

Electronic Structure Studies of the E'₈ and the Triplet Centers in *a*-SiO₂

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ABSTRACT

Ab initio Hartree-Fock calculations have been performed on the electronic structure and spin properties of model clusters representing E'₈ and triplet-state centers observed in amorphous SiO₂ (*a*-SiO₂). The calculated results strongly suggest that E'₈ centers involve a trapped hole, shared between two Si atoms adjacent to a mono-oxygen vacancy in a silicon dioxide network. The calculated spin properties of the assumed models for the triplet-state center are too large in comparison with experiment. It is suggested that the two-Si atom, mono-oxygen vacancy structure can not be responsible for the 134 G triplet splitting observed along with the E'₈ center.

INTRODUCTION

The E' centers are perhaps the most extensively studied point defects in *a*-SiO₂ [1,2] and belong to a family of five positively charged centers identified to date in thin SiO₂ films [3,4]. The E' centers, as identified via electron spin resonance (ESR) spectroscopy, are associated with an unpaired electron centered on (a) a single Si atom around vacant oxygen (V_O) sites or (b) on multiple Si atoms in the regions containing excess Si centers (ESC) in the oxide network. These centers are believed to be the primary electron trap (ET) centers in the metal-oxide-semiconductor (MOS) devices [5,6]. Therefore, an understanding of the microscopic structure, stability, and electrical characteristics of these centers have been the subject of extensive studies in the past decade.

Among the various flavors of the E' centers in *a*-SiO₂, the E'_γ center appears to be the most common high-energy radiation-induced V_O center generated in oxides prepared under different conditions. The characteristic features of the ESR spectrum of the E'_γ center are: (a) a 420 G splitting in the hyperfine spectrum and (b) an anisotropic g-tensor (g₁₁=2.0018, g₂₂=2.0006, g₃₃=2.0003). Extensive experimental [7-9] and theoretical studies [10-13], performed in the past, have identified this center as a Si⁺—Si⁺ pair around a missing O atom. The unpaired electron is mainly located in an *sp*³ bonding orbital of a tetrahedral Si center and the positive charge is located on the other Si atom. The positively charged Si atom is far removed from its tetrahedral counterpart and perhaps bonded to a triply-coordinated O atom in the oxide network. In essence then, this center involves two Si atoms adjacent to a missing O atom in which the spin is localized on a single Si atom.

The E'₈ center is a relatively new arrival as a V_O (or the ESC) center. This center was first detected by Griscom and Frieble [7] in 100 keV x-ray irradiated bulk silica containing a high density of chlorine impurity. Later, it was also detected in γ-ray irradiated high purity silica glasses [14]. Vanheusden and Stesmans [15] detected this center in buried oxide (BOX) layers formed by O⁺ implantation during the separation by implantation of oxygen (SIMOX) process. Similar observations have been reported by Warren et al.[16]. In the recent years, this center has also been detected in the thermally grown oxide films upon annealing [17-21] and in x-ray irradiated high purity silica glass [22]. The characteristic features of the E'₈ centers are (a) a 100 G doublet hyperfine splitting, and (b) a nearly isotropic g-tensor (g₁₁=2.0018, g₂₂=2.0021, g₃₃=2.0021) in the electron spin resonance (ESR) spectrum [7,22]. The hyperfine splitting and the g-tensor are attributed to ²⁹Si centers in the oxide samples [7,15,16,22]. Another important feature of this center, as observed from the ESR spectrum of irradiated glass samples [7,14,22], is the simultaneous appearance of a triplet state spectrum. The charge state of E'₈ is believed to be positive [15,16].

While the total spin and the charge state of the E'₈ center extracted from the ESR and the electrical measurements are believed to be well established, the exact nature of its microscopic structure remains uncertain. Analysis of the ESR spectrum for this center, vis-a-vis that of the more extensively studied E'_γ center in *a*-SiO₂ [1-9], suggests that the unpaired electron spin in the E'₈ center is delocalized over four, nearly equivalent, Si atoms. Since *a*-SiO₂ is a network of tetravalent Si atoms connected via divalent bridging O atoms, an atomic arrangement with four equivalent Si atoms requires multiple-oxygen vacancies or domains of unoxidized, tetrahedrally-connected Si atoms, also referred to as oxygen deficient centers (ODC), in the oxide. These arguments have led a number of groups to propose multiple-oxygen vacancy models. For example, Griscom and Frieble [7] proposed a model in which the unpaired electron spin is

delocalized on four tetrahedral bonds of equivalent but different Si atoms. The model proposed by Vanheusden and Stesmans [15] and Warren et al. [16] involves delocalization of the unpaired electron spin over four equivalent Si atoms connected to a central tetrahedral Si atom (the *five-Si atom model*). In contrast, the model proposed by Zhang and Leisure [22] involves delocalization of the electron spin over four equivalent Si atoms around a SiO₄ vacancy (the *four-Si atom model*). In addition to the multi-oxygen vacancy models, mono-oxygen vacancy models have also been proposed in the literature [14,18] to describe the local atomic configuration of the E'₈ center. In these models, the unpaired electron spin is believed to be localized either on a Si-Si dimer [14] or on a single Si atom [18] as in the case of E'_γ center (the *two-Si atom model*).

The triplet state species with two unpaired electrons having parallel spins (total spin, $S=1$, spin multiplicity, $M_s=3$) have only been detected in irradiated bulk silica samples [7,14,22]. The triplet-state center has a number of very interesting properties. For example, (a) it always appears in the samples where E'₈ is observed, (b) it is observed in the samples which exhibit a 5 eV absorption followed by a 4.4 eV photoluminescence, (c) it is only found in low-OH oxygen-deficient samples with no Cl impurity, (d) its ESR properties (a nearly isotropic g-value=2.002 and a hyperfine splitting of 134 G) are strikingly similar to those of the E'₈ center. Furthermore, its anneal behavior is also very similar to that of the E'₈ center. Due to the observed similarities in the properties of the triplet-state and the E'₈ centers, previous workers have suggested [7,14,22] that the two paramagnetic centers have common local atomic structure.

Previous attempts to establish the microscopic structure of these defects in *a*-SiO₂ via quantum mechanical calculations are limited to a single study by Chavez et al. [23] on the E'₈ center. In the study of Chavez et al. [23], the proposed atomic models for the E'₈ center [14,15,22] were examined by *ab initio* Hartree-Fock (HF) calculations of stable geometry, energy, and spin properties. The calculations by Chavez et al. [23] suggested that subsequent to the hole trapping, the free electron spin prefers to localize on a pair of Si atoms regardless of the number (five, four, or two) of Si atoms around oxygen vacancy. Furthermore, the calculated spin density and the hyperfine coupling tensor on the two participating Si atoms showed excellent agreement with the experimental ESR data. From these results, Chavez et al. [23] concluded that the E'₈ center most probably resulted from an equal distribution of the unpaired electron spin over two equivalent Si atoms. Furthermore, it was suggested that the E'₈ center was a symmetrical variant of the E'_γ center. In the latter case, the spin is asymmetrically localized on a single Si center around a mono-oxygen vacancy.

Since Chavez et al. [23] used relatively small atomic clusters to model E'₈ center, it is not clear if the size of the clusters had any influence on the calculated results for spin density. Also, Chavez et al. [23] did not study the triplet-state centers. In view of the importance of V_O related point defects on the reliability of MOS devices, we have performed *ab initio* HF calculations on the E'₈ centers employing extended sets of atomic basis functions and much larger model cluster structures than used in the previous study [23]. We have performed similar calculations on the triplet-state centers employing somewhat smaller clusters. The new results for the E'₈ centers agree with those of the previous calculations [23], suggesting that the observed ESR spectrum results from an unpaired electron distributed over a pair of Si atoms around a mono-oxygen vacancy. The calculated results for the ESR hyperfine coupling tensor for model triplet-state structures are too large compared with the experiment [7,14,22].

CALCULATIONS

The model clusters used for the E'₈ centers in the present study are shown in Figure 1 through Figure 3. Figure 1 represents a five-Si center model (model A), Figure 2 represents a four-Si center model (model B), and Figure 3 represents a two-Si center model (model C). The largest spheres in the figures represent the Si atoms, the medium spheres represent the O atoms and the small outer spheres represent H atoms. The H atoms were used to saturate the valency of the outer O atoms. In each case, the total charge (q) on the cluster is +1. Calculations on model A were performed at the *ab initio* HF optimized equilibrium geometry of the neutral cluster ($q=0$). Model B was generated from model A by removing the central Si atom. Calculations on model C were performed at the *ab initio* HF optimized geometry of the neutral oxide cluster. Model C was generated by removing a bridging O atom from the neutral cluster. As explained below, the calculations on the triplet-state centers were performed on two-Si atom model (model C) only. The atomic cluster used for this center was taken from our previous study [23].

The total energy and the spin density of the positively charged clusters were calculated via *ab initio* unrestricted HF (UHF) method. A double zeta Cartesian Gaussian basis set augmented by a six-component d polarization function on Si and O atoms and a three-component p polarization function on the H atoms

was used in all calculations. For the two-Si center model (model C), the ESR hyperfine coupling constants were also calculated using a minimal (STO-3G) and a double-zeta valence (DZV) basis

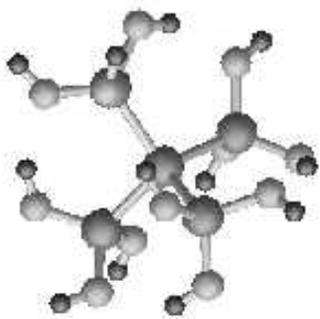


Figure 1 (Model A)



Figure 2 (Model B)

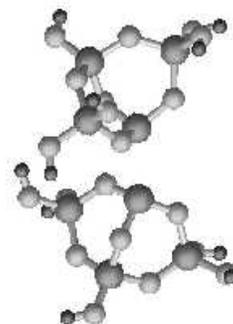


Figure 3 (Model C)

set effect. Calculations were performed using the GAMESS [24] and HONDO [25] *ab initio* electronic structure codes.

RESULTS

A. The E' center:

The five-Si atom model (model A). The Si—Si bond distances in the neutral model A (Fig. 1) cluster are calculated to be between 2.350 Å and 2.362 Å and the calculated Si—O bond distances range from 1.628 Å to 1.630 Å, in good accord with the literature data [23]. The bonds at the central silicon atom are very nearly equivalent to each other as is noted from the Si_c—Si_c—Si_o bond angles which range between 109° and 111°. The subscript *c* indicates *central* and *o* indicates *outer*. The equivalence of the outer four Si atoms is also noted from the Mulliken population analysis, which gives a net charge between 1.428389 and 1.449943 for the outer Si atoms. When a hole ($q = +1$) is placed on this cluster, the net calculated charge on the outer Si atoms is calculated to be between 1.486277 and 1.508052. The total spin density, ρ^0 , (the excess of α over β spins) calculated for the outer four Si atoms are: -0.003626, 0.175657, 0.053748, 0.013128. While the net atomic charges on the Si centers are not too different from each other, the corresponding spin densities differ greatly. It is clear that the spin density is not equally distributed on the outer four Si atoms. Moreover, the value of the calculated spin density is too small to compare with the experimental value of about 0.32 [7, 22] for the E' center.

The four-Si atom model (model B). For model B (Fig. 2), the calculated values of the spin density, ρ^0 , at the four Si centers are: 1.018086, 0.993140, -0.221734, and -0.280082. Once again, it is clear that the spin density is not equally distributed over the four Si atoms. Also, the magnitudes of the calculated spin densities are vastly different from the experimental value [7,14,22]. However, the spin density seems to be distributed on a pair of equivalent Si atoms.

The two-Si atom model (model C). For model C (Fig. 3), the calculated spin density, ρ^0 , at the two Si atoms are 0.304606 and 0.335135. These values are in good agreement with experiment [7,14,22] and the previously reported theoretical values[23]. The calculated value of ρ^0 on the first nearest neighbor (NN) O atoms varies from a low of 0.04 to a high of 0.06. Similarly, the spin density, ρ^0 , at the second NN Si atoms is calculated to have a value between 0.002 and 0.005. Further removed NN (>2) have still smaller values for ρ^0 . This suggests that the spin density in the two-Si atom model is mainly distributed over the pair of Si atoms adjacent to the oxygen vacancy.

The calculated spin properties of the two Si atoms adjacent to the O vacancy for this model structures are listed in Table I. Listed in the table are the spin density, ρ^0 , the isotropic hyperfine coupling constant, a_{iso} , and the principal components of the anisotropic hyperfine coupling tensor, \mathbf{T} . The unit for the hyperfine coupling constant (a_{iso} , \mathbf{T}) is *Gauss* (G). The spin density, ρ^0 , provides information on the *s*-electron spin density at the atomic nucleus, in this case Si, and contributes directly to the isotropic hyperfine coupling constant. Electrons in the *p* and higher order angular momentum wavefunctions have zero density at the nucleus. The anisotropic hyperfine tensor, \mathbf{T} , provides information on the spin density distribution away from nucleus and contains contributions from non-*s* type orbitals in the wavefunction. The

measured hyperfine splitting tensor, \mathbf{A} ($= a_{\text{iso}} + \mathbf{T}$), contains contributions from the isotropic and the anisotropic part. We note from the table that the minimal basis set (STO-3G) gives somewhat lower values of ρ^0 and a_{iso} than the extended DZV basis set. However, both basis sets give comparable values for the components of \mathbf{T} . This is expected. The isotropic part, which depends on the accurate evaluation of spin density at a single point, is known to be much more sensitive to the choice of basis set than the anisotropic part [26]. The later depends on the spin density in the regions of space away from the nucleus and can be evaluated accurately with a reasonable basis set. Accurate evaluation of the isotropic part, on the other hand, requires highly flexible and extended basis set.

Table I. ^{29}Si spin properties in two-Si atom model cluster. Si_1 and Si_2 refer to the Si atoms adjacent to V_{O}

Center	ρ^0	$a_{\text{iso}}(\text{G})$	$T_{11}(\text{G})$	$T_{22}(\text{G})$	$T_{33}(\text{G})$
Basis set I ^a					
Si_1	0.219676	-69.69	11.06	9.15	-20.21
Si_2	0.242067	-76.80	11.66	10.08	-21.74
Basis set II ^b					
Si_1	0.326490	-103.58	9.27	8.63	-17.90
Si_2	0.372170	-118.07	9.88	9.58	-19.46
Expt, Ref.[7,22]		100			

^aSTO-3G. Calculated total energy, $E = -3768.141957$ Hartree. ^bDZV. Calculated $E = -3814.852743$ Hartree.

We note that as the basis set improves, the calculated a_{iso} moves closer to the experimental value of 100 G [7,14,22]. In fact, the spin density, ρ^0 , calculated from our DZP basis set, as discussed above, is in excellent agreement with the experimental value for the E'_{δ} center. We also note that the magnitude of the a_{iso} is much larger than the components of \mathbf{T} , by a factor of 5 to 10 for the DZV basis. This suggests that the wavefunction of the unpaired electron has at least 5:1 ratio of the s and p characters. Note that the greater the s character in the wavefunction, the more isotropic the hyperfine coupling and the g -tensor. This may explain the observed “near isotropy” of the hyperfine splitting and the g -tensor in the ESR spectra [7,14,22] for the E'_{δ} center.

B. The triplet-state center:

Since our calculations on the E'_{δ} centers did not support the five-Si and the four-Si models as the microscopic structure, we excluded these models from our initial study of the triplet-state center. The calculations were performed on the two-Si model cluster. The reason for this selection was the assumption that the E'_{δ} and the triplet-state centers have common microscopic structure. As noted earlier, we used the model cluster C [(HO)₃Si Si(OH)₃] of Ref. [23] for this study. Although considerably smaller than the structure shown in Fig. 3, this model cluster retains all the essential features of a two-Si model. The Si atoms adjacent to V_{O} are each bonded to three O atoms. The valency of the outer O atoms are saturated by H atoms. Calculations were performed on two geometries. The first set was that of a neutral precursor containing the middle oxygen. The triplet state geometry was generated by removing the bridging O atom from the precursor cluster. This geometry, is labeled as *precursor* in the table. The other geometry, called *optimized*, was obtained from a full geometry optimization of the cluster without the bridging oxygen atom. This geometry represents a Si-Si dimer structure. The calculated values of Si—Si internuclear distance, the total energy, E , and the spin properties for the triplet state center in the two geometries are listed in Table II. Since the two Si atoms adjacent to V_{O} in this case are exactly equivalent, the spin properties for only one center in each geometry is listed.

We note that the two Si atoms move away from each other as the geometry is allowed to relax. As the Si—Si internuclear distance increases, the spin density on the Si centers decreases. However, in both geometries the calculated values of the hyperfine coupling constants are much larger than the observed value of 134 G [7,22] by a factor of four or more. Such a large difference between the calculated values of hyperfine couplings for the model structure and the experimental value for the triplet-state center rules out

Table II. Calculated ^{29}Si spin properties for the triplet-state center.

Geometry	Precursor	Optimized
R(Si—Si) (Å)	3.0894	4.0435
E (Hartree)	-1030.788045	-1030.843963

ρ^0	1.692381	1.294420
a_{iso} (G)	-536.92	-410.66
T_{11} (G)	25.46	21.77
T_{22} (G)	25.23	21.32
T_{33} (G)	-50.69	-43.08

the possibility of the former representing the microscopic structure for the latter. It then raises a question: What is the origin of the 134 G triplet observed in the ESR spectra of irradiated α -SiO₂? A straight forward answer to this question is not possible on the basis of our limited study. However, it seems plausible that the E'_8 and the triplet centers do not share a common microscopic structure. One takes note of the fact that the E'_8 center is a hole ($q=+1$) trapped at a V_{O} , while the triplet-state species is a *neutral* ($q=0$) center with two unpaired electrons. Therefore, the two species may have different geometrical features due to the difference in the local electronic environment. In order to further pursue this reasoning, we calculated the hyperfine properties of a four-Si cluster in which the valency of the Si atoms were terminated by H atoms. This structure, generated from a five-Si tetrahedral cluster by removing the central Si atom, was taken from our previous work [23]. The calculations were performed by an *ab initio* UHF method using a minimal (STO-3G) basis set. The calculated values of ρ^0 at the Si centers are: 0.5307, 0.5232, -0.2009, 0.5216. The corresponding values for a_{iso} (G) are: -168.28, -165.99, 63.72, -165.48. In this case, the calculated spin properties of three centers are closer to the experimental value. However, one of the centers has opposite sign of the spin with much lower magnitude of the spin density. Therefore, this model can not adequately explain the observed spectrum which requires four equivalent Si centers.

DISCUSSION

The results presented here for the E'_8 center show excellent qualitative and quantitative agreement with the results of our previous study [23] using smaller model clusters. This suggests that (a) further extension of the cluster size will have little effect on the spin properties, and (b) a reasonable size cluster can accurately provide the spin properties of point defects in solids. The calculations on the model E'_8 structures, similar to our previous study, suggest that the center detected in the ESR spectrum as a 100 G doublet could not involve distribution of unpaired electron spin over more than two Si atoms. In the case of the five-Si and four-Si atom model structures, the spin density is not calculated to be distributed equally. Moreover, the magnitude of the spin density calculated in these models (A and B) are incompatible with the observed spin properties for the E'_8 center.

The only model that seems plausible, on the basis of the calculated values of the spin properties, is a two-Si model. In this case, the Si atoms adjacent to V_{O} have share most of the spin density and the wavefunction exhibits at least a 5:1 ratio of the s and p characters. Greater s character of the wavefunction results in a reduced anisotropy in the hyperfine spectrum. These results, therefore, suggest that E'_8 center is a simple mono-oxygen vacancy involving two Si atoms.

The calculated results for the triplet-state center do not agree, whether in the two-Si atom or a four-Si atom model, with the experimental results for a triplet species. There can be a number of reasons for this discrepancy between the theory and experiment. First, and foremost, it is plausible that the observed triplet-state spectrum results from a species whose identity remains unknown. Second, it does involve excess Si centers, but the microscopic structure of this species is different from that of the E'_8 center. Third, the theoretical treatment used in the present study may not be adequate for characterizing a triplet state. At this moment, however, the origin of the triplet-state spectrum in the ESR spectrum of the irradiated α -SiO₂ samples remains unresolved.

CONCLUSIONS

We have presented here the results of our *ab initio* HF calculations of structure and spin properties of model clusters representing E'_8 and the triplet-state centers observed in the ESR spectra of α -SiO₂. The calculations were able to rule out the five-Si and four-Si atom models, which require multiple oxygen vacancies, to represent the local atomic structure of E'_8 center. The electronic structure and the spin properties of the two-Si atom model involving a simple mono-oxygen vacancy are calculated to be in close agreement to the experimental results for the E'_8 center. These calculated results are also in excellent agreement with our previous study on the E'_8 center using smaller model clusters. Therefore, we believe that E'_8 centers involve a trapped hole on two equivalent Si atoms adjacent to a mono-O vacancy. The two-Si atom model, however, does not seem to be a plausible structure for the triplet-state centers observed with

the E'_8 centers in the ESR spectra of irradiated α -SiO₂. The calculated results also do not favor a four-Si atom model for the triplet state. Further calculations on the triplet-state centers are underway in our laboratory and will be the subject of our future communications.

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