Structure, Properties, and Dynamics of Oxygen Vacancies in Amorphous SiO_2

Zhong-Yi Lu,[1] C. J. Nicklaw,[2] D. M. Fleetwood,[2,1] R. D. Schrimpf,[2] and S. T. Pantelides[1,3]

[1]*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235*
[2]*Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, Tennessee 37235*
[3]*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*

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Oxygen vacancies in SiO_2 have long been regarded as bistable, forming a Si-Si dimer when neutral and a puckered configuration when positively charged. We report first-principles calculations of O vacancies in *amorphous* SiO_2 supercells that unveil significantly more complex behavior. We find that the vast majority of O vacancies do not pucker after capture of a hole, but are shallow traps. The remaining vacancies exhibit *two distinct types of puckering.* Upon capturing an electron, one type forms a metastable dipole, while the other collapses to a dimer. A statistical distribution of O vacancies is obtained, and the implications for charge transport and trapping in SiO_2 are discussed.

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Silicon dioxide has been the subject of extensive experimental investigations in both its crystalline and amorphous forms. Several of its properties are dominated by a single point defect with a characteristic electron-paramagnetic-resonance (EPR) signature, known as E_1' in crystalline quartz [1] and E_γ' in amorphous SiO_2 [2]. Theoretical calculations [3–5] for small clusters, for crystalline quartz, and amorphous supercells led to the identification of the defect as the oxygen vacancy. This defect exhibits a unique bistability: In the neutral state, the two adjoining Si atoms rebond into a "dimer configuration" [Fig. 1(a)]; in the EPR-active positively charged state, one of the Si atoms relaxes back past the plane of its three O neighbors and bonds with another network O atom ("puckered configuration") [Fig. 1(b)].

In the past decade, research on radiation or high-field-stress induced defects in the amorphous SiO_2 layer of metal oxide semiconductor (MOS) field-effect transistors has revealed a broad range of complex dynamical phenomena in both the bulk oxide film and near the Si-SiO_2 interface. The origin of many of these phenomena has been traced to O vacancies [6–10]. The underlying atomic-scale processes, however, remain elusive. The phenomena are often associated with the dynamics of the E_γ' center and of a second EPR-active defect that has been labeled E_δ' and identified as an O vacancy in the dimer configuration [6,7,11]. Examples of these phenomena are as follows: (a) E_γ' centers are found to be more stable thermally than E_δ' centers; at room temperature, after irradiation or hole injection, the density of E_δ' centers has been observed to decrease, in some cases with a concomitant increase in the density of E_γ' centers [7]. (b) After irradiation or high-field stress, the accumulated positive charge in the oxide can often be neutralized by a high-temperature anneal at large positive bias, but much of the original positive charge can be restored by reverse-bias annealing [12–14]. The restored positive charge can cycle reversibly when the bias is cycled from positive to negative, but the total positive charge that gets restored during the cycling can gradually decrease with repeated cycling.

In this Letter, we report *ab initio* total-energy calculations of O vacancies in several amorphous SiO_2 supercells. The results and analysis reveal that O vacancies in *amorphous* SiO_2 exhibit a very rich structure because of the large variations in local bonding that are possible in the amorphous network as opposed to crystalline quartz. Three distinct types of O vacancy were found. Examination of the variations in local bonding in the amorphous supercells allows an analysis of the statistical probability of distinct modes of behavior. For the statistical study, the local topologies of a million-atom cell [15] were analyzed. The results are as follows.

(a) The vast majority ($\sim$ 80%) are *not* bistable like O vacancies in quartz. Instead, the dimer configuration [Fig. 1(a)] is the only stable configuration in both the neutral and positively charged state. The dimer energy level containing one or two electrons is shallow (within $\sim$1 eV from the SiO_2 valence-band edge).

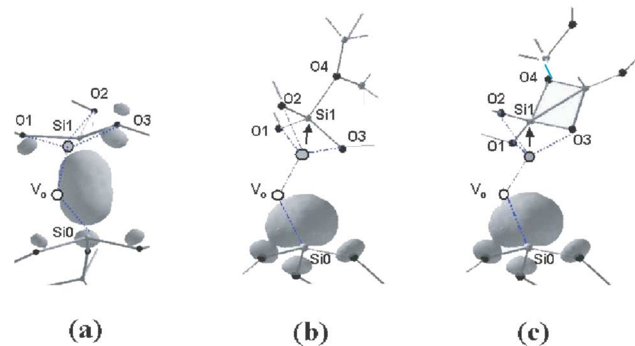

FIG. 1 (color online). Schematics of (a) "dimer," (b) "fourfold puckered," and (c) "fivefold puckered" oxygen vacancies as described in the text. Dotted lines show bonds prior to removing the O atom (V_o). The gray shading shows the unpaired electron density.

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(b) Roughly 12% are bistable in the same way as an O vacancy in quartz: In the neutral state, the dimer configuration is stable; in the positively charged state, one of the adjoining Si atoms relaxes back past the plane defined by its three O neighbors and bonds with another network O atom; the latter becomes threefold coordinated whereas the puckered Si atom becomes fourfold coordinated [Fig. 1(b)]. The localized energy level is now quite deep, nearly in the middle of the SiO_2 energy gap (~ 4.5 eV). When this center is given an electron back, *it stays in a metastable puckered configuration*, with an energy barrier ranging from 0.2 to 1.2 eV. The electron, in fact, fills the dangling bond, *making it negative*, whereas the hole is still left on the puckered Si side, resulting in a dipole. The result that a defect with such small spatial extent can sustain such a dipole is somewhat surprising, but the idea was in fact invoked in previous studies [12–14].

(c) Roughly 8% are also bistable, but with the following key differences: In the positively charged state, the puckered Si atom now bonds both to a network O and a network Si atom, becoming fivefold coordinated [Fig. 1(c)]; the localized energy level is again deep (~ 4.5 eV) and the unpaired electron has essentially the same distribution as before (suggesting a nearly identical EPR signature); however, when this center is given back an electron, *it collapses immediately to the dimer configuration without an energy barrier.*

As will be described later in detail, the above results can account for many complex dynamical phenomena associated with electron capture and release after hole trapping in irradiated or stressed SiO_2.

The calculations were done using density functional theory and the local density approximation for exchange correlation [16], ultrasoft pseudopotentials [17], and plane waves as a basis set. Integrations over the Brillouin zone were done using four special k points in the irreducible wedge [18]. The plane wave cutoff was set at 28 Ry following convergence tests with cutoffs up to 45 Ry. Atomic relaxations were carried out until the forces on each atom were smaller than 0.025 eV/Å, except when certain degrees of freedom were restricted as in calculations of energy barriers. One α-quartz supercell and four different amorphous supercells, each containing 24 SiO_2 units (72 atoms), were used. The amorphous supercells were created using the first-principles molecular dynamics [19] and reflect the observed variation of densities in various forms of a-SiO_2.

Initial calculations were performed with an α-quartz cell for calibration. The results were in excellent agreement with those of Boero *et al.* [5]. The neutral vacancy has a dimer configuration while the positively charged state undergoes puckering, with a hole residing on the puckered Si atom and the unpaired electron in the dangling bond of the other Si atom, as schematically shown in Fig. 1(b). When the puckered state is neutralized with an electron, it becomes metastable, with an energy barrier of 0.3 eV separating it from the dimer configuration, which is 2.9 eV lower in energy (the two sides are not symmetrical; the puckering can occur on either side with minor differences in the energies involved). In the metastable neutral puckered configuration, the added electron is found to go to the dangling bond, leaving the puckered Si atom still positively charged. Thus, though the defect is neutral, it has a nonzero dipole, in agreement with the original suggestion made by Lelis *et al.* for amorphous SiO_2 [12–14].

The calculations carried out in the amorphous supercells identify three distinct types of O vacancies as outlined above, which we now discuss more fully.

Dimer configuration [shown in Fig. 1(a)].—In the vast majority of sites in all the amorphous supercells we examined, the dimer configuration has the lowest energy in both the neutral and positively charged states. The Si-Si bond length (Si0 and Si1) is typically longer (2.5–3.0 Å) in the positively charged state. We calculated total-energy differences and found that a hole can be captured by a neutral defect with an activation energy of less than 1.2 eV. The localized hole is in a Si-Si bonding orbital, namely, shared by the Si0 and Si1, from which an E'_δ EPR signal results [11].

Puckered configurations.—We found two distinct puckered configurations that occur when an O vacancy is positively charged: (a) the conventional one [shown in Fig. 1(b)], similar to the one that occurs in α quartz: one of the Si atoms (Si1) relaxes back and bonds to an O atom (O4), becoming fourfold coordinated while making the atom O4 threefold-coordinated (we call this the fourfold-puckered configuration); and (b) a novel form [shown in Fig. 1(c)] in which one of the Si atoms (Si1) relaxes back and bonds to both an O atom (O4) and a Si atom, the net result being two fivefold-coordinated Si atoms and a threefold-coordinated O atom (we call this the fivefold-puckered configuration). For both puckered configurations, the puckered Si atom (Si1) is positively charged while there is an unpaired electron localized on the other Si atom (Si0) (neutral dangling bond). In both cases, when an electron is added, the dimer configuration is lowest in energy, but there is a key difference: The fourfold-puckered configuration is metastable similar to O vacancies in α quartz, with a barrier typically ranging from 0.4 to 0.8 eV, but in some cases the barrier can be as large as 1.2 eV (the saddle point always seems to be when the Si atom is at the center of the triangle defined by its three original O neighbors), while the fivefold one is unstable (barriers less than 0.05 eV may be present) (see Fig. 2). In other words, upon addition of an electron, the fourfold configuration remains puckered, whereas the added electron goes to fill the dangling bond rather than to the positively charged puckered Si atom, forming a nonzero dipole between Si0 and Si1. On the contrary, the fivefold configuration collapses to the dimer configuration without an energy barrier. In puckered configurations, the

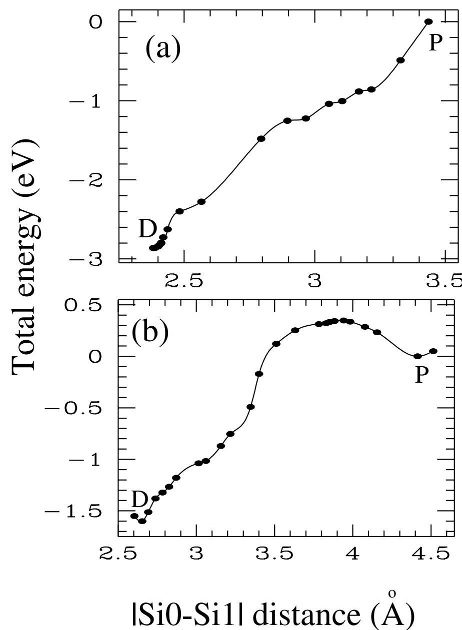

FIG. 2. Total energies following electron capture by positively charged (a) fivefold pucker and (b) fourfold pucker. P denotes pucker position and D denotes dimer position.

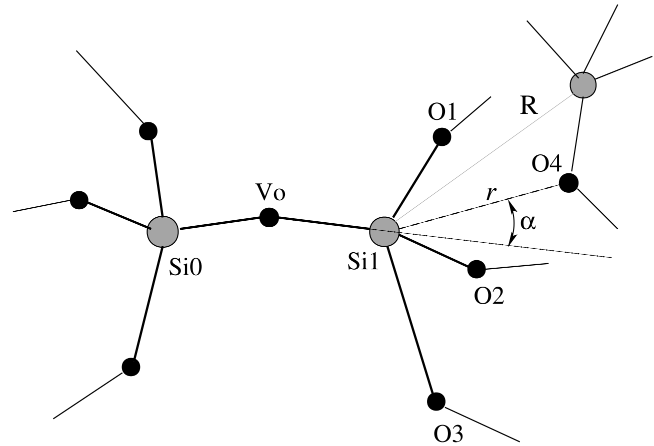

FIG. 3. Schematics illustrating the rules for fourfold and fivefold puckers after removing an O (V_o) and capturing a hole as described in the text.

localized energy levels (both one electron and two electron) are quite deep, nearly in the middle of the SiO_2 energy gap, ~4.5 eV above the valence-band edge and the centers definitely have positive U. The captured hole is bound quite strongly. That the localized energy level moves up in energy by ~2 eV is somewhat surprising because it means that, upon puckering, the energy of the unpaired electron goes up by that amount. Clearly, the backbonding makes up for all that and more. In fact, we found that, on average, E'_γ centers are about 0.6 eV lower in energy than E'_δ centers. Thus, capture of a hole by the neutral dimer configuration of either of these vacancies leads to a stable positively charged puckered defect. There is no barrier or a small barrier less than 0.1 eV found. The wave function of the unpaired electron (dangling bond) is essentially the same in the two cases [see Figs. 1(b) and 1(c)] so that they would be indistinguishable by EPR as E'_γ. Thus, the same EPR signal corresponds to two point defects with differing structures.

Examination of the local bonding that prevails at different O sites in our supercells and comparisons with the resulting type of vacancy reveal the following criteria that determine which type of behavior an O vacancy will exhibit upon hole capture (schematically shown in Fig. 3): (a) fourfold-puckered configuration [a Si atom (Si1) neighboring an O vacancy puckers through the plane formed by its three O neighbors (O1, O2, and O3) and acquires fourfold coordination if there is a fourth O (O4) on the backside within a radius r between 3.2 and 3.8 Å and an angle α less than 30° and its nearest neighbors have a radius R greater than 3.8 Å]; (b) fivefold-puckered configuration [a Si atom (Si1) neighboring an O vacancy puckers through the plane formed by its three O neighbors (O1, O2, and O3) and acquires fivefold coordination if there is a fourth O (O4) on the backside within a radius r between 2.5 and 3.2 Å and an angle α of less than 15°. In this cases, the target back side O atom typically has a Si neighbor that presents itself for the additional bond. This Si-Si bond has substantial electron density to qualify as a real bond (~ 30% of a Si-Si bond in crystalline Si, where no oxygen atoms are present to draw away electrons).]; (c) dimer configuration [all other geometries].

After the criteria were formulated, they were used to predict the behavior of vacancies at several sites and their predictions were confirmed. Overall, we collected the following statistics by performing a computerized check of the local topologies of all oxygen sites in a million-atom cell [15]: Nearly 80% of the sites are dimer precursors, 12% are fourfold-puckered precursors, and 8% are fivefold-puckered precursors. The actual percentages of defects in real devices will vary with material fabrication process, which reflects the wide variety of response that one can observe in irradiated SiO_2 [6–14]. We also checked the relative formation energies of the various types of vacancies and found them to be about the same on average. Thus, all O sites have equal probability of becoming a vacancy since the density of preexisting O vacancies in thermal oxides is governed by thermodynamics, which is consistent with this observation [7,10]. Thus, most O vacancies are indeed E'_δ precursors, with small but comparable percentages of puckered fourfold and puckered fivefold E'_γ precursors.

We are now ready to construct a composite picture of the dynamics of O vacancies in irradiated or stressed thermal oxides in the context of the experimental data. Thermal oxides usually contain significant concentrations of O vacancies. Our statistics suggest that as

many as 80% of these O vacancies may be precursors of E'_δ centers. As we saw above, the holes captured in dimers have a short lifetime. Those holes that are released either get recaptured at other dimer precursor sites or at puckered-precursor sites. Since the latter capture holes in stable states, the process will gradually lead to a reduction of the density of E'_δ centers and an increase in the density of E'_γ centers, as observed experimentally [7]. Moreover, the metastable trapping of holes in dimer defects may be difficult to distinguish from the "retarded" hole transport observed in oxides with high vacancy densities [20]. We note that hydrogen and O vacancy-hydrogen interactions can also play a significant role in determining MOS oxide trap charge, as discussed elsewhere [21,22].

We now turn to the behavior of puckered positively charged O vacancies near the Si-SiO_2 interface during postirradiation switched-bias annealing [12–14]. It is immediately obvious that, under positive bias, driving electrons to the fivefold-puckered configurations causes them to collapse to neutral dimers. Further negative or positive bias annealing has no effect. In contrast, driving electrons to the fourfold-puckered configurations simply places an electron into the dangling bond, while the puckered configuration remains, but a dipole complex forms. Reverse-bias annealing can easily destroy the dipole, driving the electron away, "restoring the hole." The hole on the puckered Si atom of course has been there all along. This is consistent with the data of both Schwank *et al.* and Lelis *et al.*, as well as much other work on the reversibility of trapped positive charge in irradiated or stressed SiO_2 [12–14]. The results further confirm the model proposed by Lelis *et al.* to account for the cycling of the restored positive charge by bias switching [13]. The cycling positive charge can diminish over time because the barriers for the collapse of metastable neutral puckered fourfold configuration are typically not large.

In summary, we have used first-principles calculations to show that O vacancies in amorphous SiO_2 have a much richer structure than in crystalline quartz because of local variations in topology. There are three distinct types of defects (dimer, fourfold pucker, and fivefold pucker) that can be used to account for the complex dynamics of electron and hole trapping and detrapping in irradiated or stressed SiO_2.

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[1] R. A. Weeks, J. Appl. Phys. **27**, 1376 (1956).
[2] D. L. Griscom, Phys. Rev. B **20**, 1823 (1979).
[3] F. J. Feigl, W. B. Fowler, and K. L. Yip, Solid State Commun. **14**, 225 (1974).
[4] J. K. Rudra and W. B. Fowler, Phys. Rev. B **35**, 8223 (1987).
[5] M. Boero, A. Pasquarello, J. Sarnthein, and R. Car, Phys. Rev. Lett. **78**, 887 (1997).
[6] W. L. Warren *et al.*, J. Electrochem. Soc. **139**, 872 (1992); J. F. Conley *et al.*, J. Appl. Phys. **76**, 2872 (1994); W. L. Warren *et al.*, IEEE Trans. Nucl. Sci. **40**, 1755 (1993).
[7] W. L. Warren *et al.*, IEEE Trans. Nucl. Sci. **41**, 1817 (1994).
[8] E. P. O'Reilly and J. Robertson, Phys. Rev. B **27**, 3780 (1983).
[9] P. M. Lenahan and P. V. Dressendorfer, J. Appl. Phys. **55**, 3495 (1984); T. H. Ning and H. N. Yu, *ibid.* **45**, 5373 (1974); D. M. Fleetwood and N. S. Saks, *ibid.* **79**, 1583 (1996).
[10] P. M. Lenahan and J. M. Conley, Jr., IEEE Trans. Nucl. Sci. **45**, 2413 (1998).
[11] J. R. Chavez *et al.*, IEEE Trans. Nucl. Sci. **44**, 1799 (1997).
[12] J. R. Schwank *et al.*, IEEE Trans. Nucl. Sci. **31**, 1434 (1984).
[13] A. J. Lelis, H. E. Boesch, T. R. Oldham, and F. B. McLean, IEEE Trans. Nucl. Sci. **35**, 1186 (1988); A. J. Lelis, T. R. Oldham, H. E. Boesch, and F. B. McLean, *ibid.* **36**, 1808 (1989); S. P. Karna *et al.*, IEEE Trans. Nucl. Sci. **47**, 2316 (2000).
[14] D. M. Fleetwood *et al.*, Appl. Phys. Lett. **74**, 2969 (1999); D. M. Fleetwood *et al.*, IEEE Trans. Nucl. Sci. **40**, 1323 (1993).
[15] This million-atom cell was generated by Laurent Van Brutzel and Aiichiro Nakano at Louisiana State University. It contains 395 136 Si atoms and 790 272 O atoms. The corresponding density is 2.21 g/cm^3.
[16] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[17] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[18] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[19] The creation procedure is documented by J. Sarnthein, A. Pasquarello, and R. Car, Phys. Rev. Lett. **74**, 4682 (1995); **52**, 12690 (1995).
[20] F. B. McLean, H. E. Boesch, Jr., and T. R. Oldham, *Ionizing Radiation Effects in MOS Devices and Circuits*, edited by T. P. Ma and P. V. Dressendorfer (Wiley, New York, 1989), pp. 87–192.
[21] V. V. Afanas'ev and A. Stesmans, Europhys. Lett. **53**, 233 (2001).
[22] S. T. Pantelides *et al.*, IEEE Trans. Nucl. Sci. **47**, 2262 (2000).