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Spectroscopic features of dimer and dangling bond E' centres in amorphous silica

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Abstract

We performed first-principle embedded cluster calculations of the hyperfine parameters, g-tensors and optical excitation energies for the dimer and back-projected configurations of the E' centre in amorphous silica. The optical transition energies of these defects are calculated for the first time. We predict a strong optical transition at about 6.3 eV for the dimer configuration and a relatively weak transition at 5.6 eV for the back-projected configuration of the E' centre. These predictions could be used for further experimental identification of these centres. Our results support the dimer model of the E'_δ centre, and for the first time provide a full range of spectroscopic parameters for the back-projected configuration of the E' centre in amorphous silica.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Charge trapping centres in gate oxides and at the silicon–silicon dioxide (Si–SiO_2) interface strongly affect the performance of metal oxide–silicon (MOS) devices. Extensive experimental and theoretical studies over the past three decades have identified intrinsic and extrinsic defects as charge trapping centres in SiO_2 and Si–SiO_2 systems [2, 3]. The former include threefold coordinated Si centres and oxygen vacancies, while the latter can be hydrogenic species, phosphorus, and boron inpurities. However, even basic details of the atomic structure, electronic properties, and spectroscopic characteristics of some of these defects are still lacking.

The well known family of E' centres in silica (reviewed in [1] and more recently in [2]) includes E'_γ and E'_α, both positively charged, as well as neutral H-decorated E'_β centres. Yet another centre, called E'_δ, has been observed in oxygen deficient (type IV) silica with low OH content after x-ray irradiation at 77 K [4]. This centre was characterized using electron paramagnetic resonance (EPR) spectroscopy.

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All E' centres share one of the principal values of the g-tensor: $g_1 = 2.0018$. However, other principal values of the g-tensor are quite different, for example, $g_2 = 2.0006$, $g_3 = 2.0003$ for the E'_γ centre [1] while $g_2 = 2.0021$, $g_3 = 2.0021$ for the E'_δ centre [4]. The 42 mT hyperfine splitting (hfs) proves to be characteristic of the E'_γ, E'_α, and E'_β centres [1].

The charge state of E' centres is difficult to verify in a direct experiment. In the case of E'_γ centres observed in thermal oxides, a linear correlation between the density of E'_γ spins and the density of trapped holes, responsible for the charge build-up in MOS gate oxide, has been demonstrated [5]. Later it was shown, however, that at least some of the dangling bond E' centres in thermal oxides are electrically neutral [6]. The correlation of the E'_γ and E'_δ centre contributions to the charge build-up in MOSFETs has been considered as an indicator of positive charge of the E'_δ centre [7].

The room-temperature microwave saturation characteristics of both E'_γ and E'_δ centres are almost identical and, in the case of silica IV glass, the intensity of the hfs doublet is of the same order of magnitude as the one observed for the E'_γ centre. At the same time there are differences: the E'_δ centre demonstrates a relatively isotropic g-tensor, whereas the E'_γ centre is almost axially symmetric; the hfs of the E'_δ centre is one-quarter of that of E'_γ; finally, it has been shown that the E'_δ centres can be annealed completely at 400 °C while the annealing temperature of the E'_γ centres is about 600 °C [4].

On the basis of their experimental data Griscom and Frieble [4] proposed a model in which the unpaired spin is delocalized over the tetrahedral bonds of four equivalent but different Si atoms. Another model proposed by Vanheusden and Stesmans [8] and by Warren *et al* [9] involved the delocalization of the unpaired electron spin over four equivalent Si atoms connected to a central tetrahedral Si atom (five-Si-atom model). A more recent model proposed by Zhang and Leisure [10] involves delocalization of the electron spin over four equivalent Si atoms around a SiO_4 vacancy (four-Si-atom model). Mono-oxygen-vacancy models have also been proposed in the literature [11]. A theoretical study of the atomic and electronic structure of the mono-vacancy model of the E'_δ centre performed by Chavez *et al* [12] and Karna *et al* [7] supported this model and predicted a value for the hyperfine splitting on the two Si atoms surrounding the vacancy in good agreement with the experimental EPR data.

The mono-vacancy model of the E'_δ centre is otherwise known as a dimer configuration of the positively charged oxygen vacancy in silica. The existence of this configuration has been predicted in many previous theoretical studies of E' centres obtained by ionizing a neutral oxygen vacancy in α-quartz. It is linked to the puckered configuration of this defect in α-quartz through a small barrier and is about 0.2–0.6 eV higher in energy than the puckered configuration. Pacchioni *et al* [13] and then Chavez *et al* [12] and Pineda *et al* [14] associated this defect with the E'_δ centre in a-SiO_2 only on the basis of the calculated hyperfine splitting. These calculations described the E'_δ centre as metastable due to existence of the lower energy puckered configuration of the positively charged oxygen vacancy accessible through a relatively low barrier. Recently Pineda *et al* [14] suggested that for some precursor sites in the a-SiO_2 structure used in the calculations only the dimer-like centres can exist. Boero *et al* [15] also observed both metastable and single-minimum configurations of positively charged vacancies in their calculations of a-SiO_2 and suggested that there should exist a continuous distribution of different configurations.

Thus, there is still a controversy regarding the structure of the E'_δ centre in amorphous silica and whether it is a stable or a metastable defect. In particular, the experimental results of Griscom *et al* and Zhang *et al* suggest that this is a rare defect with quite an exotic structure that may involve four Cl atoms in the SiO_4 vacancy. On the other hand, if the silicon dimer model proposed by the theory is correct, this could in fact be a very common defect with one of the simplest structures in silica. The recent theoretical results by Lu *et al* [16] suggested

that the vast majority of positively charged oxygen vacancies are not bi-stable as in α-quartz, but the silicon dimer configuration is in fact the only stable defect in 80% of the oxygen sites.

Another structural type of E' centre in a-SiO_2 has been proposed by Griscom and Cook [17], again on the basis of EPR data. They analysed the EPR spectra of several samples and found E' centres with hyperfine (hf) constants similar to those for the classical puckered E' centre (42.0 mT) but with a distinctly different set of super-hyperfine (shf) constants: in the shf observed for puckered E'_γ they are typically close to 1.3 mT, while in the new centre they were smaller than 1.0 mT. On the basis of theoretical modelling of spectral features Griscom and Cook proposed that, unlike in the E'_γ centre, in this configuration the Si dangling bond with an unpaired electron points away from the vacancy site, i.e. is *back projected*, and the other Si is in the plane of its three oxygen neighbours. Recently [18] we have demonstrated theoretically that such a configuration of the E' centre can be stable and found that the calculated hyperfine parameters are in good agreement with the experimental data. However, no further theoretical analysis of this centre has been made so far.

Thus the dimer and the back-projected configurations of the E' centre have been characterized so far mainly through their hyperfine parameters. In this paper, we present for the first time the calculations of their optical absorption energies and g-tensors. For that purpose we use a model of amorphous silica obtained using the classical molecular dynamics (MD) approach, and employ an embedded cluster method to study the defect properties. This approach was used recently to study the conditions for the formation of positively charged oxygen vacancies obtained by hole trapping at neutral oxygen vacancies (NOVs) in amorphous silica [18], which could be the prevalent mechanism of the E'_δ centre formation as suggested in [12]. There we demonstrated that, depending on the precursor state in the amorphous structure, the positively charged vacancy can have one or two energy minima. The oxygen sites with small average distances to their Si neighbours are prone to the formation of stable dimer centres. Incidentally, these sites also have the lowest neutral vacancy formation energies. Therefore, dimer configurations are likely to be formed in thermal oxides where NOVs are thermodynamically equilibrated. Their concentration relative to other types of E' centres will be different in other, e.g. x-ray irradiated, glass samples. Hence, the results of this work may help in identifying different E' centres using EPR and optical spectroscopies.

In this paper, we use two representative configurations obtained in [18] to calculate the properties of dimer and back-projected E' centres. In the case of the dimer, the calculated hyperfine parameters and the components of the g-tensor are in good agreement with those measured experimentally for the E'_δ centre, supporting the mono-vacancy Si–Si dimer model of this defect. We predict that both centres will have optical absorption at around 6 eV and discuss the nature of optical transitions involved. Finally, we discuss the defect structures formed as a result of electron trapping by either centre: the issue that is related to the mechanism of anneal of MOS devices [19, 20, 7].

In the next section we discuss the methods of calculations. The results of our modelling are given in section 3 and we conclude in section 4.

2. Calculation methods

The amorphous SiO_2 structure used in this work was generated using the periodic molecular dynamics (MD) method and classical inter-atomic potentials. We followed earlier work by Vollmayr *et al* [21] as described in detail in [18]. The DL_POLY code [22] and Buckingham-type inter-atomic potentials were used in these calculations. The original potentials developed by van Beest *et al* [23] (BKS) were slightly modified as described in [18]. The a-SiO_2 model has a continuous random network structure where all Si ions are coordinated by four oxygen

ions, and all O ions are coordinated by two silicon ions. The density of this a-SiO_2 structure is close to 2.37 g cm^{-3}.

The electronic structures of a-SiO_2 and of the defect centres were calculated using an embedded cluster technique developed in our group and implemented in the GUESS computer code [24, 26]. In this method, a crystalline or amorphous system with a single point defect is divided into several regions. A spherical region I is centred at the defect site and includes a quantum mechanically treated cluster (QM cluster), an interface region connecting the QM cluster to the rest of the solid, and a classical region that surrounds the QM cluster and includes up to several hundred atoms. Region I is surrounded by a finite region II, also treated atomistically and containing several thousand atoms. The QM clusters are terminated by interface Si atoms (Si^* thereafter) which have one of their Si–O bonds treated quantum mechanically and the other three bonds treated classically. The detailed description of Si^* atoms and of the whole method as applied to α-quartz and a-SiO_2 is given elsewhere [25, 18, 26, 27, 30]. Some of our previous calculations employed the Hartree–Fock method [25, 18, 26, 27]. In this work we used density functional theory (DFT) and a modified density functional built on the basis of the standard B3LYP functional [32, 33]. In the modified functional the amount of the exact exchange was increased from 20% to 32% [28]. The back-projected and the dimer configurations of the E' centre were considered using $Si_8O_{24}Si^*_{16}$ and $Si_8O_{24}Si^*_{18}$ QM clusters respectively; a standard 6-31G basis set was used in this work. The optical transition energies were calculated using the time-dependent DFT method (TD-DFT) as implemented in the GAUSSIAN-03 package [29]; g-tensors were calculated using the same code.

To form an E' centre at a selected oxygen site we first calculate the electronic structure of the non-defective lattice. Then we form a neutral oxygen vacancy there and minimize its total energy with respect to the coordinates of all centres in region I. Finally, the NOV is ionized and the total energy of the system is minimized again. Since the positively charged vacancies were obtained by ionizing the neutral vacancies and relaxing the resultant structures, the E' centre configurations appear naturally as a result of relaxation of the continuous amorphous network rather than by construction of a specific cluster [31].

3. Results and discussion

In [18] we created NOVs in 70 different randomly selected sites in the amorphous structure and studied distributions of their properties. We demonstrated that hole trapping by these vacancies will lead to formation of broadly two types of E' centres—dangling bond (DB) and dimer type centres (see figure 1). We found several configurations of dangling bond centres, which include the classical puckered configuration, as well as unpuckered and back-projected ones. Some of the dimer configurations could transform into the dangling bond configurations. The conditions for formation of these different defect structures are discussed in [18]. In this paper we are concerned with the properties of two of them—the dimer and back-projected configurations. The unpuckered configuration is discussed in detail in [18] and here we only report the calculated g-tensor and the optical absorption energy for comparison with other configurations.

3.1. Dimer configuration of E' centre

The highest occupied orbital for a typical dimer centre is shown in figure 1. The calculated hf splittings due to the interaction of the unpaired spin with two Si ions of the dimer are 10.5 and 10.0 mT. They are close to those measured experimentally for the E'_δ centre [17, 10]. These

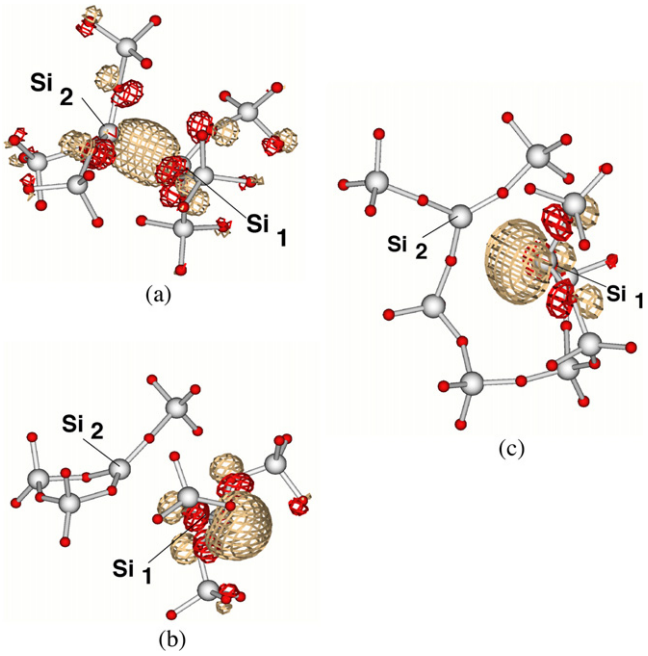

Figure 1. Atomic structures and iso-surfaces of the highest occupied orbitals for the three E' centre configurations: (a) dimer, (b) back-projected dangling bond, and (c) unpuckered dangling bond. The Si neighbours of the oxygen vacancy are indicated. In (b) and (c), Si_1 hosts the dangling bond while Si_2 occupies a site at the centre of the plane formed by its oxygen neighbours.

hf constants are not equal due to the lattice disorder, which affects the local structure of this particular site. The width of the distribution of hyperfine parameters due to disorder estimated from several configurations found in our calculations is 5.0 mT. The main reason for these relatively small values of the hf splitting is seen in figure 1—the unpaired electron density in the dimer configuration is delocalized to a large extent *between* the two Si ions reducing the s-orbital contribution on the Si nuclei. The components of the g-tensor given in table 1 are much more isotropic than those for the DB configuration and are close to those attributed to the E'_δ centre [4].

A schematic energy diagram of the dimer configuration is shown in figure 2. It is instructive to compare its electronic structure to that of the NOV. Both centres have similar geometric structures but there is only one electron localized in the positively charged vacancy. The Si–Si distance of 2.68 Å in the relaxed dimer centre is significantly longer than the Si–Si distance of 2.33 Å in the parent NOV. At the same time, the electron–electron repulsion is smaller in the charged vacancy. The effects of these two factors on the position of the occupied σ state tend to compensate each other. As a result, the σ state is at approximately 0.5 eV above the top of the valence band in both positively charged and the parent neutral oxygen vacancies. The unoccupied anti-bonding σ^* state and two π states are at 7.6 and 8.7 eV above the σ state respectively. There are two more unoccupied π^* states in the gap at 9.2 and 9.3 eV above the σ state.

We used TD-DFT to calculate the optical transition energies for this centre. The main optical transition is due to $\sigma \rightarrow \sigma^*$ excitation; it has an energy of 6.3 eV and an oscillator strength of $f = 0.35$. The $\sigma \rightarrow \pi$ transition has an energy of 7.3 eV and an oscillator strength of $f = 0.03$. The higher energy transition at 7.9 eV, which has a mixed character with contributions from $\sigma \rightarrow \pi^*$ excitations and from VB $\rightarrow \sigma^*$ excitation, has a higher oscillator strength of 0.12. These transitions overlap with the broad spectrum attributed to the E'_γ centre and NOV in irradiated glass samples [2].

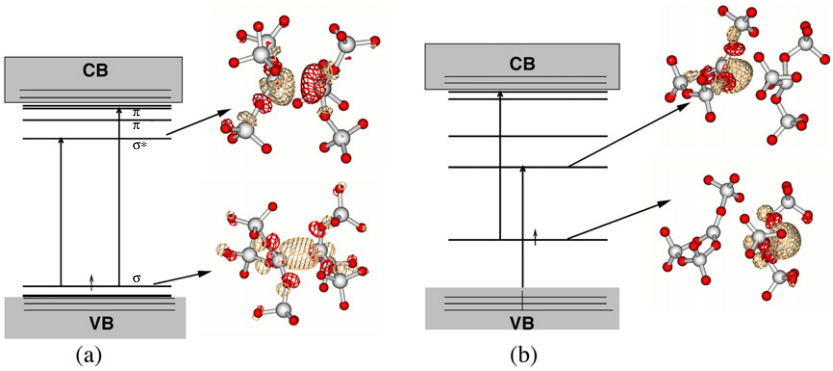

Figure 2. Schematic diagram of one-electron energy states induced by the dimer (a) and the back-projected DB (b) configurations of the E' centre. Only the energy levels corresponding to 'spin-up' states are shown.

Table 1. The theoretical and experimental values of the g-tensor components and optical absorption energies for the E' centre configurations discussed in this paper (see also figure 1).

Structural configurations	g-tensor		Optical excitation energy (eV)	
	Theory	Experiment [4]	Theory	Experiment [34]
E'_δ (dimer)	2.0018 2.0034 2.0043	2.0018 2.0021 2.0021	6.33	—
E'_γ (DB)	2.0018 2.0008 2.0007	2.0018 2.0003 2.0006	4.0 and 5.8	5.8
Back-projected E' centre	2.0018 2.0010 2.0008	—	5.5–5.6	—

3.2. Back-projected configuration of E' centre

In [18] we discussed the structure of the back-projected configuration of the E' centre and the conditions for its formation in amorphous silica. Essentially, such a configuration can be formed if a silicon ion that hosts the unpaired electron (Si_1 in figure1(b)) puckers through the plane of three nearest neighbour oxygen ions. The conditions for formation of this configuration were first formulated in [17]. Our results demonstrate that stable back-projected configurations can be formed if the inverted dangling bond faces the ample free space provided by the surrounding ring structure. However, the barrier for the formation of this configuration is about 1.5 eV and the barrier for the reverse process is about 1.0 eV. The typical values of hyperfine and super-hyperfine constants are 43.1 and 0.26, 0.23, and 0.29 mT, respectively [18] and the calculated components of the g-tensor of this centre are shown in table 1.

The calculated energy levels for the back-projected configuration are shown in figure 2(b). The singly occupied defect level is located at 2.54 eV above the top of the valence band. The first unoccupied 'spin-up' state is just 3.5 eV above the occupied defect level and is associated with the other silicon (Si_2 in figure 1(b)) on the opposite side of the vacancy. The second unoccupied level is located at 1.5 eV above the first one and corresponds to the p state of Si_2. Several unoccupied 'spin-down' states in the gap located close to the bottom of the conduction band are associated with the back-projected Si ion.

The optical absorption spectrum is formed by a group of transitions with energies close to 5.6 eV and relatively small oscillator strength of about 0.012–0.025. Most of these transitions can be described as excitations from the valence band states perturbed by the defect to the unoccupied p states associated with the back-projected Si ion. The nature and energies of these transitions are again close to those attributed to the E'_γ centre in irradiated silica samples [2].

3.3. Inter-conversion between E' centres and NOV

It has been demonstrated experimentally that positive charges accumulated in MOS oxide due to irradiation or high-field stress can often be neutralized by a high-temperature anneal at positive bias [20]. This implies that the positively charged oxygen vacancies, which are thought to be responsible for positive charge accumulation in the oxide, can be restored reversibly to NOVs after electron trapping. Whether this is indeed true is not clear, especially in the case of the back-projected configuration. Therefore, it is of interest to study the relaxation of E' centres after they capture an extra electron. We have considered one dimer, one unpuckered E' centre, and two back-projected E' centre configurations. The dimer and the unpuckered E' centre, upon capturing an electron, relax to the neutral vacancy configuration with almost the same geometrical parameters as their parent NOVs: the differences in Si–Si distances and O–Si–O angles are within 0.02 Å and 2°, respectively. The electron capture is accompanied by a strong network relaxation with characteristic relaxation energies of about 3 eV. This large energy is dumped into the local vibrations and could lead to local reconstruction of the amorphous network. This issue cannot be addressed by static calculations and requires further studies for clarification.

The situation is less clear cut in the case of the back-projected E' centre as the result depends on the method of calculation. In the Hartree–Fock calculations the system remains in the back-projected configuration after electron trapping and network relaxation. This indicates the existence of some local minimum in this configuration. However, in DFT calculations the same defect returns to the NOV configuration after being neutralized. The relaxation energy in this case is 6.6 eV. This may indicate that the electron correlation accounted for in DFT calculations eliminates the barrier between the NOV and back-projected configurations in the neutral state. Again, this question requires a more detailed study.

4. Conclusions

In this paper we have calculated the hyperfine parameters, g-tensors and optical excitation energies for the dimer and back-projected configurations of the E' centre in amorphous silica. The EPR parameters are in good agreement with the experimental values attributed to the E'_δ centre and the back-projected configuration of the E'_γ centre in silica glass. The optical transition energies are calculated for the first time and could be used for further experimental identification of these centres. We should note that the optical spectrum of these centres will be broadened due to the varying local and medium-range environments of different sites in an amorphous network. The predicted energies at around 6.3 and 5.6 eV overlap strongly with the broad spectrum attributed to the E'_γ centre. This implies that confident identification of these configurations may require analysis of both optical absorption and photo-luminescence spectra.

Our results support the dimer model of the E'_δ centre and for the first time provide a full range of spectroscopic parameters for the back-projected configuration of the E' centre in amorphous silica. However, they do not exclude the existence of the other models of E'_δ centre in specific types of silica glass described in section 1. Since the optical absorption of other models of E'_δ is expected to differ considerably from the one considered here, our results may

help to identify particular types of E'_δ centres. Thus, the embedded cluster method combined with classical MD for generating the amorphous structure can be used for predictive modelling of defect properties in amorphous silica.

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