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Defects in amorphous SiO_2: Valence alternation pair model

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The structure of the intrinsic coordination defects in amorphous SiO_2—namely, a nonbridging oxygen and a threefold-coordinated silicon—is studied using a modern *ab initio* method, aiming at elucidating their actual structure and possibly their contribution to mass transport. We show that the silicon part adopts a planar configuration and does not make any new bonds. Conversely the nonbridging oxygen develops spontaneously a new bond with an already fourfold-coordinated silicon, which becomes now fivefold coordinated. We discuss the energetics of this defect, including the energy gain due to the formation of the fivefold-coordinated silicon, as well as the possible contribution it could give to oxygen self-diffusion.

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INTRODUCTION

Existing models for intrinsic defects in SiO_2 pertain to two groups: point defects and coordination ones. Defects belonging to the first group, vacancies and interstitials, are well documented, at least for oxygen defects. Most of the experimental information comes from electron spin resonance (ESR) studies done on the paramagnetic form of the defect produced from the intrinsic diamagnetic precursor under ionizing radiation.[1] The high level of local chemical order in SiO_2 allows defining very clearly the notion of vacancies and interstitials, as a missing or an extra oxygen atom on a given tetrahedron. Silicon defects received theoretical attention only recently, probably because their experimental knowledge was much less developed; nevertheless, their structure and energetics are being gradually elucidated.[2–5] However, silica is a noncrystalline material with a mixed ionic-covalent bonding, so a second kind of defects can be defined: the broken bonds i.e., pairs formed of a threefold-coordinated silicon atom and of a singly coordinated oxygen one. Various authors proposed long ago that similar pairs of dangling bonds could be the intrinsic defect in glassy chalcogenides semiconductors. A low enough formation energy could result from a charge transfer between both members of the pair, despite the high formation energy of a broken bond. The defect would then be stabilized by the formation of a dative bond between the undercoordinated positively charged part of the pair and a normal lattice chalcogen atom, thanks to the lone pair of *p*-like electrons available on the latter.[6,7] The strong electron-phonon coupling gives rise to a negative effective correlation energy from neutral to charged pair. In the early state of the model the energy cost of the defect pair with respect to perfect bonding was proposed to be the sole correlation energy, the well-known U term, of the electron pair in the nonbonding level of the negatively charged part. This model explains quite satisfactorily many properties of glassy chalcogenides semiconductors, mostly the absence of paramagnetism, despite the high concentration of gap states, and the pinned Fermi level. The term "valence alternation pair" (VAP) was coined for this defect.[7]

Oxygen is also a chalcogen, so similar models have been proposed for silica too, involving various specific reactions for the dative bond rooting for the low formation energy of the defect.[8–11] Broken bonds, invoking or not the specific aspects of the VAP, indeed have been frequently proposed as a self-diffusion and creep mechanism in silica, among many others.[12–14] Although this idea is qualitatively well supported by the well-known effect of extrinsic bond breakers, like OH groups and alkali solutes, on both properties, we are not aware of detailed models going beyond the qualitative step. Indeed we lack solid models either of mass transport based on broken bonds or VAP or simply of their true structure in SiO_2. The aim of the present work is to make the first step in this direction and present the actual structure of the broken bonds in silica using modern *ab initio* tools in the framework of the density-functional-theory local-density-approximation (DFT-LDA) approach. The more ambitious purpose of developing quantitatively a complete model of mass transport based on the idea of broken bonds will be developed in a forthcoming publication.

VALENCE ALTERNATION PAIR MODELS FOR SILICA

The available models for VAP defects in silica propose three possible structures. In the original formulation the VAP concept supposes that dangling bonds are present in three charge states: +1, 0, and −1, each charge state being able to change by capture of electrons or holes, either from external charge injection or by exchange between other similar defects. This scheme explains the pinning effect on the Fermi level observed in chalcogenides. In Mott's original proposal for silica[8] the bond severing produces a pair of dangling bonds, one on the oxygen and the other on the silicon, but the sole oxygen orbital plays the role of the amphoteric defect, like the chalcogenide selenium. The VAP defect is constituted from a negative oxygen and a positive one, after a charge exchange between the neutral dangling bonds of the oxygen atoms of two pairs of dangling bonds. The defect should be stabilized by the energy which is gained by the dative bond formation between the positively charged oxygen and a normal lattice oxygen, using the lone pair of the latter, as depicted in Fig. 1. But Mott noticed that this defect

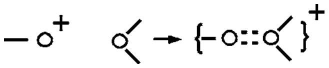

FIG. 1. Atomic configuration corresponding to Mott's proposal for the structure of the VAP. The amphoteric pair in this model is constituted by two oxygen atoms coming from two different pairs of broken bonds. Here we show the reaction of the sole positive oxygen with a normal "network" atom, not the negative one or the two silicon parts, since none of them are involved in a new bond formation.

should have a very low concentration in the bulk, probably a larger one at the Si-SiO$_2$ interface in the oxide formed on silicon surfaces. He also considered the E' center associated with the oxygen vacancy as a possible candidate for the VAP defect.

The original scheme of Mott was modified by Greaves owing to the electronegativity difference between silicon and oxygen.[10,11] According to this author the bond-breaking process is supposed to leave directly a positively charged silicon atom and a negatively charged oxygen one, forming then the VAP. The electronegativity difference stabilizes the Si$^+$-O$^-$ pair, rather than a negative effective correlation energy as in Mott's scheme. Further energy can be gained by the formation of what Greaves calls a "quasibond" of the Si$^+$ with a normal oxygen. In the course of later irradiation by ionizing particles or due to charge injection during operation in a microelectronic device, charge exchanges can occur by electron or hole capture on either the silicon or oxygen part. This effect would be at the root of the role of the defect in perturbing the behavior of devices. After capturing a hole the negative oxygen becomes neutral and a partial bonding can occur with a normal lattice oxygen. This scheme is depicted in Fig. 2.

A third model has been proposed by Lucovsky.[15,16] Considering the rather high formation energy of the pair involved in Greaves's model, since this model keeps more or less a broken bond, he proposes that the Si$^+$ makes a full new bond with a normal lattice oxygen using the available lone pair of the latter, recovering the full energy of the missing bond. The formation energy of the defect amounts then to the sole correlation energy of two electrons in the nonbonding level of the O$^-$ member of the pair. This scheme is depicted in Fig. 3. Once more, the defects can act as electron and hole traps and change their bonding accordingly, as shown also in the same figure, noting that in Fig. 3 pairs of charge are supposed to be trapped, according to Lucovsky.

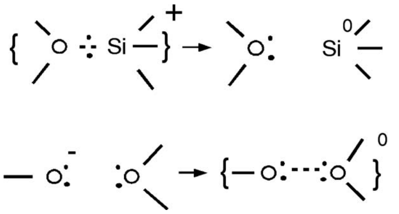

FIG. 2. Atomic configuration of Greave's proposal for the VAP. The pair is constituted by a negative oxygen and a positive silicon. On the left of the figure we show the intrinsic diamagnetic state of the two parts of the defect before any charge exchange. On the right we display the paramagnetic state, resulting from an electron or hole capture. On top the positive silicon experiences a weak dative bond, symbolized by the dashed line plus two dots, with a normal oxygen atom, and can capture an electron (not shown) breaking then the bond. On the bottom we see the negative oxygen part capturing a hole (not shown) and becoming able to form a weak dative bond, symbolized by the dashed line, with a normal lattice oxygen. The lone pairs of the oxygen atoms are shown as pairs of dots.

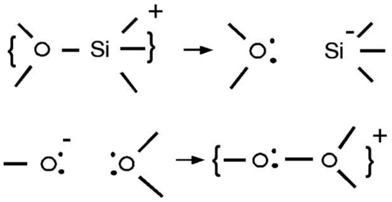

FIG. 3. Lucovsky's proposal for the VAP defect. Here is sketched also the capture of two electrons (top), or two holes (bottom), so all defects are diamagnetic. The dative bond between the positive silicon and a normal lattice oxygen (top left), supposed to be a full one, is represented by a solid line; this is also the case of the oxygen part which can form a full dative bond with a normal lattice oxygen (bottom right) after the capture of a pair of holes (not shown).

The equilibrium concentration of any defect is determined by its formation free enthalpy. The early efforts done for calculating the formation energy, using *ab initio* total energy methods in the case of the selenium at the origin of the VAP idea, already provided evidence that the energy estimates sketched on the above qualitative grounds could be vastly erroneous.[17] The energetics of the qualitative models formerly proposed for SiO$_2$ has been tackled by Robertson[14] using the semiempirical molecular orbital method MINDO/3 for the calculation of the formation energies. The calculations are based on the use of small clusters of atoms, containing from three to eight tetrahedra, neglecting then the role of the amorphous lattice in the structural relaxation. According to this author the formation energy of a broken bond could amount to 4.6 eV, much higher than expected from former qualitative models and approximately half the formation energy of an oxygen Frenkel pair, determined at 8.4 eV. For the latter our results for quartz[18] and silica[5] amount, respectively, to 7.4 and 6.9 eV i.e., quite lower than this early evaluation. The use of small clusters of tetrahedra precludes a rigorous determination of the final equilibrium structure of the defect. Nevertheless, similar semiempirical methods have been used with success to determine the equilibrium structure of the oxygen vacancy in quartz, in either the zero or the +1 charge state, using clusters of increasing size as computer power increased.[19,20] We can probably compare these results with our problem, since the positively charged oxygen vacancy contains a positive silicon akin to the Si$^+$ member of the VAP. These calculations show that the positive silicon, showing initially the longest bond with the missing oxygen, relaxes backward through the basal plane of its tetrahedron and forms a new dative bond with a normal oxygen, gaining then a puckered configuration. This result, in quite good agreement with experimental facts,[1] has been later confirmed by a lot of authors using either semiempirical methods too, or DFT techniques, in either quartz or silica.[21–24] All these results agree to propose that in quartz the zero-charge oxygen vacancy takes the form of a *c*-Si-like silicon-silicon bond, the dimerized form. Conversely in the +1 charge state the puckered configuration is the stable form with respect to the dimerized one, by approximately 0.3–0.4 eV in the LDA and by less than 0.1 eV in generalized gradient approximation (GGA) calculations. Conversely, in the neutral state, the dimer structure is the stable one by roughly 2 eV. It must be noted that the relevance of this structural model, deduced mostly from calculations done on quartz, has been questioned for silica[25] and should probably be partly reconsidered as the main equilibrium structure of the positively charged oxygen vacancy.[3,4] Whatever the actual status of the puckered structure of the +1 oxygen vacancy in silica, it should be at least a plausible model for the charged-silicon dangling bond. Conversely very little attention, if any, has been given to the oxygen dangling bond. In Mott's original VAP scheme, as well as in Greaves's one, the positive oxygen forms a dative bond with a normal lattice one, but the negative part is supposed to remain isolated.

We will present here a model of the most frequent equilibrium structure of the Si^+-O pair of dangling bonds. In the following section we will describe only very briefly the DFT-LDA approach we have used, since it has already been reported in greater details elsewhere.[5,18,26] Then we will present our results on the structure of the pair of broken bonds, and finally we will discuss them with respect to the above-mentioned models.

CALCULATION METHODS

Silica is a disordered, nonequilibrium material. As such one must cope with two critical problems when using *ab initio* methods. First, any physical property is distributed and can only be determined on a statistical basis, each atom in a given block of silica having a specific environment. Second, this block of silica itself, which is necessarily very small if one wants to do structural relaxations using *ab initio* approaches, should be proved to be representative of a bulk silica.

The first aspect, the disorder, requires calculating the defect properties on a large number of sites of the model, pointing to the need for a fast quantum approach. In this prospect we chose to do a systematic study of point defect formation energies using a method based on the use of a local basis for expanding the electron orbitals, using the SIESTA code.[27] Here the main interest is the capability to realize statistical studies for a reasonable amount of computation time. As we shall see below, the validity of the calculation has to be checked versus a plane-wave method, for in the latter the completeness of the wave basis can be safely controlled. We used for this purpose the PWSCF code.[28] In the present study we have used the DFT-LDA approach for two reasons, discarding the DFT-GGA which is frequently shown to describe more accurately the bonding properties of solids. First we are aiming, as said above, to build a complete picture of the dynamics in SiO_2. In this prospect we have to compare all the proposed mechanisms on an equal footing, and our former studies have been developed using this approximation. Moreover, the errors in the binding energy coming from the use of the LDA, instead of the GGA, are one order of magnitude lower than defect formation energies,[23] and the actual interest in the GGA approximation for silica has been strongly cast in doubt by the bad ordering of the energies of the different tetrahedral crystalline phases of SiO_2 it leads to.[29] On the other hand, in our specific perspective of defect studies, the interest of the GGA is less obvious since generally this approximation leads to slightly less precise formation energies. The origin of the better bonding description in the GGA lies indeed in an error cancellation which does not occurs in defect calculations, at least for vacancies.[30]

In the second prospect, getting a "good" silica, the most useful route is to use molecular dynamics, in periodic boundary conditions, for preparing a small block of silica by melting a crystal, equilibrating it at a high temperature, and then cooling it as slowly as possible down to ambient conditions. It is here feasible to use *ab initio* calculations,[31] but the price is quite heavy in terms of computing time. Instead one can combine a preparation by empirical molecular dynamics followed by a careful relaxation using an *ab initio* approach.[3,26,32,33] In this last method the cooling rates can be much slower, so the structure is closer to an actual silica. In particular we proved that despite the very small size of the silica models we have built, their structure can be shown to be fully converged with respect to density, to defect formation energies, and, to a smaller extent, to the distribution of closed rings.[3,5,26]

The silica models prepared with the empirical molecular dynamics method along this line contain 108 or 192 atoms. They are prepared by successively melting a cristobalite crystal in the *NVT* ensemble using the Van Beest–Kramer–Van Santen potential,[34] equilibrating the liquid, and then slowly quenching it. The potential is slightly modified for allowing high-temperature annealing.[26] The structures obtained in this way are then relaxed in the local basis approach (SIESTA code), with respect to atomic positions but also to lattice parameters, allowing one to get a silica model at ambient pressure. We have checked the results obtained by relaxing a few of these models within the plane-wave method (PWSCF code). As we shall show below, if the agreement is good between both quantum approaches for nondefective models, one has to be careful in cases when complex defects are formed. The quench rates used in the empirical step are either 10^{12} K/s or 2.3×10^{14} K/s. With the first quench rate the models of silica obtained are free of coordination defects and the ring statistics is as good as can be done in such small systems, in particular free of three-membered rings. In the second case one can observe either defective systems, containing overcoordinated and undercoordinated silicon and oxygen atoms, or not.[3,5,26] The interesting point here is that all models prepared with the slow quench rate have nearly the same total energy, within a tenth of an eV. Conversely the models quenched with the high rate, although still clearly grouped by energy, display, however, a larger dispersion, of the order of half an eV. Their average energy is roughly 8 eV above the energy of the "good" silica models prepared with

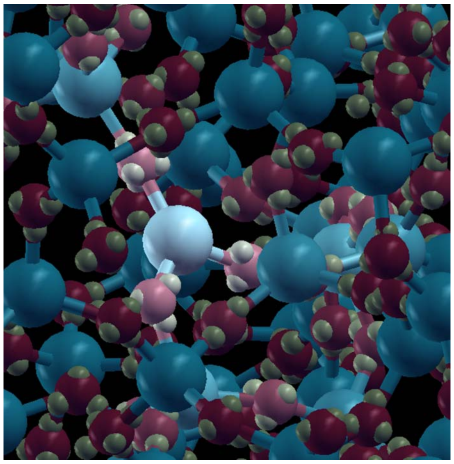

FIG. 4. (Color online) Atomic configuration of the silicon part of the broken bond. From larger to smaller spheres: silicon atoms, oxygen atoms, and Wannier functions centers. Here the positively charged silicon remains stable in the planar, sp^2, electronic structure. The lighter silicon atom in the center of the figure is surrounded by its three oxygen neighbors. The centers of the Wannier functions are situated on the oxygen atoms near the root of the stick representing the bond (color online).

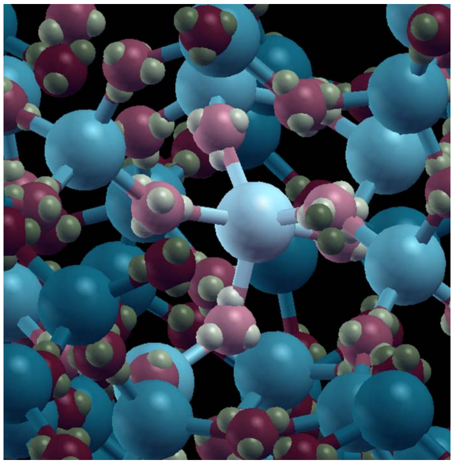

FIG. 5. (Color online) Atomic configuration of the oxygen part. From larger to smaller spheres: silicon atoms, oxygen atoms, and Wannier functions centers. The oxygen of the VAP, in the forefront, forms a new bond involving three centers: itself, a normal lattice silicon in the center of the figure, and the one of the normal oxygen neighbors which was in the rear of the tetrahedron. The other three oxygen neighbors come in a planar equatorial configuration around the silicon (color online).

the slow quench rate.[3] The usual structural tests, pair distribution functions, distributions of structural angles, or rings statistics do not allow one to discriminate very clearly these two groups of models, but the former have an equilibrium density of 2.18 $\mathrm{g/cm^3}$, the latter amounting to 2.33 $\mathrm{g/cm^3}$. It looks as if the spontaneous formation of a pair of coordination defects is only possible beyond a certain level of structural disorder. One of these defective samples, containing a single pair, a threefold-coordinated silicon and a singly coordinated oxygen—i.e., a VAP—is used here to study the actual structure of this kind of defect.

RESULTS

The equilibrium structures of both end members of the VAP defect determined using the plane-wave basis approach are shown in Figs. 4 and 5. We have analyzed the electronic charge distribution using maximally localized Wannier functions (MLWFs) after both the local basis and plane-wave steps.[35] The decomposition of the charge density into a MLWF is particularly interesting in the case of defects, where localized states in the band gap can appear. For these levels the Bloch function at the Γ point coincides with the MLWF, but then a comparison with the other MLWFs, which are obtained on identical footing, can give very interesting insights into the role of electrons on the atomic structure and bonding. In all cases the structures we have obtained for the VAP corresponds effectively to a spontaneous dissymmetric bond severing, with a negative oxygen and a positive silicon, both before and after the plane-wave basis step.

The silicon member, Fig. 4, corresponds to a threefold-coordinated silicon atom, in a planar sp^2 hybridization scheme. The plane-wave approach did not produce noticeable changes with respect to the structure observed after the local basis step. If the silicon end member bears effectively a positive charge, in agreement with Greave's model, the defect was not observed to be stabilized by the formation of a new bond with a normal oxygen atom, as supposed at least partially, in all VAP models. The silicon atom remained threefold coordinated. This result is at variance with the better known configurations of the various E' defects in $\mathrm{SiO_2}$, which, as recalled above, correspond mostly to the stable configuration of the positively charged oxygen vacancy, called E_1' center in quartz and E_γ' in silica. For these defects the silicon atom on the long bond side of the missing oxygen forms a new bond with a back oxygen. This is not the case here. Since the dimer configuration of the positively charged oxygen vacancy is metastable, not unstable, with respect to the puckered one, we have searched for this possibility, using a relaxation method under the constraint of a fixed distance between the silicon atom and the most favorable oxygen neighbors. We have searched for all the oxygen neighbors which would not correspond to the formation of edge-sharing tetrahedra or a three-membered ring after the possible new bond formation. According to former results, the equilibrium $\mathrm{Si^+}$-O bond length should be of the order of 2 Å.[20] The energy versus Si-O distance curves we obtained show indeed in some cases a slight inflection for this distance, but no energy minimum corresponding to an equilibrium position, either stable or metastable for any of the neighbors we have studied. We present as an example in Table I the evolution of the total energy, with respect to the energy of the initial position, as a function of the distance between the silicon and an oxygen. The energy increases without any minimum, even metastable or, in this case, any inflection at the proposed distance of 2 Å. It was already known that in silica only a small fraction of the oxygen vacancies of charge +1, of the order of 10%, were able to

TABLE I. Evolution of the total energy of the VAP-containing silica model as a function of the distance between the silicon bearing the broken bond and a neighboring oxygen. The calculation is done by constraining the distance while relaxing all the other degrees of freedom, whether atomic or cell parameters. There is clearly no rebonding in the puckered position, in this case, nor a reminiscence of a possible (meta)stable position around 2 Å.

Silicon-oxygen distance (Å)	Energy (eV)
3.45	0
3.18	0.02
2.73	0.19
2.27	0.3
1.82	0.37
1.62	0.82
1.47	1.71

establish spontaneously such a stabilizing backbond.[3,4] The present result, totally negative, could therefore be due either to the higher disorder of the silica model containing the pair of broken bonds, as compared to the good silica models, or to the lack of a large enough statistical basis, defect configurations elsewhere in the system being possibly able to give rise to a puckered configuration. In both cases anyway, this means that in most sites the silicon part of the VAP should remain unreconstructed. The dative bond between the silicon member of the VAP and a normal oxygen atom is not the origin of a low formation energy, if any.

Conversely the oxygen end member of the VAP, Fig. 5, presents an equilibrium structure which is quite different from the various VAP proposals. The oxygen suffers a strong reconstruction which was not foreseen in any of them. After the relaxation step using the local basis approach, the stable configuration was still the unreconstructed oxygen dangling bond. But as shown in Fig. 5, at the end of the relaxation within the plane-wave approach, the oxygen atom has formed a new bond with a normal silicon atom. The unreconstructed form of the oxygen is clearly an artifact of the specific basis used for expanding the electronic wave functions, favoring the tetrahedral configuration of the silicon atoms, an artifact that has already been noted.[3] The local basis approach is of invaluable interest in studies of amorphous solids for its efficiency, but has to be checked against a safer approach when exotic configurations are studied, in the present case the broken bonds. A proper improvement of the pseudoatomic basis could probably be worth here.

The silicon atom involved is now pentacoordinated in a bipyramidal structure. Three oxygen atoms form an equatorial plane with distances of 1.656, 1662, and 1.679 Å from the silicon; the Si-O-Si angles in this plane measure 109°, 117°, and 133°. The other two oxygen atoms form the apexes and are at 1.825 and 1.856 Å from the silicon with angles with respect to the equatorial plane close to the normal, within less than ±5°. The energy gained in this last relaxation step amounts to 0.5 eV. This pentacoordinated structure of the silicon atom is quite common for negatively charged defects in SiO_2, as already observed for the hydrogen impurity, associated or not with an oxygen vacancy.[23] The novelty here is the relatively high value of this energy gain, in contrast with the energy *increase* observed during the formation of the puckered configuration of the silicon part of the VAP, varying between 0.7 eV and 1.5 eV. At variance with the original ideas, the stability source of the VAP, if any, will be mostly due to the reconstruction of the oxygen part and not of the silicon one. This result is also fully coherent with the remark already made in the past that the VAP were not visible in a concentration compatible with the expected formation energy.[36] Whatever the formation energy of the defect, the VAP bears only orbitals containing an even number of electrons.

THERMODYNAMICS AND MIGRATION

In equilibrium at temperature T, the defect concentration is controlled by their formation free enthalpy G^f_{VAP} according to

$$c_{\mathrm{VAP}} = \exp\left(-\frac{G^f_{\mathrm{VAP}}}{k_BT}\right) = \exp\left(\frac{S^f_{\mathrm{VAP}}}{k_B}\right)^{*} \exp\left(-\frac{E^f_{\mathrm{VAP}}/2}{k_BT}\right). \tag{1}$$

Here S^f_{VAP} is the vibrational entropy and E^f_{VAP} the formation energy at zero pressure. The factor of 2 in the last factor of Eq. (1) comes from the configurational part of the entropy of the pair. We have already shown that in quartz the entropy factor, the first one, although not negligible, does not change by orders of magnitude the concentration.[18] The same remark is certainly valid here. However, the definition of a formation energy for a broken bond is not a trivial task. The cohesive energy of SiO_2 corresponds to a bond energy amounting to 4.55 eV.[18,26] However, this is certainly a lower limit to the actual formation energy since the breaking of a bond does not correspond to the whole of the lattice distortion needed to stabilize the pair and separate the two parts. Conversely, if, as said above, all "good" silica models prepared using the slow quench rate have a quite well-defined energy and rapidly quenched models, exhibiting a broken bond, also have also a well-defined but higher-energy level, we can define then the energy difference between the two groups of models as the formation energy of a VAP. This value in turn should be an upper limit since the models obtained by fast quenching correspond to a high-temperature equilibrium. So the formation energy of the pair should be contained in the 4.55–8 eV interval, a relatively wide range indeed. The probable value should then be slightly higher than the former Robertson estimate of 4.6 eV.[14] This is to be compared to the mean energy of the oxygen Frenkel pair, 6.9 eV, quite lower than Robertson estimate at 8.4 eV.[26]

Lacking the experimental determination of true VAP concentrations, we can only try to check the validity of our calculations with respect to the activation energy of transport in the hypothesis that these defects are involved in the self-diffusion mechanism of either oxygen or silicon, provided that we know the migration part. Let us examine the case of oxygen, for which the activation energy in the intrinsic regime amounts to 4.7 eV.[37] As already said there is presently no complete diffusion model available based on the broken

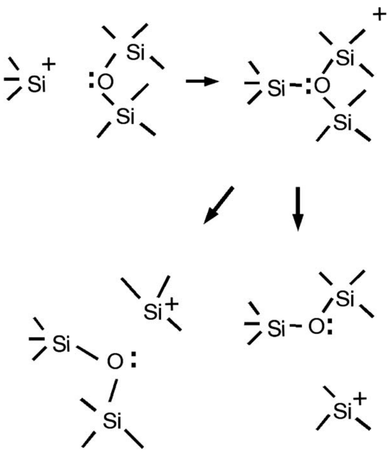

FIG. 6. Scheme of an oxygen migration mechanism involving the silicon end member of the VAP. On the top left the positive silicon is isolated; then, a dative bond formation occurs (top right). This bond can decay in any of the three bondless configurations shown, the initial one or two others involving a bond with an other silicon (bottom, left and right). At the end of these two last sequences the oxygen atom has jumped over one intertetrahedron distance.

bond concept. However, it is easy to realize that in order to produce oxygen migration, the mechanism proposed must allow for an oxygen to jump from one tetrahedron to an other. The silicon member of the pair, at least, can allow oxygen diffusion. Indeed, if a puckered configuration is formed, the threefold-coordinated oxygen, after breaking a normal bond, can be left on any of the three tetrahedra involved, as shown in Fig. 6. In this picture the puckered configuration of the defect is an intermediate step in the migration path of the oxygen defect, whether stable or not. If this is not the stable configuration, it can be viewed as a step toward the saddle position during the migration of an oxygen atom from one tetrahedron to the next. Assuming that the total migration energy cost involves a significant fraction of a Si-O bond—energy, say, 2 eV as a low estimate—corresponding to the severing of one of the two normal bonds of the oxygen, then, in the intrinsic regime of defect formation, the diffusion activation energy should be in the range 4.2–6 eV. A more rigorous and complete study of the broken bond mechanism is underway.

It is nevertheless clear that in the intrinsic self-diffusion regime, both the broken bond mechanism and the interstitial one, could compete for the oxygen self-diffusion. Both mechanisms correspond to an activation energy matching, at least roughly in the case of VAP, the experimental value of 4.7 eV.[18,37]

CONCLUSION

In the present work we have studied the atomic structure of the frequently evoked broken bonds in silica, formed by a pair of dangling bonds, one on a silicon and another on an oxygen atom. We compare our results to the formerly proposed models of the valence alternation pair. Using modern *ab initio* methods for determining the energy and the structure of the pair of dangling bonds, we show that the dative bond formation between the silicon part of the pair and a normal lattice oxygen is not the source of the relatively low energy of formation of this defect, at variance with all existing models. Nevertheless, this point could have been inferred from previous studies of the E' defect in silica. In addition we show that the proper stabilizing source of this type of defect lies in the formation of a complex bond on the oxygen part. The negatively charged oxygen indeed forms a three-atom bond with a neighboring silicon, lowering the formation energy by 0.5 eV. A first and rough estimate of the possible contribution of broken bonds to oxygen self-diffusion in intrinsic silica shows that these defects could compete with the interstitials and gives an activation energy which is compatible with known experimental results.

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[1] D. L. Griscom, in *The Physics and Technology of Amorphous* SiO_2, edited by R. A. B. Devine (Plenum Press, New York, 1988).
[2] G. Roma and Y. Limoge, Phys. Rev. B **70**, 174101 (2004).
[3] L. Martin-Samos, Ph.D. thesis, Cergy-Pontoise University, 2004.
[4] N. Richard *et al.*, J. Non-Cryst. Solids **351**, 1825 (2005).
[5] L. Martin-Samos, Y. Limoge, J. P. Crocombette, G. Roma, N. Richard, E. Anglada, and E. Artacho, Phys. Rev. B **71**, 014116 (2005).
[6] R. A. Street and N. F. Mott, Phys. Rev. Lett. **35**, 1293 (1975).
[7] M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. **37**, 1504 (1976).
[8] N. F. Mott, Adv. Phys. **26**, 363 (1977).
[9] N. F. Mott, J. Non-Cryst. Solids **40**, 1 (1980).
[10] G. N. Greaves, Philos. Mag. B **37**, 447 (1978).
[11] G. N. Greaves, J. Non-Cryst. Solids **32**, 295 (1979).
[12] P. Donnadieu, 3rd cycle thesis, Paris-Sud University, 1984.
[13] N. F. Mott, Philos. Mag. B **56**, 257 (1987).
[14] J. Robertson, in *The Physics and Technology of Amorphous* SiO_2, edited by R. A. B. Devine (Plenum Press, New York, 1988), p. 113.
[15] G. Lucovsky, J. Non-Cryst. Solids **35**, 825 (1980).
[16] G. Lucovsky, Philos. Mag. B **39**, 513 (1979).
[17] D. Vanderbilt, Solid State Commun. **35**, 535 (1980).
[18] G. Roma, Y. Limoge, and S. Baroni, Phys. Rev. Lett. **86**, 4564 (2001).
[19] J. K. Rudra and W. B. Fowler, Phys. Rev. B **35**, 8223 (1987).
[20] K. C. Snyder and W. B. Fowler, Phys. Rev. B **48**, 13238 (1993).
[21] D. C. Allan and M. P. Teter, J. Am. Ceram. Soc. **73**, 3247 (1990).
[22] M. Boero, A. Pasquarello, J. Sarnthein, and R. Car, Phys. Rev. Lett. **78**, 887 (1997).
[23] P. E. Blöchl, Phys. Rev. B **62**, 6158 (2000).
[24] C. M. Carbonaro, V. Fiorentini, and F. Bernardini, Phys. Rev.

Lett. **86**, 3064 (2001).

[25] T. Uchino, M. Takahashi, and T. Yoko, Phys. Rev. Lett. **86**, 5522 (2001).

[26] L. Martin-Samos *et al.*, Europhys. Lett. **66**, 680 (2004).

[27] P. Ordejon, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996).

[28] S. Baroni *et al.*, URL http://www.pwscf.org

[29] T. Demuth *et al.*, J. Phys.: Condens. Matter **11**, 3833 (1999).

[30] L. M. Almeida, J. P. Perdew, and C. Fiolhais, Phys. Rev. B **66**, 075115 (2002).

[31] J. Sarnthein, A. Pasquarello, and R. Car, Phys. Rev. B **52**, 12690 (1995).

[32] M. Benoit *et al.*, Eur. Phys. J. B **13**, 631 (2000).

[33] R. M. Van Ginhoven, H. Jonsson, and L. R. Corrales, Phys. Rev. B **71**, 024208 (2005).

[34] B. W. H. van Beest, G. J. Kramer, and R. A. van Santen, Phys. Rev. Lett. **64**, 1955 (1990).

[35] N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997).

[36] E. P. O'Reilly and J. Robertson, Phys. Rev. B **27**, 3780 (1983).

[37] J. C. J. Mikkelsen, Appl. Phys. Lett. **45**, 1187 (1984).