Theory of the Self-Trapped Hole in a-SiO$_2$

Arthur H. Edwards

Department of Electrical Engineering, University of North Carolina at Charlotte, Charlotte, North Carolina 28223

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We present the first calculation of the self-trapped hole in a-SiO$_2$ that exhibits strong localization on one oxygen atom. This calculation was performed using both semiempirical and *ab initio* molecular orbital methods applied to finite clusters of atoms. The self-trapping is accompanied by a network distortion in which the two nearest-neighbor silicon atoms relax away from the self-trapped hole site along the Si-O bond directions. Our calculated ^{17}O and ^{29}Si hyperfine interactions are in very good agreement with experiment.

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Understanding the charge traps in a-SiO$_2$ is crucial for reliable fabrication of radiation tolerant metal-oxide semiconductor devices. Many groups have contributed to this understanding, using a variety of experimental [1–8] and theoretical [9–13] techniques. In Fig. 1 we show the three most prevalent room temperature, intrinsic defects that have been identified unambiguously to date: The E_γ' center [Fig. 1(a)], the nonbridging oxygen-related hole center (NBOHC) [Fig. 1(b)], and the superoxide radical [Fig. 1(c)]. While these defects are intrinsic, they require local nonstoichiometry, either vacancies or interstitials, in the idealized SiO$_2$ network. Another class of intrinsic defects, considered more fundamental, arise from carrier self-trapping within the ideal structure. Self-trapping is not guaranteed, but depends on the strength of the electron-phonon interaction, on the width of the band from which the carrier self-traps, and, in some cases, on disorder [14]. Self-trapping has been explored earlier in the alkali halides. The self-trapped hole (STH), or V_k center, arises when a hole localizes on two halogen atoms through a large lattice relaxation [15]. The self-trapped exciton (STE) has also been studied. This defect has as its core the V_k center [16].

Self-trapping had been predicted in SiO$_2$ [17] sixteen years ago. Only recently, however, two self-trapped species have been observed. First, Hayes and co-workers observed the self-trapped, triplet exciton in α-quartz [18]. Second, the ESR experiments of Hayes and Jenkin [19] and of Griscom [20] have led to the identification of the STH in a-SiO$_2$. To review briefly, Hayes and Jenkin identified a hole trap in α-quartz wherein the hole is completely localized on a bridging oxygen with one nearest-neighbor germanium. While this group was unable to observe a similar ESR spectrum in undoped α-quartz, Griscom has seen it in irradiated a-SiO$_2$. In fact, Griscom identified two ESR spectra, labeled STH$_1$ and STH$_2$, that he has attributed to self-trapped holes. According to Griscom's models, STH$_1$ is the intrinsic analog to the germanium-trapped hole observed by Hayes and Jenkin. The STH$_2$ signal is assumed to arise from a hole trapped on two oxygen atoms. The STH and the STE are not observed above 160 K.

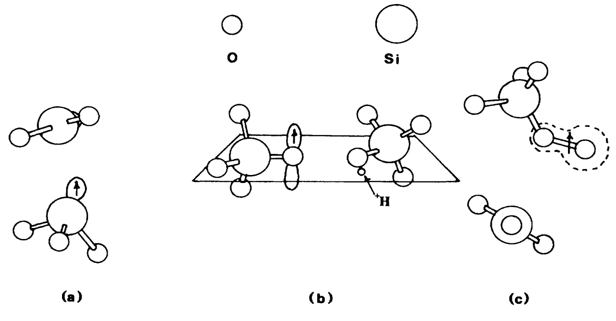

FIG. 1. The three principal, room temperature intrinsic defects in a-SiO$_2$. (a) The E_γ' center, (b) the nonbridging oxygen hole-trapping center (NBOHC), and (c) the superoxide radical.

In addition to the ESR data, there are optical data for both the Ge-trapped hole in α-quartz [21] and the STH in a-SiO$_2$ [22]. These defects have absorption bands centered at 2.25 eV.

Theoretical studies of the STH and STE have also been undertaken recently. Fisher and co-workers have reported the first calculation of a self-trapped exciton in α-quartz [23], while Shluger and Stefanovich have studied it in a finite cluster [24], and in ideal β-cristobalite [25]. All three calculations indicate that the hole localizes on one oxygen atom, and that the electron localizes on the two nearest-neighbor silicon atoms. To date, the STH has eluded correct theoretical treatment. Chernov and co-workers have reported a calculation of a hole in a-SiO$_2$ [22]. In this calculation, the hole was delocalized over all of the oxygen atoms in the cluster. In this Letter, we report the first calculation of a truly self-trapped hole in a-SiO$_2$. Our calculations support Griscom's model for STH$_1$ and they reveal the lattice relaxation that leads to self-trapping. We obtained this result using the same semiempirical Hamiltonian as Chernov *et al.* on a similar molecular cluster. However, our results are dramatically different. Furthermore, we were unable to reproduce their results. We have also performed *ab initio* calculations on a smaller cluster (Si$_2$O$_7$H$_6$) that agree with our semiempirical calculations.

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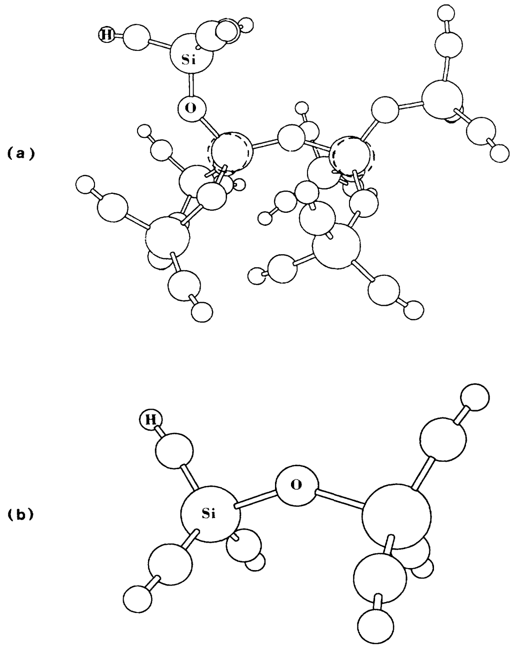

FIG. 2. Atomic clusters used in the present calculations. (a) Cluster used for large, semiempirical calculations. (b) Cluster used for *ab initio* calculations, and for small semiempirical calculations.

TABLE I. Equilibrium geometry for the neutral and positively charged unstrained cluster shown in Fig. 2. Subscripts: c = central; NN = nearest neighbors; NNN = next-nearest neighbors; o = outer; LHS and RHS are with respect to the central oxygen atom.

Geometric parameter	Neutral	Positive
$R_{\mathrm{O}_c,\mathrm{Si}_{\mathrm{NN}}}$	1.65 Å,1.64 Å	1.722 Å,1.759 Å
$\measuredangle \mathrm{Si}_{\mathrm{NN}} - \mathrm{O}_c - \mathrm{Si}_{\mathrm{NN}}$	146°	147°
$R_{\mathrm{Si}_{\mathrm{NN}}-\mathrm{O}_{\mathrm{NNN}}[\mathrm{RHS}]}$	1.64 Å	1.615 Å
$R_{\mathrm{Si}_{\mathrm{NN}}-\mathrm{O}_{\mathrm{NNN}}[\mathrm{LHS}]}$	1.65 Å	1.61 Å
$\langle R_{\mathrm{O}_{\mathrm{NNN}}\mathrm{Si}_o[\mathrm{RHS}]}\rangle$	1.64 Å	1.65 Å
$\langle R_{\mathrm{O}_{\mathrm{NNN}},\mathrm{Si}_o[\mathrm{LHS}]}\rangle$	1.62 Å	1.65 Å
$\langle \measuredangle \mathrm{Si}_{\mathrm{NN}} - \mathrm{O}_{\mathrm{NNN}} - \mathrm{Si}_o \rangle_{[\mathrm{RHS}]}$	140°	141°
$\langle \measuredangle \mathrm{Si}_{\mathrm{NN}} - \mathrm{O}_{\mathrm{NNN}} - \mathrm{Si}_o \rangle_{[\mathrm{LHS}]}$	145°	141°

Method of calculation.— In the semiempirical calculations we have used a finite atomic cluster shown in Fig. 2(a). We have chosen the cluster geometry in the following manner. All Si-O bonds were set at 1.63 Å (the equilibrium Si-O bond length for the semiempirical Hamiltonian we use), all O-Si-O angles were set at 109.5°, and all Si-O-Si angles were set at 144°. The dihedral angles were varied arbitrarily to simulate the amorphous network. Finally the O-H bond lengths were fixed at 0.92 Å and the Si-O-H angles were fixed at 170°. To calculate the total energy for this cluster we used MOPN [26], an unrestricted Hartree-Fock version of MINDO/3 [27]. We used a version of MOPN that was modified by Deak and co-workers to include several algorithms that improve convergence dramatically. In our calculation, we hold the outer $\mathrm{Si(OH)_3}$ units fixed, but allow the inner seven oxygen atoms and two silicon atoms to relax. We have calculated equilibrium geometries and electronic structures in both the neutral and positive charge states. The *ab initio* calculations were performed on the cluster shown in Fig. 2(b) using Gaussian-92 [28] and GAMESS [29] with the 6-31G** basis. We compared these results to semiempirical calculations on the same cluster.

Calculated results.— In the second column of Table I we show the geometrical parameters for the internal atoms ($\mathrm{O_1}$-$\mathrm{O_7}$,$\mathrm{Si_1}$-$\mathrm{Si_2}$) for the neutral charge state. The bond lengths are within 0.04 Å of the experimental value for α-quartz. This is to be expected because of the constraints placed on the outer $\mathrm{SiO_3H_3}$ groups. In the second column of Table II we show the calculated net charges on all the heavy atoms in the neutral cluster. Note that the oxygen atoms all have nearly identical charges, as do all silicon atoms. We believe this indicates that termination in OH groups results is a relatively mild perturbation of the electronic structure. This belief is reinforced by the very small component ($< 0.3\%$) of H 1s character in the molecular orbitals that correspond to the top of the $\mathrm{SiO_2}$ valence band.

In the third column of Tables I and II we show the calculated geometry and atomic charges in the +1 charge state. We note several features of these results. First, the positive charge is strongly localized on the central oxygen atom. This is reflected in the net change in charge on $\mathrm{O_1}$ ($+0.424e$). Second, as shown in Fig. 2(a), the network relaxation is also strongly localized on the central three

TABLE II. Charges on silicon and oxygen atoms in units of e for the neutral and positively charged cluster. Subscripts are the same as in Table I.

Atom/Group	Neutral	Positive
O_c	-0.673	-0.249
$\mathrm{Si}_{\mathrm{NN}}$	1.375	1.371
$\mathrm{O}_{\mathrm{NNN}}$	Between -0.637 and -0.670	Between -0.639 and -0.662
Si_o	1.46	Between 1.473 and 1.479
O_o	Between -0.681 and -0.704	Between -0.672 and -0.696

TABLE III. Calculated and experimental values for the ^{29}Si hyperfine tensor for the STH$_1$ defect.

	$A_1(1)$ (mT)	$A_2(1)$ (mT)	$A_3(1)$ (mT)	$A_1(2)$ (mT)	$A_2(2)$ (mT)	$A_3(2)$ (mT)
Calculated	0.75	0.71	0.62	0.63	0.60	0.52
Expt. Ref. [20]	0.8	0.8	0.8	0.8	0.8	0.8

TABLE IV. Calculated and experimental values for the ^{17}O hyperfine tensor for the STH$_1$ defect.

	A_1 (mT)	A_2 (mT)	A_3 (mT)
Calculated	12.1	0.77	0.58
Expt. Ref. [20]	11.4	~1.7	~1.7

atoms. The network relaxation is comprised almost completely of the motion of the two silicon nearest neighbors *away* from the central oxygen atom, along the silicon-oxygen bond direction.

The calculated distortion for the STH is different from that predicted for the STE where there is a lengthening of only one Si-O bond [23,25]. Fisher and co-workers [23] have postulated that, like the V_k center in alkali halides, the STH forms the core of the STE. The recent calculation of Shluger, Grimes, and Catlow [30] indicate that the trapping of the electron at the V_k center in LiCl is accompanied by an asymmetric motion of the Cl_2^- ion, so that even though the STH is the driver for the STE the final configuration is quite different. In SiO_2, this may well also be the case. The hole may trap first, but trapping the electron at the STH will require the shortening of one of the Si-O bonds.

Because these results were obtained from an oxygen-centered cluster there is the possibility that localization on the central atom is an artifact of this choice. However, there are several metastable states where the charge and spin are localized on one of the six second-shell oxygen atoms. These metastable states can be obtained by changing the initial positions of the nine interior atoms in the same fixed cage of $Si(OH)_3$ units. For example, if instead of placing Si$_1$ in Fig. 2(a) at the tetrahedral site, 1.63 Å from each nearest-neighbor oxygen atom, we displace it 0.1 Å away from O$_5$, along the Si$_1$-O$_5$ bond direction, and allow the cluster to relax, the equilibrium geometry retains this displacement and the charge and spin reside on O$_5$. While this geometry is metastable by 0.28 eV, part of this energy difference is an artifact of the rigid, terminating $Si(OH)_3$ units.

We turn now to the electron spin resonance (ESR) data. Recently, Griscom has published ESR data from samples enriched with both ^{29}Si and ^{17}O [20]. From these data he obtained a set of hyperfine parameters that fit the ESR spectra. The ^{29}Si parameters for that fit were taken from Ref. [19]. Also, only the largest of three principal values for the ^{17}O hyperfine parameters were optimized (fit to experiment). The other two were set equal to $A_\perp$ for the NBOHC. We have calculated values for the STH$_1$ model using a method described elsewhere [31]. Our calculated results, shown in Tables III and IV, are in very good agreement with Griscom's experimental data (also shown for comparison). We have also calculated the directions of the principal values. The ^{29}Si hyperfine tensors are essentially isotropic (the largest value points 3.4° away from the Si-O bond direction), while the ^{17}O hyperfine tensor has the principal axis for the largest value normal to the Si$_1$-O$_1$-Si$_2$ plane. The diagonal elements of the spin density matrix indicate that the spin is 94% localized in a 2*p* state on O$_1$. While our results are for a particular arrangement of nearest and next-nearest neighbors, the ^{17}O hyperfine results follow our expectations—the orbital composition of the top of the valence band of α-quartz is almost purely nonbonding O 2*p*.

The results reported here are in stark contrast to those reported by Chernov and co-workers [22]. Using the same semiempirical Hamiltonian they obtained results that indicated almost no localization. Because we were unable to reproduce their results, we performed *ab initio* calculations on a smaller cluster [Fig. 2(b)]. We allowed the central oxygen atom and the two silicon atoms to relax. The results were consistent with our semiempirical results. In the positive charge state, the silicon atoms moved 0.2 Å away from the central oxygen atom. The spin density was strongly localized (0.97) in a lone-pair oxygen *p* state, and the excess charge was localized on the central oxygen to an extent similar to our semiempirical results. Thus, the *ab initio* calculation is in essential agreement with our prediction of strong localization, and with experiment.

Finally, we have used the *ab initio* results to calculate the optical absorption cross section for this defect as a function of photon energy for excited states that could contribute to the 2.25 eV band. It is well known that the Hartree-Fock theory underestimates systematically the binding of unoccupied states. We recognized, however, that the valence band edge was a good lower bound for the excitation energy. Thus, we looked for large excitation cross sections from states within 2.25 eV of the highest occupied β-spin molecular orbital. The results are shown in Table V. These cross sections are very small because the transitions involve charge transfer from the defect atom to neighboring oxygen atoms. This could have been predicted from the following simple argument. The upper valence bands of SiO_2 are composed primarily of nonbonding oxygen 2*p* states. Thus, a strong, on-site *s*-*p* transition is not possible within 2.25 eV of the valence band edge. We would expect, then, that the dominant excitation would involve *p* orbitals from other oxygen atoms, and that the dipole matrix elements would scale

TABLE V. Calculated optical absorption cross sections for transitions that could contribute to the 2.25 eV absorption band.

$\varepsilon_{vb} - \varepsilon$ (eV)	σ (eV cm^{-2})	Polarization
0.73	1.1×10^{-18}	x
1.92	2.6×10^{-19}	y
2.48	3.6×10^{-19}	y
2.17	2.7×10^{-19}	z

with the overlap. We expect that the near neighbors contribute most strongly, so that the size of the *ab initio* cluster is less important than it might initially appear.

In summary, we have calculated the equilibrium geometry, ESR parameters, and optical properties for the STH_1 model of the self-trapped hole in *a*-$\mathrm{SiO_2}$. Our calculations are in very good agreement with Griscom's ESR data and lend support to the STH_1 model. Furthermore, the calculations indicate that there is a strongly localized network relaxation wherein the nearest-neighbor silicon atoms move 0.1 Å away from the oxygen on which the hole is self-trapped. Finally, our calculations of the optical properties reinforce the notion that the optical transitions involve charge transfer from the central oxygen to neighboring oxygen ions in the network.

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