Oxygen vacancies in amorphous silica: structure and distribution of properties

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Abstract

We used an ab initio embedded cluster method to study and compare three charged states of the Si-Si dimer configurations of oxygen vacancies in α-quartz and amorphous silica. The Si–Si bond in the neutral vacancy remains largely the same in both crystalline and amorphous SiO_2. In α-quartz the positively charged dimer E' centre exists only as a meta-stable configuration, whereas in amorphous silica stable dimer configuration can be formed at favorable precursor sites. Our results demonstrate that negatively charged dimer oxygen vacancies can be formed in α-quartz.

Keywords: SiO_2; oxygen vacancies; ab inito calculations; structure; spectroscopic properties

1. Introduction

Capture and emission of carriers at oxygen vacancy centers near Si/SiO_2 interface is thought to be responsible for $1/f$ noise in MOS devices [1]. Recent development of high-k oxides highlighted the potential importance of ultra-thin SiO_2 layers between Si and high-k oxides as well as amorphous HfO_2 and Hf silicates. However, theoretical modeling of effects of structural disorder and film thickness on distributions of defect properties and relative abundance of different defect configurations in amorphous materials is only starting to develop. In this paper we discuss some of the approaches to address these issues. We study the distributions of defect properties using an embedded cluster method.

We present the new results for oxygen vacancy defects in a-SiO_2 and compare the properties of neutral, positively and negatively charged oxygen vacancies in a-SiO_2 and in quartz. Our calculations predict the existence of negatively charged oxygen vacancies in α-quartz and their spectroscopic properties.

2. Method of calculations

The a-SiO_2 structure used in this work was generated using the periodic Molecular Dynamics (MD) method and classical inter-atomic potentials. It has a continuous random network structure where all Si ions are coordinated by 4 oxygen ions, and all O ions are coordinated by 2 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 centers were calculated using an embedded cluster technique developed in our group and implemented in the GUESS computer code [2,3]. In this method, a crystalline or amorphous system with a single point defect is divided into several regions. A spherical region I is centered 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, which is treated atomistically and contains several thousand atoms. The QM clusters are terminated by interface Si atoms (Si*), which have one of their Si – O bonds treated quantum-mechanically and the other three bonds treated classically. The detailed description of interface Si atoms and of the whole method as applied to α-quartz and a-SiO$_2$ is given in refs. [2,3]. Our approach differs from those used in previous studies in several respects. The calculations employing molecular clusters are not based on any particular a-SiO$_2$ model and so can capture only those defect properties which are determined by the most stable local properties of the material. Our calculations explore a well-established model of an amorphous structure and allow us to treat consistently the local, medium range and long range environment of each defect site. In addition we can build a statistical distribution of defect properties and relate these properties to the structure of the amorphous network. Besides, the embedded cluster model allows one to properly account for variations of the electrostatic potential in the amorphous network and for its polarization by the charged defect and to treat defects at interfaces.

3. Results and discussion

In this work we discuss the results of our modeling of neutral, positively and negatively charged oxygen vacancies in a-SiO$_2$ (see Fig. 1). We treat neutral vacancies first and then consider positively and negatively charged vacancies created by trapping a hole or an electron by a precursor neutral vacancy. This does not exhaust all mechanisms for creating these centers, but provides an effective method for studying their structure and properties in amorphous network.

To study the effect of structural disorder on the structure and properties of neutral oxygen vacancies,

up to fifty atoms large quantum clusters were embedded at about seventy different oxygen sites of continuous random network amorphous structure generated using classical MD. The distribution of these sites follows the distribution of Si – O bond-lengths, O – Si – O angles and rings in the amorphous structure. The results demonstrate a wide distribution of local defect configurations with Si – Si bonds ranging from 2.3 to 2.7 Å. In all cases we find that the removal of an oxygen atom is accompanied by a Si–Si bond formation. The distance between the two Si ions becomes much shorter than the original distance and, as Si ions move closer to each other they pull the network ions with them. However, the bond length and details of the lattice relaxation in the vicinity of the defect depend on the structure of local- and medium-range environments of the original site. Further analysis of the medium and long-range relaxation of the amorphous network induced by the formation of neutral vacancies demonstrates that this relaxation is very long ranged and propagates up to 10 Å from the vacancy site [2,3].
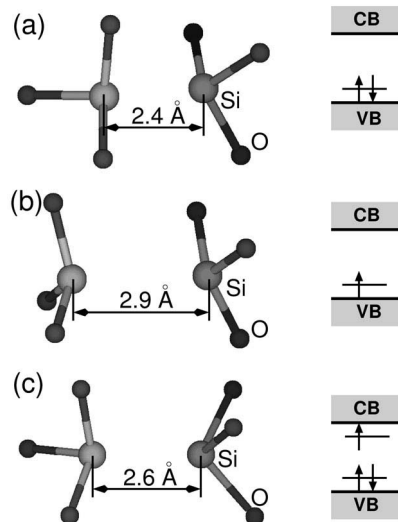

Figure 1. Local atomic structure and schematics of occupied energy levels relative to the band edges for several charge states of oxygen vacancies in silica: (a) neutral vacancy, (b) positively charges vacancy (E′ centre in a dimer configuration), (c) negatively charged vacancy (also in a dimer configuration).

The formation of a neutral oxygen vacancy induces a doubly-occupied energy level in silica band

gap. The full width of the distribution of defect levels calculated for neutral vacancies at 75 sites is about 1.5 eV. This broad distribution clearly demonstrates the extent of inhomogeneous broadening of defect levels in amorphous silica.

Positively charged vacancies were obtained by the hole trapping at neutral vacancies. Our modeling predicts the two major structural types of positively charged vacancies (E' centers): dimer and dangling bond centers [3]. The local structure of both types of centers depends on the medium range structure of the surrounding amorphous network. The majority of the dangling bond centers are unpuckered. We used structural "fingerprints" [3,6] to find two other structural types of dangling bond centers: the puckered configuration and the back-projected configuration of E' centers. In each case we find a distribution of both structural and EPR parameters and calculate the optical absorption spectra. We found that the average values of the EPR parameters for all dangling bond configurations are similar. We formulated the structural criteria, which favour the formation of different types of centers in the original amorphous structure in terms of the average Si – O distance of oxygen ion with its two neighboring silicon ions [3].

One can distinguish two types of displacements of Si ions following the relaxation from a neutral vacancy into an ionized configuration. The formation of dimer type centers is characterized by relatively small displacements of atoms from their positions in the precursor neutral vacancy. In this case the two Si ions do not fall far apart so that Si–Si bond could still be preserved. In most dangling bond centers, the two Si ions find themselves much further apart with a large displacement (maximum of 1.0 Å) from the initial neutral vacancy configuration. This relaxation is determined by both the initial short and medium range structures and is accompanied by the reorientation of surrounding tetrahedra.

We focus in more detail on the structure of the E'_δ centre, which is thought to serve as meta-stable electron trap near Si/SiO$_2$ interface. However, there is still a controversy regarding its structure in amorphous silica and whether it is a stable or a metastable defect. In particular, the experimental results of Griscom and Friebele [4] 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 [5] is correct, this could in fact be a very common defect with one of the simplest structures in silica. The recent theoretical results [1] 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.

The results of our calculations support the dimer model of the E'_δ centre. The calculated *hf* splittings due to the interaction of the unpaired spin with two Si ions of the dimer are about 10.0 mT. They are close to those measured experimentally for the E'_δ centre [6]. The width of the distribution of hyperfine parameters due to disorder estimated from several configurations found in our calculations is 5.0 mT. The unpaired electron density in the dimer configuration is delocalized to a large extent *between* the two Si ions. The calculated components of the g-tensor are much more isotropic than those for the dangling bond E' centre configuration and are close to those attributed to the E'_γ centre [6]. We used TD-DFT to calculate the optical transition energies for this centre. The main optical transition has an energy of 6.3 eV and an oscillator strength of about 0.35. It overlaps with the broad spectrum attributed to the E'_γ centre in irradiated glass samples.

The flexibility of the SiO$_2$ lattice suggests that the lattice relaxation could promote trapping of an extra electron by a neutral vacancy. Such a possibility has been suggested in earlier molecular cluster calculations [7,8]. To test this idea, in this work we have calculated the electronic structure of the negatively charged oxygen vacancy in α-quartz. For that purpose we used a small, Si$_2$O$_7$Si*$_6$, and a large, Si$_8$O$_{25}$Si*$_{18}$, QM clusters, where the stoichiometry is given for the non-defective case. In both sets of calculations we considered a fully relaxed neutral oxygen vacancy as a precursor state for trapping an electron. First, the electronic structure of the vacancy with an extra electron was calculated using the neutral vacancy geometry. We found that the one-electron state occupied by the additional electron (highest occupied molecular orbital or HOMO) is slightly split from the bottom of the Conduction band (CB) as represented by the lowest unoccupied molecular orbital (LUMO). The nature of the HOMO state in the unrelaxed vacancy depends on the size of the QM cluster: is the case of the small cluster it is a π-like state induced by the oxygen vacancy, in the case of the large cluster it is anti-bonding $\sigma*$-like

state. The HOMO–LUMO splittings are 1.4 eV and 0.8 eV respectively. In both clusters, the additional electron appears to be predominantly localized in the vicinity of the vacancy, which allows us to suggest that the unrelaxed vacancy in α-quartz is a shallow electron-trapping center. The total energy of the negatively charged vacancy was then minimized with respect to the atomic coordinates of all centers in region I. The electronic structure and calculated properties of the fully relaxed negatively charged oxygen vacancy are similar in both small and large clusters, therefore we only report the results obtained using the large cluster. The most prominent feature of the geometry relaxation is the increase of the Si–Si distance in the vacancy by approximately 0.2 Å. The total energy gain in this relaxation is 1.7 eV. The HOMO state after the relaxation has an anti-bonding σ^* character and the HOMO–LUMO splitting increases to 3.5 eV.
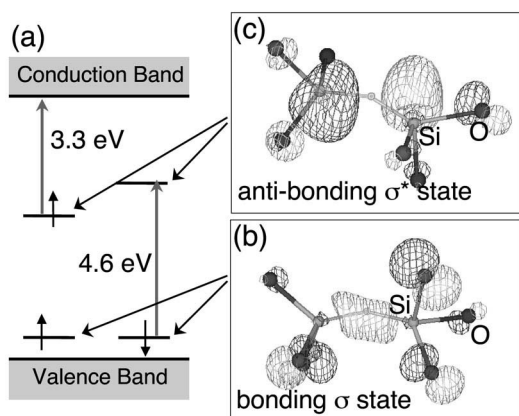

Figure 2. (a) Energy levels diagram for the negatively charged oxygen vacancy; (b) and (c) show the one-electron wave-functions for the doubly occupied σ and singly occupied σ^* states respectively. The nature of optical transitions is indicated with red arrows. The excitation energies are calculated using spin-unrestricted TD-DFT approach.

The negatively charged vacancy can be characterized by its magnetic properties and optical absorption. Our calculations suggest that the hyperfine interaction of the unpaired electron spin with neighboring ^{29}Si atoms is 32 mT and the principal values of the g-tensor are 1.9993, 2.0023, and 2.0027. The most intensive optical absorption transitions were found at 3.3 eV and 4.6 eV, as shown in Fig. 2(a). The former corresponds to the

excitation of the unpaired electron from the anti-bonding σ^* state (Fig. 2c) to the states at the bottom of the CB, while the latter is a so-called β-spin transition in which an electron is excited from a doubly occupied σ-type bonding state of the vacancy (Fig. 2b) to the singly occupied σ^* state (Fig. 2c).

4. Conclusions

In this work we considered three charged states of the dimer configurations of oxygen vacancies in silica. The results demonstrate the wide distribution of defect levels of positively charged and neutral oxygen vacancies in the bulk a-SiO$_2$ and illustrate a potential for electron trapping at neutral vacancies. Similar effect is expected to take place near the Si/SiO$_2$ interface. Since the structural relaxation around these defects is long-range, it can be constrained by the oxide film boundaries. The network disorder and structural constraints imposed by the film thickness and by the position of a defect with respect to the interface may therefore strongly affect the position of the defect level in the band gap.

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