First-Principles Investigation of Low Energy E' Center Precursors in Amorphous Silica

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We show that oxygen vacancies are not necessary for the formation of E' centers in amorphous SiO_2 and that a single O deficiency can lead to two charge traps. Employing molecular dynamics with a reactive potential and density functional theory, we generate an ensemble of stoichiometric and oxygen-deficient amorphous SiO_2 atomic structures and identify low-energy network defects. Three-coordinated Si atoms appear in several low-energy defects both in stoichiometric and O-deficient samples where, in addition to the neutral oxygen vacancy, they appear as isolated defects.

Amorphous silicon dioxide (a-SiO_2) is important in many technological applications, from microelectronics to optical transmission media. Whether generated by manufacturing, irradiation, or even mechanical deformation, defects capable of trapping charge in a-SiO_2 are responsible for degrading device performance, leading to threshold voltage shifts in metal-oxide-semiconductor transistors, actuation voltage changes in microelectromechanical systems, and attenuation in optical fibers. The experimentally observed families of E' centers are associated with trapping charge and are believed to play an important role in this degradation [1,2].

The correlation between three-coordinated Si precursors (III-Si) and E' centers in silica is firmly established, with electronic structure calculations on proposed atomic models [1,2] predicting spectroscopic features in good agreement with electron paramagnetic resonance (EPR) experiments [3,4]. However, significant challenges remain; the high concentration of E' centers observed experimentally in stoichiometric a-SiO_2 (see, for example, Ref. [5]) cannot be explained by current models of a-SiO_2, all of which assume an oxygen vacancy to be the origin of the defects. Besides their local coordination, definitive structural models for these defects remain debatable, as does their formation under differing glass forming conditions. Using a combination of molecular dynamics (MD) and density functional theory (DFT), we predict that III-Si precursor centers occur as part of several low-energy defects both in oxygen-deficient and stoichiometrically perfect a-SiO_2 samples, showing that an oxygen vacancy is not necessary to form E' centers in a-SiO_2 (similar to findings in α-quartz by Boero, Oshiyama, and Silvestrelli [6]).

The commonly proposed E'_γ and E'_δ precursor in a-SiO_2 is a neutral oxygen vacancy (NOV), a missing O atom that leaves behind a Si-Si pair. Theoretical calculations have shown that an EPR-active center occurs when one of the silicon atoms retreats from the oxygen vacant site and

becomes tetrahedrally coordinated with another oxygen atom in the amorphous network, known as the puckered configuration [3]. The resulting structure leaves an unpaired electron spin localized on a single silicon sp^3 hybrid orbital and has spectroscopic signals consistent with the EPR experiments on the E'_γ center. Electronic structure calculations have also shown that if the Si-Si bond in a NOV captures a hole and remains a dimer, the resulting properties agree well with the E'_δ EPR signals [3,4]; this time the unpaired electron spin is delocalized over a pair of silicon sp^3 hybrid orbitals. Our calculations predict the NOV to be a common defect in oxygen-deficient samples but, more interestingly, that isolated III-Si atoms appear in several common native defects. This indicates the presence of a more direct precursor to the E'_γ center than the NOV in both oxygen-deficient and stoichiometric samples.

One of the key factors hindering progress in this field is that the prediction of well-equilibrated atomic structures representative of amorphous materials remains a significant computational challenge. It requires both an accurate atomistic description of configurational energies, including defects, and an extensive exploration of configuration space to avoid getting trapped in unphysical high-energy structures, as often occurs with fast quenches. To address this challenge, we combine MD simulations using the reactive potential REAXFF with a slow annealing procedure designed to minimize artifacts seen in previous studies, followed by energy minimization using DFT to refine the candidate amorphous models and obtain their energies. The REAXFF force field we use is based on *ab initio* calculations of silicon and silica [7] including the equation of state of various phases as well as the structure and energetics of small molecules. The MD simulations are performed with a Berendsen thermostat and barostat with coupling constants of 10 fs and 5000 fs, respectively. The DFT calculations use SEQQUEST [8], in the generalized gradient approximation by Perdew, Burke, and Ernzerhof [9] with Troullier-Martins

pseudopotentials [10] for oxygen and a Hamann pseudo-potential [11] for silicon, and double-zeta plus polarization basis sets. The Γ point was adequate for Brillouin-zone integration for the large supercells used in the amorphous models [12]. Additional simulation details are described in the supplemental material together with the REAXFF force field parameter file [12].

Initial structures with 72 and 192 atoms were generated by replicating the 9-atom trigonal α-quartz and 24-atom β-cristobalite unit cells twice along each cell vector and transforming the resulting structures into orthogonal cells. We then performed 5 independent 1500 ps long MD simulations for each supercell at 4000 K and a density of 2.3 g/cm^3 (atmospheric pressure) to melt and randomize the structures. From each MD run we selected 12 independent liquid configurations, the first at 400 ps and one every 100 ps thereafter, for a total of 60 well-equilibrated, stoichiometric liquid samples for each cell size. We generated 60 oxygen-deficient samples for each size repeating the procedure above, first removing one oxygen atom at random from each initial structure prior to the $T = 4000$ K liquid runs. Each sample, stoichiometric and oxygen-deficient, was then slowly annealed from 4000 K to 300 K under isobaric conditions at a rate of 1.67 K/ps. This rate is slower than those used in previous studies [13,14], and results in well-annealed a-SiO$_2$ structures with a lower incidence of unphysical network artifacts. All samples were treated as neutral, with no net charge.

Each resulting amorphous structure (60 stoichiometrically perfect and 60 oxygen deficient for each size) was relaxed using DFT energy minimization with respect to atomic positions. The average density of the cells (predicted by REAXFF) 2.22 ± 0.18 g/cm^3 is in good agreement with the experimental values of 2.20 g/cm^3 (applicable to high purity fused silica used in optical fibers [15]), and 2.23–2.27 (applicable to thermally oxidized silica used in metal-oxide-semiconductor field-effect transistor devices [16]). Finally, a structural analysis was performed to identify and classify the structures and their defects. A defect-free a-SiO$_2$ structure is defined as a continuous random network of SiO$_4$ tetrahedra with twofold coordinated bridging oxygen atoms. To identify defects, we calculate the coordination number of every atom using a bond cutoff of 2 Å. For the stoichiometric samples, 75% and 37% of the 72- and 192-atom cells are defect-free, respectively. Most of the remaining stoichiometric cells exhibit a single isolated defect or defect pair. For the oxygen-deficient samples, 97% of the 71-atom cells and 70% of the 191-atom cells contain only a single isolated defect or minimum defect pair needed to accommodate a missing oxygen atom. All 240 structures obtained together with a description of their defects are available electronically as supplemental material [12].

Figures 1 and 2 show typical atomic configurations of defects in stoichiometric and oxygen-deficient a-SiO$_2$, respectively; Figs. 3(b)–3(f) show the distributions of formation energies of each defect type. All energies quoted here correspond to DFT relaxed structures for the 192- and 191-atom systems at $T = 0$ K (zero point energy is not taken into account). The smaller cells yield similar defect energies, shown in the supplemental material [12]. It is important to note the large variations in defect formation energy (see Fig. 3) due to the amorphous nature of the structures. As was discussed in Ref. [17] this underscores the importance of generating and analyzing ensembles of representative structures as opposed to drawing conclusions from a single calculation.

Defect formation energies are presented with respect to amorphous silica in the oxygen rich limit. The amorphous silica reference cell energy, $E_{a\text{-SiO}_2}$, is taken to be the average energy of all defect-free stoichiometric samples [see Fig. 3(a)], and the oxygen reference E_{O_2} is the energy of a spin-polarized DFT calculation of an oxygen molecule in the triplet ground state. The formation energy (E_f) for the defects in oxygen-deficient samples is obtained from the energy of the defective sample ($E_{a\text{-SiO}_2}^{\text{def}}$), E_{O_2}, and $E_{a\text{-SiO}_2}$:

$$E_f = E_{a\text{-SiO}_2}^{\text{def}} + \frac{1}{2}E_{O_2} - E_{a\text{-SiO}_2} \qquad (1)$$

The defect formation energies in the Si-rich limit (given in the supplemental material [12]) can be obtained from the O-rich values using the computed heat of formation of α-quartz from diamond Si and O$_2$ (8.12 eV/SiO$_2$) and the computed heat of amorphization to form a-SiO$_2$ from α-quartz (0.23 eV/SiO$_2$).

The most common defects observed in stoichiometric samples are (i) a pair of threefold and fivefold coordinated Si atoms (III-Si/V-Si), Fig. 1(a), and (ii) a threefold oxygen and fivefold silicon pair (III-O/V-Si), Fig. 1(b). The III-Si/V-Si has the lowest formation energy of all reported defects at about 1.7 eV [Fig. 3(b)]. This is a surprisingly low-energy, similar to the amorphization energy of only 8 SiO$_2$ formula units. Three- and fivefold Si have been reported in previous simulations [13,17]—fast cooling rates in MD simulation tend to artificially trap large numbers of these defects—however, their formation energy has not been reported. Their appearance as isolated defect pairs in our simulations with slower cooling rates and low formation energies indicates that III-Si and V-Si are likely native defects in a-SiO$_2$. Fivefold silicon atoms,
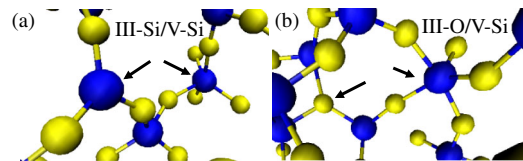

FIG. 1 (color online). Defects in stoichiometric samples. (a) A pair of threefold and fivefold coordinated silicon atoms (III-Si/V-Si). The undercoordinated silicon has a dangling bond and could be a precursor to the E'_γ center without an oxygen vacancy. The low formation energy suggests that this is likely a native defect in a-SiO$_2$. (b) A pair of 3-coordinated oxygen and 5-coordinated silicon atoms (III-O/V-Si). We find that III-O forms with a formation energy ~0.5 eV higher than III-Si.
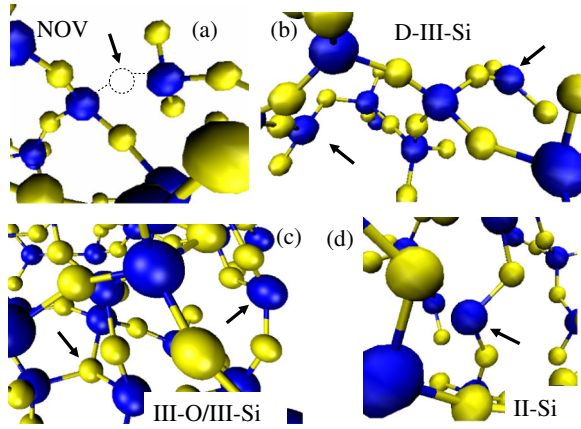
FIG. 2 (color online). Defects in oxygen-deficient samples.
(a) A NOV in which two silicon atoms share a missing oxygen
site and usually form a Si-Si bond; this is the typically assumed
E' precursor. (b) Two dissociated 3-coordinated silicon atoms
(D-III-Si); the Si atoms do not share a single oxygen vacancy site
resulting in two more direct E'_γ precursors than the NOV.
(c) A 3-coordinated oxygen and 3-coordinated silicon pair
(III-O/III-Si); the III-Si is a E'_γ precursor and the III-O occurs
with formation energy ~ 0.7 eV higher than the III-Si. (d) A
twofold coordinated silicon atom (II-Si), hypothesized as a
precursor to an E'_α center.

FIG. 3. Histograms of defect formation energies. The long-
dashed line indicates the average energy of *all* defect-free
samples ($E_{a\text{-}SiO_2}$) and short-dashed lines indicate the average
formation energy E_f of each defect. (b) and (c) show data for
defects found in the stoichiometric samples, and (d), (e), and
(f) for the oxygen-deficient samples.

V-Si, in a-SiO$_2$ have been tentatively identified in solid-
state nuclear magnetic resonance studies [18], thus
suggesting the existence of a compensating companion
III-Si, a direct precursor to E'_γ centers. The second impor-
tant defect found in stoichiometric systems is the
III-O/V-Si pair with formation energy about 0.5 eV higher
than the III-Si/V-Si [Fig. 3(c)]. Overcoordinated oxygen
has been observed in prior MD and DFT studies of vitreous
silica and has been hypothesized to play a significant role
allowing the amorphous network to generate during silicon
oxidation [19]. Our DFT calculations show the III-O to
form approximately planar structures with three Si-O
bonds that are, in average, 0.2 Å longer than those among
perfectly coordinated Si and O atoms. The III-O, just as
overcoordinated O atoms bonding with hydrogen [20],
may trap holes and III-O atoms have been hypothesized
in aluminosilicate glasses to explain NMR [21].

We now turn our attention to oxygen-deficient samples.
As expected from prior studies, the NOV is frequently
observed in these samples; shown in Fig. 2(a) this defect
is the typically assumed precursor for E'_γ and E'_δ centers.
Previous DFT–local-density-approximation calculations
have reported the average NOV formation energy as
5.6 eV [22] (O-rich limit), which is significantly higher
than our average value of 4.4 eV [see Fig. 3(d)]. This is
likely a product of strain relaxation with some influence
from the different choice of functional; each simulation
cell in our work is annealed with a missing oxygen from
the melt and relaxed, as opposed to annealing a stoi-
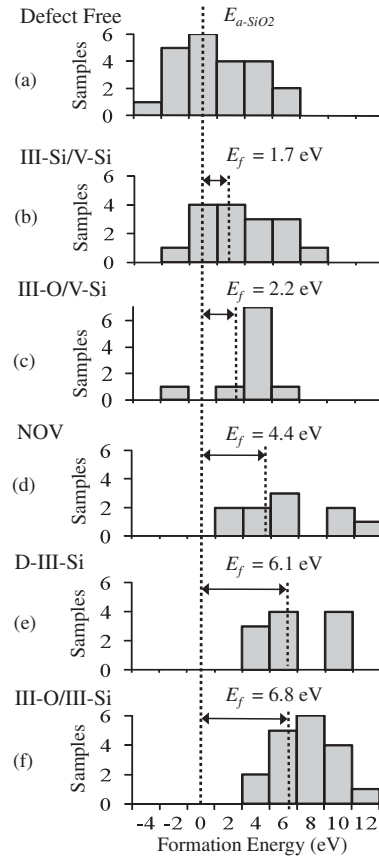chiometric sample and then removing a network
oxygen.

A more interesting defect to emerge from these oxygen-
deficient simulations is a pair of dissociated threefold
silicon atoms (D-III-Si) [see Fig. 2(b)]. This defect can
be described as a dissociated oxygen vacancy; the two
threefold silicon atoms in the D-III-Si pair do not share
an oxygen vacancy site (as in the NOV). Each of the two
III-Si defects is a more direct structural precursor to an E'_γ
center than the NOV; it does not require a Si atom to pucker
away from a dimer configuration. Furthermore, both under-
coordinated Si atoms are E'_γ precursors, leading to two
charge traps per oxygen deficiency. While the average
formation energy of the dissociated III-Si pair is
~ 1.5 eV [Fig. 3(e)] higher than of the NOV, it is entropi-
cally favored since the location of the two Si atoms need
not be correlated. In our simulations both defects appear
with very similar probabilities (17% for NOV and 18% for
D-III-Si). This indicates that isolated III-Si are likely com-
mon defects in oxygen-deficient a-SiO$_2$.

Another common defect observed in the oxygen-
deficient samples has an overcoordinated oxygen and
an undercoordinated silicon (III-O/III-Si) [see Figs. 2(c)
and 3(f)]. This pair of defects again yields a possible E'
precursor with the III-Si, and the appearance of III-O is

analogous to the III-O/V-Si defect observed in stoichiometric samples. Finally, three of the oxygen-deficient samples contained an isolated divalent silicon (II-Si) with average formation energy of 3.0 eV. This defect, denoted ODC(II) in the past, is shown in Fig. 2(d) and has been attributed an optical absorption peak in luminescence polarization experiments [2]. The II-Si has been hypothesized as a precursor to other types of E' centers [1].

It is interesting to note that III-O/V-Si and III-Si/V-Si defects in stoichiometric samples have average formation energies within an electron volt, as do the D-III-Si and III-O/III-Si defects in oxygen-deficient samples. This indicates that formation energy of the III-O is fairly close to the III-Si, and that these defects may be present in a-SiO$_2$ in comparable concentrations.

In summary, we used MD simulations with an accurate reactive force field and DFT calculations to identify nonvacancy network defects in a-SiO$_2$ that can act as precursors to E' centers. We have shown that III-Si atoms, known precursors to E' centers, are low-energy defects not only in O-deficient environments but also in samples with perfect stoichiometry down to the ~$(1.5 \text{ nm})^3$ scale, which provides a plausible explanation for the unexplained abundance of E' centers observed experimentally in stoichiometric a-SiO$_2$ [5]. Furthermore, we find that in oxygen-deficient cases III-Si atoms appear not only as NOV's but also as dissociated defects, and yield two E' precursors per oxygen deficiency. We also find that over-coordinated O atoms are low-energy defects both in stoichiometric and oxygen-deficient samples; these defects can also play an important role in charge trapping. These low-energy defects and defect pairs emerge directly from well-equilibrated samples obtained via unbiased MD simulations from the melt, rather than from assumptions in the construction of the model. This statistical relaxed-defect approach is generally applicable to a wide range of amorphous materials including those for which little is known about possible defects and to explore new materials where no experimental data are available. The accuracy and reliability of the predictions depend on analysis of an extensive ensemble of structural models generated by MD simulations that contain a statistically meaningful sampling of the dominant defects. This requires fast and accurate interatomic MD potentials and quenching rates slow enough to avoid freezing in high-energy artifacts.

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