New Fundamental Defects in α -SiO₂

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Abstract

The atomic structure and spin properties of two previously undescribed amorphous silicon dioxide fundamental point defects have been characterized for the first time by *ab initio* quantum mechanical calculations. Both defects are electrically neutral trivalent silicon centers in the oxide. One of the defects, the X-center, is determined to have an O₂Si≡Si[↑] atomic structure. The other defect, called the Y-center, is found to have an OSi₂≡Si[↑] structure. Calculated electronic and electrical properties of the new defect centers are consistent with the published characteristics of the oxide switching trap or border trap precursors.

I. INTRODUCTION

Throughout the three decades of research into radiation-induced degradation of metal-oxide-semiconductor (MOS) devices, investigators understood that point defects in the Si-SiO₂ structure (localized deviations from stoichiometrically pure Si and SiO₂) are responsible for many observed anomalies. Basic research in this area has progressed along two tracks: (i) differentiating the anomalies based upon subtle differences in their characteristic behavior, and (ii) precise description of the defects responsible for the anomalous behavior. These two research tracks are complementary since often a discovery in one area provides insight and ultimately leads to discoveries in the other.

The work reported here explores the electronic structure and spin properties of model defect clusters through extensive *ab initio* quantum-mechanical calculations. Comparing our calculated results for ESR hyperfine coupling constants with experimental results obtained by other researchers, we show that the local atomic structure of the X-center [1] is O₂Si≡Si[↑]. Furthermore, we show the S-center [2,3] to have the same origin and atomic structure as the X-center. The remaining member of the O_{3-n}Si_n≡Si_p[↑] defect family, i.e., the defect corresponding to n=2 which we call the Y-center, has not yet been observed.¹ However, our calculations suggest that the Y-center should be observable in Si-rich oxides. Analysis of the electrical properties of the X- and Y-centers suggest that, in their charge neutral state, both are relatively poor electron traps. Using a combination of the calculated electrical properties and geometrical features, we argue that the X- and Y-

centers belong to border trap family as suggested earlier by Fleetwood, *et al.* [4].

II. BACKGROUND

Extensive experimental studies of Si-SiO₂ point defects have identified two major species as charge traps in MOS systems: (i) trivalent Si centers at the Si-SiO₂ interface and (ii) oxygen vacancy centers (V_O) in the oxide. The interface trivalent Si defect, represented by a Si₃≡Si[↑] atomic structure and commonly referred to as the P_b center [5,6], is a neutral species with an unpaired electron in a dangling bond pointing into the oxide [7-14]. The V_O defects, on the other hand, have complex structure [1], involving more than one Si atom and often carry a positive electric charge [11]. A recent article by Helms and Poindexter [15] provides an excellent review on the microscopic structure of point defects in Si-SiO₂ systems. Among the neutral point defects in the oxide, an all-oxygen equivalent of the P_b center having an O₃≡Si[↑] atomic structure [16-18] is known as the hemi-E' center [17] (called E'_h-center hereafter), or the E'_s-center [19] (not to be confused with the S-center described later). Similar to the P_b center, the central Si atom of the E'_h-center contains an unpaired electron in a dangling bond. Both P_b and the E'_h-centers are known to be charge traps in MOS systems.

Between the structure of E'_h-centers in the oxide and the P_b-centers at the interface, there are two atomic structures, O₂Si≡Si[↑] and OSi₂≡Si[↑], that represent partially oxidized trivalent Si-centers. These centers constitute fundamental, V_O-related, native defects in SiO₂ and can exist in the oxide layer of the Si-SiO₂ system. These two E'-type centers (*three-fold coordinated paramagnetic Si centers bonded to varying number of O and Si atoms*) should possess electronic and electrical properties intermediate between the E'_h and the P_b centers. Thus one anticipates that these centers also play an important role as charge trap centers and, therefore, affect the reliability of MOS devices. Indeed, Fleetwood, *et al.* [4], have suggested the neutral E'-type centers with the atomic structure O_{3-n}Si_n≡Si_p[↑] (n=1 or 2) to be candidates as border trap precursors in MOS devices. There is also recent experimental evidence that reveals neutral E'-type centers are generated in Si-SiO₂ structures during post-oxidation high-temperature anneal [3].

¹ In the notation used here, an upward arrow, ↑, represents an unpaired electron and the p subscript denotes the paramagnetic Si center.

III. EXPERIMENTAL DATA

The first experimental evidence suggesting the existence of E'-type centers in α -SiO₂ was reported by Holzenkämpfer, *et al.* [20]. These authors observed a broad line in the electron spin resonance (ESR) spectrum of 250 keV He-ion implanted amorphous SiO_x ($1 < x < 2$) films and suggested that E'-type centers were responsible for part of the ESR signal. Later, Griscom, *et al.* [2], observed a solitary peak in the ESR spectrum of x-ray irradiated phospho-silicate (P₂O₅-SiO₂) glasses (PSG) upon vacuum annealing at an anneal temperature, $T_{an} \sim 727$ °C. Based on the similarity between the g-value they observed (2.0030) and those reported by Holzenkämpfer, *et al.* [20], Griscom, *et al.*, concluded that the source of the solitary peak in the ESR spectrum of the irradiated PSG was an E'-type center with O_{3-n}Si_n≡Si[†] (n=1 or 2) atomic structure. Due to the solitary nature of the ESR signal, Griscom, *et al.*, named this center the "S-center."

Recently, Stesmans and Afanas'ev [3] have observed similar ESR signals in standard oxide grown on Si after exposing the oxide to (post-oxidation) high-temperature vacuum anneal at $T_{an} \geq 960$ °C. The features of the ESR spectrum observed by these authors are strikingly similar to those observed by Griscom, *et al.* [2]. For example, the singlet peak has a broad and symmetric line shape with $g=2.0028$. Therefore, following Griscom, *et al.* [2], Stesmans and Afanas'ev [3] called the paramagnetic defect they observed "the S-center" and assigned it to an E'-type center with an unknown atomic structure. Additional experimental evidence suggesting the existence of E'-type centers in high-purity silica glass under heavy ion implantation has been reported by Hosono, *et al.* [21-23]. Hosono and Weeks [21] reported the ESR signals of E'-type centers which they called X-centers, in Cr⁺ implanted amorphous silicon dioxide (α -SiO₂). Similar ESR signals were later detected by Hosono, *et al.* [22], in other transition-metal-ion implanted α -SiO₂.

Figure 1. Energy minimized equilibrium structures of the model clusters used for the calculations on (a) E'_h-center, (b), (c) E'-type centers, and (d) Pb-center

It is important to note that none of the experiments [2,3,20-22] were successful in resolving the hyperfine structure of the ESR spectrum. Hyperfine spectra provide the most detailed information about the atomic structure of a paramagnetic center. The first hyperfine resolved ESR spectrum attributed to E'-type X-centers was reported by Hosono, *et al.* [23], in Si-implanted α -SiO₂. These authors were able to isolate signals corresponding to E'_h-, D- (P_b-center equivalent in α -SiO₂) and X-centers. The X-center was identified with a hyperfine doublet splitting of 230 G in the ESR spectrum. The hyperfine splitting of the ESR spectrum in combination with other known characteristics [2,20] lead Hosono, *et al.* [23] to identify the X center as one of the E'-type defects. However, these authors were unable to establish whether the X center resulted from an O₂Si≡Si[†] or an OSi₂≡Si[†] atomic structure. Thus, the uncertainty concerning the microscopic structure of the X center remained.

It is evident that the S- or the X- E'-type centers are fundamental defects that are present in a wide variety of oxides. It has been demonstrated that these defects can be generated by energetic photons and heavy particles as well

as by post-oxidation annealing in an O-deficient ambient. Due to the ease of generating the S- and X-centers as well as the qualitative similarity of their physical characteristics to known charge trapping centers, a clear understanding of the structure and properties of these fundamental defects is deemed essential. Such an understanding assumes added importance because of the apparent relationship between these centers and border traps [4] which implies they may play an important role in the reliability of MOS devices [24-26]. In order to gain insight into the fundamental physical and chemical properties of these defects, we investigated their electronic structure and spin properties by *ab initio* quantum mechanical calculations on several candidate atomic clusters.

IV. CALCULATIONS

The O₃≡Si[†], O₂Si≡Si[†], OSi₂≡Si[†], and Si₃≡Si[†] atomic models were studied by performing calculations on the first-nearest-neighbor (1-NN) atomic clusters shown in Figure 1. H atoms were used in each cluster to terminate

the valency of the O and Si atoms attached to the paramagnetic Si center. The cluster in Figure 1a represents the E'_h -center [17] while Figure 1d represents the P_h -center. [5,6]. The intermediate two structures (Figures 1b and 1c) represent the E' -type centers generated by successively replacing two O atoms in Figure 1a by Si atoms. All four clusters are neutral ($q=0$) species. The bond distance and bond angles in the energy minimized stable geometry of the four model clusters are listed in Table I.

In order to examine the cluster-size-dependence of the calculated results, we also performed calculations using

two nearest-neighbor (2-NN) model clusters. The model 2-NN clusters, with the chemical compositions $(\text{SiO})_3\equiv\text{Si}$, $(\text{SiO})_2(\text{Si}_3)\text{Si}\equiv\text{Si}$, $(\text{SiO})(\text{Si}_6)\text{Si}_2\equiv\text{Si}$, and $(\text{Si}_9)\text{Si}_3\equiv\text{Si}$ were obtained from the corresponding 1-NN clusters (Fig 1) by adding Si atoms to form the second atomic layer. These four model clusters represented the E'_h , the two E' -type, and the P_h -centers, respectively. Once again, H atoms were used to terminate the valency of the outer atoms (Si here). The energy minimized stable geometries were very similar to their 1-NN counterparts from Figure 1.

Table I. Calculated equilibrium bond distances and bond angles in 1-NN clusters

Model Cluster	R(Si-O) [Å]	R(Si-Si _n) [Å]	<O-Si _n -O [°]	<Si-Si _n -O [°]	<Si-Si _n -Si [°]
$\text{O}_3\equiv\text{Si}^\uparrow$	1.643, 1.635, 1.637	—	113.8, 107.2, 105.5	—	—
$\text{O}_2\text{Si}\equiv\text{Si}^\uparrow$	1.653, 1.652	2.355	110.3	106.2, 112.7	—
$\text{OSi}_2\equiv\text{Si}^\uparrow$	1.664	2.356, 2.356	—	112.35	115.23
$\text{Si}_3\equiv\text{Si}^\uparrow$	—	2.351, 2.351, 2.351	—	—	115.8

The choice of Si as the second nearest-neighbor atom in the cluster was made from our focus in this study on the "near-interfacial" region. However, as is clear, even in the near-interfacial region, there is a greater probability of the network forming Si atom(s) in the hybrid E' -type centers to be bonded with O atoms than with other Si atoms, unless the Si atom in question is a part of the Si-SiO₂ interface. Therefore, it is important to model mixed next neighbor (e.g., Si-O-Si-O) environment in order to obtain a more detailed picture of the microscopic properties of the E' -type centers. Such calculations are underway in our laboratory. Our preliminary calculations on these mixed 2-NN E' -type clusters, in which the first nearest-neighbor O atom(s) is(are) bonded to Si and vice versa to form the second nearest neighbor atomic layer, give results for spin properties, which are only marginally different from those obtained from the all-Si 2-NN cluster calculations. Results of these on-going modeling efforts will be presented in our subsequent communications.

The stable geometry of the clusters was obtained from *ab initio* unrestricted Hartree-Fock (UHF) calculations using a 6-31G** Cartesian Gaussian basis set. This basis set includes polarization and semi-diffuse functions (denoted by the **) to represent bonding in the molecular environment with atomic functions represented by a split valence basis set. The spin properties, ionization potential (IP), and electron affinity (EA) of the four paramagnetic species were calculated using *ab initio* HF method with an extended double zeta and polarization (DZP) basis set.

The UHF spin density was used without removing the spin components higher than the doublet species. It is well known in the literature [27-29] that the UHF method often overestimates the spin density at the paramagnetic nucleus due to the presence of high-spin components in the wavefunction. This anomaly is known as spin contamination [30,31]. We investigated the effect of spin contamination on the spin properties of Si atoms in the case of a paramagnetic SiH₃ radical [32]. Our calculations revealed that the UHF spin density for the Si-center has relatively small (<15%) contributions from the high-spin components. Small contribution of the spin contamination effect to the spin density has also been noted in other second-row paramagnetic atoms [33,34]. Therefore, no attempt was made to remove spin contamination from the UHF wavefunction in this study.

The spin properties calculated in the present study are: (a) spin density ρ^s at the site of the nucleus, (b) the ESR isotropic hyperfine coupling constant, a_{iso} , and the components of the anisotropic hyperfine coupling tensor, $\mathbf{T}$. The a_{iso} results from the interaction of the electron-spin magnetic moment in contact with the nuclear-spin magnetic moments. The isotropic hyperfine coupling (hfc) thus yields information about the unpaired electron spin density at the site of the paramagnetic nucleus. The anisotropic part, given by the principal components of $\mathbf{T}$, results from the interaction of the electron-spin dipole and nuclear-spin dipole, and provides information about the electron spin density in the valence region of the magnetic nucleus. The theory of ESR hfc and the details of our computational methods have been described in an earlier

publication [35]. To examine the effect of our choice of basis functions on the calculated results, the spin properties of the 1-NN clusters were also calculated using a triple-zeta plus polarization (TZP) basis set. The results differed only marginally from those obtained using the DZP basis set.

V. RESULTS AND DISCUSSION

A. Geometry

The structural parameters of the 1-NN model clusters (Figure 1) obtained from the total energy minimization are listed in Table I. The optimized Si-O bond distances are slightly larger than the average value of 1.61 – 1.62 Å found in α -SiO₂. The average Si_p-Si distance is about the same as that calculated for the Si-Si dimer [35, 36]. It is interesting to note that the Si_p-O bond distance increases as the number of Si_p-Si bond in the network increases. The changes in bond distance are accompanied by corresponding changes in the angles formed by the O and Si atoms at Si_p. We note that the Si_p-center moves from a nearly pyramidal position in the O₃≡Si_p cluster, to a nearly planar one containing the three Si atoms in Si₃≡Si_p cluster. This is consistent with the electronegativity of the atoms in an AB₃ cluster. In accordance with the Walsh rules [37] for the AB₃-type structure, atom A (here, Si_p) moves toward the plane defined by the three B atoms (O and/or Si) as the electronegativity of B decreases.

B. Spin Properties and Structural Assignment

The calculated ²⁹Si spin properties for the paramagnetic Si-center (Si_p) in the 1-NN model clusters for the E'_h-, E'-type, and P_b-centers are listed in Table II. Also listed in the table are the experimental values of a_{iso} for the E'_h-center [22], the E'-type (X) center [22], and the P_b-center [10] for comparison. The corresponding calculated results for the 2-NN cluster models along with the experimental values a_{iso} taken from references [10] and [22] are listed in Table III.

Calculated spin properties at the paramagnetic Si-center reveal a number of interesting features of the E'-type structures. First, we note that upon successive replacement of an O-atom by a Si atom, the spin density, ρ^s , at the Si_p-center decreases. As a result, the magnitude of the contact term (a_{iso}) in the hyperfine coupling decreases. The dipolar part, T , of the hyperfine coupling, which accounts for the spin density in the bonding region of the paramagnetic nucleus, shows a gradual increase upon successive replacement of the O atoms. Such changes are caused by the decrease of the 3s-character in the spin-containing orbital of the Si_p center due to an increased overlap with the similar orbitals of the substitutional Si atoms. An increased overlap between the Si 3p orbitals also increases the directional character of the spin containing dangling bond at the paramagnetic center. These two effects together lead to an increase in the magnitude of the dipolar or anisotropic part of the hyperfine coupling tensor.

Table II. Calculated spin density, ρ^s , and hyperfine coupling constants (G) for trivalent ²⁹Si-center in 1-NN model clusters

Cluster	ρ^s	a_{iso}	T_{11}	T_{22}	T_{33}
O ₃ ≡Si [†]	1.173380	-372.26 (440) ^a	21.17	20.18	-41.35
O ₂ Si≡Si [†]	0.778456	-246.97 (230) ^a	25.02	22.20	-47.22
OSi ₂ ≡Si [†]	0.612943	-194.46 (--)	26.11	24.70	-50.81
Si ₃ ≡Si [†]	0.395341	-125.42 (111) ^b	28.61	28.61	-57.22

^aExperimental data from Ref. [23]. ^bExperimental data from Ref. [10].

Before comparing the calculated results for the hfc constants with experimental data, it is worthwhile to note that the ESR measurements do not unambiguously identify the sign of hfc tensor. This is the reason for the difference in sign between the calculated and experimental results for hfc listed in Table II. A unique advantage of *ab initio* quantum theoretical calculations is that they provide accurate values for the magnitude as well as the sign of the hfc constants, the latter is often used to resolve the sign of the experimental hfc tensor. The theoretical calculations provide the accurate sign for the hfc constants. Referring to the results for the 1-NN clusters (Table II), one notes that the calculated value of $a_{\text{iso}}(^{29}\text{Si}_p)$ in O₃≡Si[†] (E'_h-center)

is slightly smaller than the corresponding experimental value [23]. For Si₃≡Si[†] (P_b-center), on the other hand, the calculated value is slightly larger than the corresponding experimental value [10]. However, in both cases, the calculated value of $a_{\text{iso}}(^{29}\text{Si}_p)$ is within 10% of the corresponding experimental value. This gives us confidence in our theoretical approach, choice of model clusters, and the calculated results for hfc constants.

Proceeding to the E'-type centers, we note that the calculated $a_{\text{iso}}(^{29}\text{Si}_p)$ in O₂Si≡Si[†] cluster is in excellent agreement with the experimental value of 230 G measured for X-centers in Si-implanted α -SiO₂ [23]. The calculated $a_{\text{iso}}(^{29}\text{Si}_p)$ in the other E'-type structure, OSi₂≡Si[†], is too

small compare with the experimental value for the X center [23]. This comparison lets us identify the X center with $O_2Si \equiv Si_p^\uparrow$ atomic structure. We call the other E'-type center with an $OSi_2 \equiv Si_p^\uparrow$ atomic structure the "Y-center". To the best of our knowledge, there is no prior report, experimental or theoretical, on the structure and properties of the Y center in SiO_2 . The present calculations have allowed us, for the first time, to establish the microscopic identity and properties of two distinct members of the E'-type defect family.

A comparison of the calculated results for the 1-NN clusters (Table II) and 2-NN clusters (Table III) sheds light on the effect of cluster size on the calculated values of the spin properties. We see marginal differences between the calculated values of hfc of 1-NN and 2-NN clusters. Specifically, the isotropic hfc constants (a_{iso}) change by as little as 2% for the $OSi_2 \equiv Si_p^\uparrow$ model cluster, identified here with the X-center [23], and as high as 10% for the $O_3 \equiv Si_p^\uparrow$ model cluster, representing the E'-center. Changes in the values of a_{iso} for the model $OSi_2 \equiv Si_p^\uparrow$ cluster, called the Y-center, and $Si_3 \equiv Si_p^\uparrow$ representing the P_b-center fall between these two extremes. The changes are not always an increase of the magnitude of a_{iso} in going from 1-NN cluster to 2-NN cluster. In fact, in the case of the Y-center, we note a small decrease in a_{iso} as the size of the cluster

increases. The components of the anisotropic hfc tensor **T**, similarly exhibit small but finite changes that range from less than 1% to about 14% in going from the small (1-NN) to the large (2-NN) clusters. It is important to note, however, that the overall changes are too small to affect our assignment of the observed paramagnetic centers.

The next question we wish to address is, "What is the identity of the S-center?" In order to answer this question it is worthwhile to examine and compare the various experimental data. One notes that the experimental g values ($g \sim 2.0030, 2.0028$) for the S center reported by Griscom *et al.* [2] and Stesmans and Afanas'v [3] are very close to the corresponding value ($g \sim 2.0022$) measured by Hosono, *et al.* [23] for the X-center. Furthermore, an estimated value of hfc constant ($\sim 270 \pm 10$ G) for the S center reported by Stesmans and Afanas'v [3] is much closer to the corresponding measured and calculated values for the X-center than the calculated value for the Y center. In fact, the estimated value of hfc constant for the S-center (~ 270 G) [3] is about 19% larger than the corresponding experimental value for the X-center (230 G) but about 39% larger than the calculated value for the Y-center (194 G) in the 1-NN model cluster. The difference between the S center estimated hfc constant and the calculated value for the Y-center in the 2-NN model clusters is even larger.

Table III. Calculated spin density, ρ^s , and hyperfine coupling constants (G) for trivalent (p) ^{29}Si -center in 2-NN model clusters

Cluster	ρ^s	a_{iso}	T_{11}	T_{22}	T_{33}
$O_3 \equiv Si^\uparrow$	1.289025	-408.95 (440) ^a	20.05	20.04	-41.09
$O_2Si \equiv Si^\uparrow$	0.795805	-252.47 (230) ^a	23.77	19.95	-43.72
$OSi_2 \equiv Si^\uparrow$	0.566788	-179.82 (--)	23.18	23.84	-47.02
$Si_3 \equiv Si^\uparrow$	0.411289	-130.48 (111) ^b	25.37	25.37	-50.74

^aExperimental data from Ref. [23]. ^bExperimental data from Ref. [10].

This allows us to rule out the possibility of S being assigned to the Y-center. Therefore, if we accept the assignment made in Refs. 2 and 3 (i.e., the S-center is an E'-type center), our results suggest that it has the same atomic structure as the X-center. Based upon these analyses, we list in Table IV the assignment of the paramagnetic E'-, X-, Y-, and P_b-centers with their respective atomic structures.

C. Generation Mechanisms & Electrical Properties

The X- and Y-centers can be generated near the Si/SiO₂ interface in a number of ways. Considering the atomic structures shown in Figure 1, it is not difficult to envision the existence of E'-type centers in partially oxidized and Si-excess α -SiO₂ samples. Since the oxidation of Si surfaces or formation of buried-oxide precipitates does not proceed with simultaneous formation of four Si-O bonds, it

is possible that some of the Si atoms remain partially unoxidized, i.e., preserve one or two Si-Si bonds, in the post-oxidation samples.

Therefore, depending upon the processing conditions, one can expect the presence of the X- and Y-centers in Si-excess (or O-deficient) regions of SiO₂. In fact, since the probability of complete oxidation decreases as one approaches the Si-SiO₂ interface, it is reasonable to expect the density of these defects to increase in the vicinity of that interface.

It has already been shown by Hosono, *et al.* [21 – 23], that heavy-ion bombardments can also generate the E'-type centers by knocking out bridging O atoms from the oxide network. The Si atoms adjacent to the O-vacancy created in the knock-on process will tend to form Si-Si dimer bonds. This leads us to propose that the E'-type (X- and Y-) centers would have a higher probability to occur in the

near-interfacial regions than in the bulk oxide in the Si-SiO₂ systems.

Table IV. Atomic structure assignment of trivalent paramagnetic Si-centers

Atomic Structure	Assignment
O ₃ ≡Si [↑]	E' _h
O ₂ Si≡Si [↑]	X (S)
OSi ₂ ≡Si [↑]	Y
Si ₃ ≡Si [↑]	P _b

One can also utilize the electronic structure arguments to derive useful information on the charge trapping behavior of the E'-type centers. In the case of the Si-excess E'-centers, such as the X- and Y-centers, the unpaired electron spin is delocalized over the overlapping orbitals of Si atoms forming a Si-Si dimer. It is well known that the delocalized electrons in the chemical environment are less strongly bound and can be detached more readily than the localized electrons which need greater energy for detachment. These arguments suggest that the Si-rich X- and Y-centers can lose their delocalized unpaired electron more easily than their all-O counterpart, E'_h center.

Further qualitative and semi-quantitative information on electrical properties of these defects can be obtained from their electron affinity (EA) and ionization potential (IP). The EA of a species is defined as, $EA = E(q=0) - E(q=-1)$, where $E(q=0)$ is the absolute total energy of the species in the neutral charged state and $E(q=-1)$ is the corresponding energy of the species in its negative charge. As is clear from the definition, the EA provides information on the ability of a neutral species to capture and stabilize an electron. Since absolute total energies are negative numbers, a positive value of EA for a species suggests that the negative charge state will be stable, which in turn suggests a favorable electron capture process. A negative value for EA suggests the converse.

The IP relates to the opposite of the electron capture process. The IP is defined as, $IP = E(q=+1) - E(q=0)$. The higher the value of the IP, the greater the energy needed to eject an electron from the system. In other words, systems with a high IP will be less likely to lose an electron or capture an hole. Therefore, in order to gain insights into the electron/capture characteristics of the E'-type centers, we obtained the EA and IP from the total energy calculations. The total energy calculations were performed at the optimized equilibrium geometry of the neutral ($q=0$) species.

Table V. Calculated vertical EA (eV) and IP (eV) for 1- and 2-NN clusters

	Cluster	EA(1-NN)	EA(2-NN)	IP(1-NN)	IP(2-NN)
E' _h	O ₃ ≡Si [↑]	-1.45	-1.02	8.34	8.15
X-center	O ₂ Si≡Si [↑]	-0.92	-0.32	7.47	6.87
Y-center	OSi ₂ ≡Si [↑]	-0.19	0.32	7.45	6.67
P _b	Si ₃ ≡Si [↑]	0.28	0.90	7.43	6.68

The calculated EA and IP for the model 1-NN and 2-NN clusters are listed in Table V. Our calculated values of EA indicate that the $q=-1$ charge state of the X- and Y-centers, similar to that of the E'_h-centers in the 1-NN cluster models are unstable with respect to the $q=0$ charge state. This suggests that, similar to the E'_h center, the X- and Y-centers either cannot capture an electron or are very poor electron traps. Upon increasing the cluster size, we note that the EA of the Y-center becomes positive, suggesting that for this center, the $q=-1$ state is stable with respect to its $q=0$ state. However, again, the X-center does not show stabilization of an electron with respect to the $q=0$ state (negative EA), suggesting a metastable electron trap center. Since the EA exhibits appreciable changes due to the cluster size, it is difficult to draw a definite conclusion from this set of results alone. However, assuming that the trend continues, it is reasonable to expect that in the bulk phase (solid, thin-film), the X- and Y-centers would form a stable $q=-1$ state, although the

stabilization energy would be small. This suggests that similar to the P_b-center, the X- and Y-centers would be able to capture an electron, albeit with a shallow minimum. However, due to a relatively small EA of the X- and Y-centers, the electron would be only weakly bound and could be easily released. Our calculated IP for the X- and Y-centers are about 1.1 – 1.2 eV lower than that for the E'_h-center and about the same as that for the P_b-center in both 1-NN and 2-NN clusters. This suggests that the energy required to remove an electron from (or conversely, to attach a hole to) the X- and Y-center, is close to the Pb center and much smaller than that for the E'_h center. The energetic consideration thus favors the X- and Y-centers as hole traps rather than electron traps in their charge neutral state.

D. X- and Y-Centers, and Border Traps

Now we shall examine the relationship of the X- and Y-centers with the border traps proposed by Fleetwood *et al.* [4]. We have already noted that the X- and Y-centers in their charge-neutral state have a very small likelihood of capturing an electron. Furthermore, their assigned atomic structures provide a clue to their spatial location in Si/SiO₂ systems. We recognize the fact that the X- and Y-centers involve at least one O atom bonded to a paramagnetic Si-center away from the interface. Therefore, the minimum distance from the interface required for such atomic arrangements to occur in the oxide will be two atomic layers. Since the average distance between two Si atoms separated by an oxygen in α -SiO₂ is about 3.5 Å, we estimate this to be the minimum distance between the true interface and the first monolayer containing the trivalent Si_p as part of the X- and/or Y-center in the oxide. This estimated distance is close to the region in the oxide where experiments suggest border traps occur [8,24-26]. The similarity in the characteristics (electron/hole trapping and location) of these E'-type centers and border traps [8, 24-26] indicates that the X- and Y-centers are likely border trap precursors.

In addition to being "near-interface" traps, the important characteristics of border traps are the presence of trapped holes and their switching behavior, i.e. the trapped holes trap and detrapp electrons under alternating bias conditions. These characteristics of the border traps are similar to the "oxide switching traps" which have been extensively studied by Oldham and coworkers [38-41]. According to Oldham and coworkers [38], the switching traps generally extend on the order of 5 to 10 nm from the Si interface into the oxide and their annealing process involves a time scale that ranges from a few milliseconds to several decades [41]. According to the Lelis model [39-41], the switching behavior of these "near-interface" charged traps results from electron trapping and detrapping by the E'_v centers, which are oxygen vacancies with a complex atomic structure that involves an unpaired electron at a three-fold coordinated tetrahedral Si atom and a hole trapped at another, strained Si atom. The switching behavior of the E'_v centers under alternate hole and electron injection have been verified through a combination of ESR and electrical measurements by Warren *et al* [42] and by Conley *et al* [43,44]. Surprisingly, the ESR measurements by Warren *et al* [42] and Conley *et al* [43,44] were unable to detect paramagnetic species other than the E'_v centers. As is clear from the consideration of the spatial distribution of the switching traps, as described by Oldham and coworkers [38], the X and the Y centers studied here are potential candidates as precursors to the oxide switching traps. We hope that further improved ESR measurements will be able to detect the X and the Y centers along with the E'_v centers in oxides which exhibit switching behavior of trapped holes.

VI. SUMMARY

We have obtained results on the atomic structure and the spin properties of model clusters representing the E'_h and the P_b-centers as well as two intermediate structures generated by successive replacement of O atoms in the E'_h-center by Si atoms. Replacement of O atoms by Si in the E'_h structure leads to (a) a decrease in the spin density and the magnitude of a_{iso} , and (b) an increase in the value of dipolar hfc, T, for the paramagnetic Si-center. From a comparison of our calculated results with the available experimental data on ESR hfc constants, we identify the X-center [1,21-23] with an O₂Si≡Si_p atomic structure. We further suggest that the S-centers observed in x-ray irradiated PSG [2] and in post-oxidation vacuum annealed simple oxides [3] have the same identity as the X-center. To the best of our knowledge, no experimental or theoretical data exists for E'-centers having an O₂Si≡Si_p atomic structure, which we call the Y-center. We cannot explain the lack of experimental data on this center in Si-SiO₂ systems. Our calculated values of the hfc constant for this (Y-) center is large enough to suggest that it should be easily detectable in high-resolution ESR measurements. The electronic structure considerations also suggest this center to have a greater density in the near-interfacial region of the Si-SiO₂ system. We hope that the present study will stimulate careful ESR measurements to observe this center in silica glass as well as in Si-SiO₂ structures.

The atomic structure of the X- and Y-centers as Si-rich E'_h permits us to suggest that both these centers should exist in the near interfacial region of the Si-SiO₂ systems. The calculated EA and the IP for the X- and Y-centers suggest them to be poor electron traps. A comparison of their electron/hole trapping characteristics and estimated spatial location with the known data on the "near-interface" traps [4,38] suggests that the X- and the Y-centers are likely precursors to the members of the oxide switching trap or the border trap family. Results of additional calculations on the electrical levels of the X- and Y-centers involving mixed and expanded atomic clusters with the third nearest-neighbor atoms and in various charge states will be communicated in a separate communication.

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