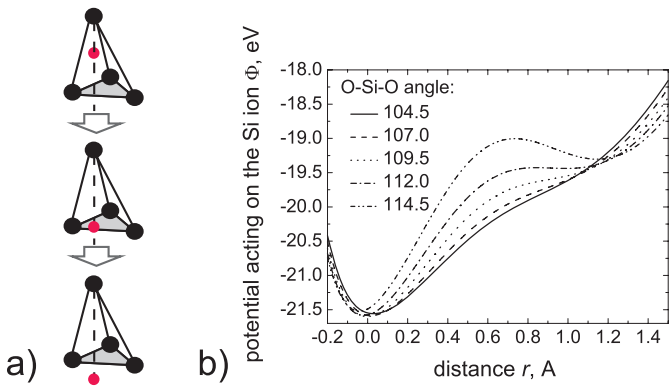

Fig. 1. Geometrical and energetical positions of the secondary minimum: (a) Si transition from the 4-fold to the 3-fold position; (b) barrier transformation with O-Si-O angle.

Although it has been speculated that the secondary minimum becomes more/less energetically pronounced with O-Si-O angle φ deviations and, thus the bond-breakage rate may be drastically changed, this issue has not been quantitatively addressed. At the same time there is a bulk of either theoretical [5-7] or experimental [8,9] publications where a distribution of O-Si-O and Si-O-Si angles is reported for amorphous SiO_2. Therefore, the McPherson model is only suitable for α-quartz and has to be extended in a way to capture the effect of fluctuations of these angles typical for SiO_2 films employed as gate oxides. We study the impact of O-Si-O angle variations on the breakage rate.

2. General Considerations

As a starting point the McPherson model for Si-O bond-breakage is used [3,4]. We employ the Mie-Grüneisen interatomic potential to describe Si-O interactions:

$$\Phi(r) = \Phi_B\left[A\left(\frac{r_0}{r}\right)^9 - B\left(\frac{r_0}{r}\right)^2 - C\left(\frac{r_0}{r}\right)\right], \quad (1)$$

where r is the interatomic distance, $\Phi_B = 5.4$ eV and $r_0 = 1.7$ Å are the bond strength and length. Constants $\{A,B,C\}$ are found in order to represent energetical and geometrical positions of the minimum corresponding to the equilibrium ($\Phi(r_0) = \Phi_B$; $\delta\Phi/\delta dr(r_0) = 0$) as well as the bond polarity.

In this model the position of the secondary saddle point is determined by the tetrahedral symmetry. The secondary ledge lies on the symmetry axis of the tetrahedron, i.e. in the direction from the center of the SiO_4 cell perpendicular the O_3 plane (Fig. 1a). While moving the Si atom in this direction – due to the symmetry – the contributions of 3 oxygen ions in the plane are identical featuring a maximum when Si penetrates the plane and 2 minima situated symmetrically respectively to this maximum. The contribution of the last O ion demonstrates the sole minimum corresponding to the equilibrium ion position and thus the common action of all ions leads to the pronounced primary minimum and a shallow secondary minimum/saddle point separated by a barrier (Fig. 1b).

While shifting one of O ions from its regular position corresponding to α-SiO_2 or, in other words, while deviating the O-Si-O angle, the symmetry is distorted and the position of a ledge is shifted both geometrically and energetically. With the increase of φ the saddle point becomes more pronounced and at the same time the barrier separating the primary and the secondary minima grows, Fig. 1b. This means that thermionic contribution decays with φ while it is not clear *a priori* how the tunnel component behaves. Since the Si ion tunnels from those levels in the quantum well of the primary minimum situated above the bottom of the secondary minimum, there is a trade-off between aggravation of the tunnel probability due to the higher barrier and its growth due to involvement of a larger number of levels into tunneling. The tunneling rate is calculated as $P_{tu} = \Sigma T_n f_n/\tau_n$, where the summation is undertaken over all levels situated above the secondary minimum, T_n, f_n and τ_n are the barrier transparency, level occupation and aller-retour time ($1/\tau_n$ is the attempt rate) [3,4,10]. The thermionic rate is $P_{th} = \nu\cdot\exp(-E_a/k_BT)$ with $\nu \sim 10^{13}$ s^{-1} [3,4] being the attempt frequency, E_a is the barrier height and k_B and T are Boltzmann constant and the temperature.

3. Bond-Breakage rate vs. O-Si-O bond angle

It is obvious that the direction in which the secondary minimum appears is determined by the SiO_4 tetrahedron symmetry. Thus if one of the O ions is shifted (φ is not equal to its conventional value 109.48^O, see Fig. 2a) the minimum should be observed in another direction. However, we consider here the overall bond-breakage rate, i.e. a path between the primary and the secondary minima providing a highest rate will be "found" by the Si ion while breaking Si-O bond. Therefore, it is more reasonable to reformulate the problem in terms of "bond-breakage rate" rather than "potential profile", i.e. to find the direction at which a maximum of bond-breakage rate P is observed. Fig. 2b demonstrates the dependence of the angle θ between the SiO_4 symmetry axis and the direction corresponding to the maximum of P as a function of φ. Note that this dependence features $\theta = 0$ for $\varphi = 109.48^O$ as it should be (the case of the regular α-quartz).

To determine θ we used the downhill simplex method in 2 dimensions (while searching the maximum we examined directions connecting the SiO_4 center and a point in the O_3 plane parameterized by 2 coordinates), see e.g. [6]. Note that only directions demonstrating a pronounced secondary minimum have been taken into account (a zero bond-breakage rate was assigned to a direction with no secondary minimum observed). Fig. 3 shows the dependence of P on φ calculated for different values of fields F. One can see an abrupt increase of P at $\varphi_{cr} = 107.75^O$ corresponding to the appearance of the secondary minimum. The following decrease of bond-breakage rate with φ reflects the interplay between the barrier strengthening and deepening of the secondary minimum mentioned above. Note that the dependencies $P(\varphi)$ calculated with a certain step on F are situated

equidistantly in a log-lin scale that means that the bond-breakage rate grows exponentially with field, supporting the thermo-chemical model [12] even in a case of fluctuating φ. The rate P as a function of F calculated for various values of φ is plotted in Fig.4, explicitly demonstrating linear trend for log P vs. F. Note that all the curves $P(F)$ have the same slope.

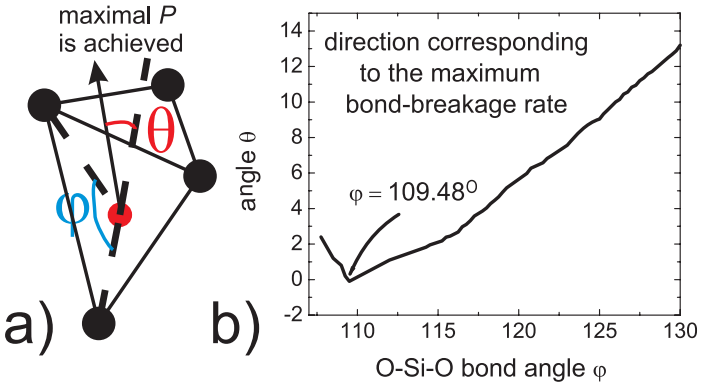

Fig. 2. Direction at which the maximum bond-breakage rate is observed (represented by angle θ): (a) schematically depicted; (b) as a function of angle φ.

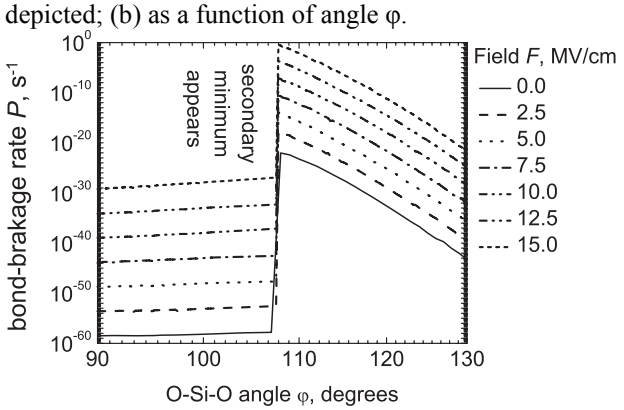

Fig. 3. Bond-breakage rate as a function of the O-Si-O angle φ calculated for various fields F.

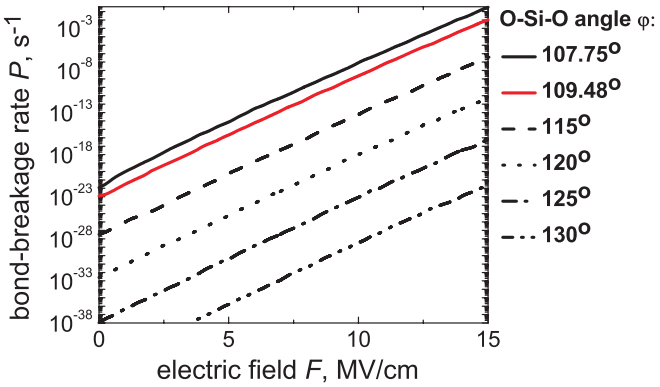

Fig. 4. Bond-breakage rate vs. the electric field F obtained for diverse angles φ.

4. Statistical analysis

For the statistical analysis of bond-breakage rate deviations due to the fluctuations of O-Si-O angles we borrowed the probability density distribution of O-Si-O angle, $D_\varphi(\varphi)$, from [7], see Fig. 5, inset. The mean value $<P>$ and the standard deviation σ_P of the variate P have been calculated as

$$< P >= \int_0^\pi P(\varphi) D_\varphi(\varphi) d\varphi \text{ and } \sigma_P = \left(\int_0^\pi (P - < P >)^2 D_\varphi(\varphi) d\varphi \right)^{1/2}.$$

Fig. 5 shows the mean value of the bond-breakage rate $<P>$ and its standard deviation σ_P as a function of the electric field F. As a reference, the nominal breakage rate P_n calculated for a fixed φ = 109.48^O (corresponding to the crystalline configuration of α-quartz) is also plotted. One can see that for a wide range of the applied electric field F = 5.0…10.0 MV/cm the mean value $<P>$ is more than 5 times higher than that calculated with φ = 109.48^O. Moreover, the standard deviation σ_P is comparable to P_n implying a quite wide span of variate P. Such a finding means that huge bond-breakage rates – realized with a small but still finite (nonzero) probability – may warrant the build-up of precursors for the formation of a percolation path. In fact, as it has been reported in the literature (e.g. [8]), while the trap cluster is being formed, new defects are most probably created in the vicinity of the pre-existed ones and thus the spot with the highest P acts as a precursor for formation of a percolation path.

A linear dependence of the bond-breakage rate on the electric field has also been observed in a case of fluctuating O-Si-O angle. Moreover, the standard deviation $\sigma_p(F)$ reveals the same slope in the semi-log scale (Fig. 5). These circumstances reflect the fact that the thermo-chemical model for

TDDB developed for crystalline SiO_2 is also applicable for amorphous material characterized with deviations in O-Si-O and Si-O-Si bond angles. In fact, the model demonstrates a linear aggravation of the logarithmic time-to-failure with the electric field. It treats the bond-breakage process in terms of chemical reactions with a certain activation energy and shows that this energy decreases proportionally *F*. In our case the same result has been obtained when the logarithmic (mean) bond-breakage probability is being enlarged proportionally to the applied field.

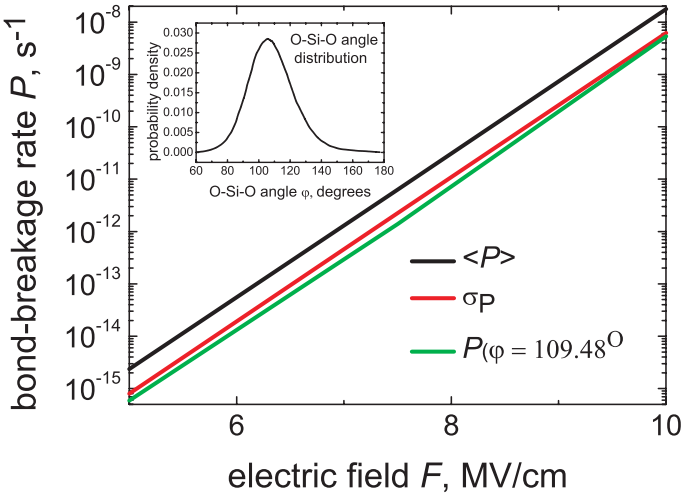

Fig. 5. The mean value, the standard deviation and the value calculated for $\varphi = 109.48^{O}$ of bond-breakage rate. Inset: O-Si-O angle distribution borrowed from [7].

5. Conclusions

Using the McPherson model for Si-O bond rupture we analyzed the effect of O-Si-O bond angle φ variations on the breakage probability. While varying φ the potential profile changes, i.e. the secondary minimum becomes deeper accompanied by a growth of the separation barrier height. Hence, there is a trade-off between a lower barrier transparency and involvement of a larger number of energy levels to tunneling. Since the Si ion "finds" a way for bond-breakage corresponding a highest probability we examined different directions to determine the one featuring a maximum of the bond-breakage rate. A secondary energetical minimum was shown to appear at $\varphi_{cr} = 107.75^{O}$. Due to the trade-off mentioned above an abrupt increase of *P* is found at $\varphi = \varphi_{cr}$ followed by an exponential decrease of *P* on φ. Using the probability density of φ we calculated the mean value $\langle P \rangle$ and the standard deviation σ_p. In a large range of *F*, $\langle P \rangle$ is more than 5 times higher that the nominal rate P_n (for $\varphi = 109.48^{O}$ typical for α-quartz) while σ_P is comparable with P_n. The dependencies of P_n, $\langle P \rangle$ and σ_P on the field *F* are linear on a log-lin scale. This circumstance supports the thermo-chemical model (showing the linear dependence between the logarithmic time-to-failure and the electric field) also in the case of fluctuating O-Si-O bond angles.

References

1. S. Mahapatra et al, *IEEE Trans. El. Dev.*, v. ED-53, p. 1583 (2006).
2. M. Kimura et al, *J. Appl. Phys.*, v. 85, p. 7671 (1999).
3. J.W. McPherson, *J. Appl. Phys.*, v. 99, pap. No. 083501 (2006).
4. J.W. McPherson, *45th Annual International Reliability Physics Symposium*, p. 209 (2007).
5. Carré et al, *Lett. Journ. Expl. Front. Phys.*, v. 82, p. 17001 (2008).
6. S.V. Alfthan et al, *Phys. Rev. B*, v. 68, p. 073203 (2003).
7. S. Munetoh et al, *Comput. Mater. Sci.* v. 39, p. 334 (2007).
8. M.G. Tucker et al, J. Phys.: *Condens. Matter*, v.17, p. S67 (2005).
9. C.R. Helms, E.H. Poindexter, *Rep. Prog. Phys.*, v. 57, p. 791 (1994).
10. M.I. Vexler, *Solid-State Electron.*, v. 47. p. 1283 (2003).
11. W.H. Press et al, *Numerical Recipes in C* (1997).
12. K.P. Cheung, *Microel. Reliab.*, v. 41, p. 193 (2001).
13. G. Bersuker et al, *Microel. Engin.*, v. 69, p. 118 (2003).