

Oxygen and Silicon Self-Diffusion in Quartz and Silica: The Contribution of First Principles Calculations

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Abstract. Despite its importance as a material in many domains, SiO_2 is still a very badly known material from the point of view of materials science. Experimentally the silicon and oxygen diffusion has been determined in silica as well as in quartz, but several discrepancies arise between different authors. From a theoretical point of view the various possible atomic defects have mostly been studied in an electronic perspective, so even the simplest ones remained quite poorly known till recently, the silicon related ones remaining completely unknown. The great similarity between silica and quartz properties is in favour of a common model. The determination of the precise formation and migration energies of the various defects is then of paramount importance for the understanding of the kinetic properties of SiO_2 . We will present in this paper the results of a study of the formation and mobility properties of oxygen and silicon defects in the view of determining the self-diffusion mechanism(s). Our work relies on up to date ab-initio methods: total energy calculations in a DFT-LDA approach, using either plane wave or pseudo-atomic basis for the wave functions and pseudopotentials. We shall discuss the role of the various parameters controlling the kinetic behaviour: chemical potential of the species, nature of the main impurities, cristallinity, and preparation mode of the sample.

Introduction

Todays microelectronics is still based on silicon and its oxide; tendency towards downscaling of devices has suggested the quest for new oxide materials, looking in the direction of high-k dielectrics like hafnium or zirconium oxides, which would allow thicker oxide layers than SiO_2 , once given the gate surface size. The problem with silicon dioxide is that, under 2 nm thickness, the tunnelling currents are not any more negligible; in this respect, also diffusion properties are very important, as leakage currents can results from ionic conduction (i.e. diffusion of charged ions/defects).

As unexpected as it can seem, diffusion properties, even silicon and oxygen self-diffusion, in SiO_2 , are not thoroughly understood. In spite of being a very common material, used in several applications in its crystalline and amorphous phases, the available experimental results are not always in agreement with each other, not only with respect to the measured activation energy but also regarding the order of magnitude of the self-diffusion constant. This can be clearly seen if one looks as the results reported in the review article by Lamkin *et al.* [1] on oxygen mobility in silicate glasses. For oxygen self-diffusion in amorphous SiO_2 alone, activation energies ranging between less than 0.9 eV and 4.7 eV have been reported. The latter value [2] can be distinguished from the others, as it has been obtained in closed conditions (SiO_2 sample

capped with silicon nitride to prevent oxygen intake from the atmosphere); but still other values obtained in open conditions are as high as 3.3 eV [1].

The situation is only slightly clearer for silicon self-diffusion; the pioneering work by Brebec [3] in 1980 reports an activation energy of 6 eV for silicon self-diffusion in amorphous SiO_2 ; fifteen years later Si self-diffusion was measured in quartz [4]; the result was similar in diffusivity with a somewhat higher activation energy (7.6 eV). Starting from the work of Celler and Trimble in 1989, several authors studied intrinsic diffusion in thin oxide films on silicon substrate. Celler reported diffusivity several orders of magnitude higher with lower activation energy (4.4 eV), which was attributed to SiO molecules, following the interpretation of SiO_2 dissolution according to the reaction: $Si + SiO_2 \rightleftharpoons 2SiO$ proposed by Tromp [5]. Similar figures obtained later from experiments on thin oxide films [6] were attributed to the migration of silicon interstitials. More recent works [7, 8] and in particular works with varying oxide thickness [9, 10] clarified that the diffusivity lowers with the thickness of the oxide layer; the measured activation energies are around 5-5.5 eV.

The spread of experimental results for oxygen and silicon self-diffusion suggests, on one side, that a richer theoretical framework is necessary in order to interpret the experimental findings; on the other side, that experiments are not always performed in the same conditions, and that there are parameters, whose influence is important, which have not been duly controlled. In the following we describe some results obtained from first principles calculations on the atomic mechanisms for diffusion. These quantities are not directly available from experiments, and can help to determine diffusion regimes and activation energies that can be compared with experiments.

First principles calculations of the formation energy of defects

Diffusion in quartz and silica can be controlled by many kinds of defects, like point defects or topological defects. Let us consider here the contribution of usual point defects, oxygen and silicon vacancies and interstitials, and possibly antisites; we will postpone to a forthcoming paper a discussion on topological defects. The tracer self-diffusion coefficient, be it for silicon or oxygen, contains contributions from all the defects whose migration can, in principle, provide the transport of, respectively, silicon or oxygen atoms:

$$D_0^* = \sum_i \nu_0^i a_i^2 f_i c_i \Gamma_i \quad (1)$$

where ν_0 is the attempt frequency, a the jump distance, f the correlation factor, and Γ the jump frequency. All these quantities are labelled by i , the type of defect. The concentration, c_i , and the jump frequency, Γ_i , are Boltzmann exponentials of the formation and migration free enthalpies, respectively. We concentrate here on the quantities that give the main temperature dependence of diffusion, which are the formation and migration energies. We neglect the vibrational entropies, which we have calculated in a previous work for oxygen vacancies and interstitials [11]. We will discuss several results of calculations of formation and migration energies using first principles calculations based on Density Functional Theory (DFT) in the Local Density Approximation (LDA) for quartz and silica. For the first we used fully converged plane waves pseudopotentials calculation performed with the PWSCF code [12].

For silica we used the SIESTA code [13], based on Linear Combination of Atomic Orbitals (LCAO). The latter allows a gain in computing time, at least on single processor scalar machines; the drawback is that there is no variational principle allowing to improve systematically

the quality of the basis set. For this reason, even for silica, a comparison with converged plane waves results [14, 15] is necessary, together with a particular care in choosing the location of the atomic basis functions for each type of defect.

The parameters and quality of our plane waves calculation have been discussed elsewhere [11], we just remind that lattice parameter and atomic distances are accurate to less than 1% with respect to experiment and bond angles to less than 3%; the formation energy of quartz has less than 2% error. Similar accuracies have been found with the SIESTA calculations [14].

We have relaxed all atomic positions and the volume of the supercell, in order to calculate the zero pressure formation energy (i.e. the formation enthalpy) of defects. In some cases we obtained positions which we discovered to be metastable, as we will discuss later discussing the migration of defects. Nevertheless, the fact of relaxing the volume of the supercells together with atomic positions helps to avoid being stuck in metastable configurations.

Charged Defects The treatment of charged defects, which is necessary to take into account all possible defects type in an insulator, present special problems. Indeed the interaction of periodic images in periodic boundary conditions cannot be neglected as the Coulomb interaction decays as $\frac{1}{r}$. The way of getting rid of these spurious interactions is still controversial, the Madelung electrostatic correction or its extended version by Makov and Payne [16] seems to be overcorrecting in certain cases [17, 18], at least when the top of the valence band (VBT) of charged supercells is correctly lined-up [19].

In our present case the line up of the VBT by the calculation of the macroscopic average, as described in ref. [19] is not feasible, as the flat region of the macroscopic average is not clearly attained with our supercell size; nevertheless it is possible to line up the VBT by comparing the defected and undefected density of states. Our method consists in a maximisation of the overlap of the two electronic density of states (eDOS) by shifting the energy reference for the eDOS of the charged supercell. A clear maximum as a function of the energy shift makes it easy to locate the correct VBT line up $\Delta\bar{V}$. The contribution to the formation energy is $Q\Delta\bar{V}$, where Q is the charge of the defect.

The formation energy of a charged defect depends on the position of the Fermi energy (or electron chemical potential) in the same way as the formation of, say, an oxygen vacancy depends on the oxygen chemical potential. For example the formation energy of a charged oxygen vacancy is given by:

$$E_f(V_O^Q) = E^{V_O^Q}(nSiO_2) - E(nSiO_2) - \mu_O - Q(\mu_e + \Delta\bar{V}) \quad (2)$$

where Q is the charge of the defect, μ_O is the oxygen chemical potential, μ_e is the electron chemical potential and $E^{V_O^Q}(nSiO_2)$ and $E(nSiO_2)$ represent the energies of supercells with n stoichiometric units, containing or not the defect. In the limit of low concentrations the value of μ_e has to be the one of the perfect crystal, but in reality it depends on the actual concentration of impurities and also of intrinsic defects [20].

Formation Conditions: Open Mode The value of chemical potentials, which is a measure of the cost of adding/removing a particle, depends on the way the particle is added or removed, i.e. on the particle reservoir that defines the grand canonical ensemble in which we are working. In practice the value of chemical potentials depends on experimental conditions. If experiments are performed on a sample which is exchanging atoms with a surrounding oxygen atmosphere (and we assume that the permeation energy is not limiting the reaction) then defects can be

formed by exchange with the atmosphere and the oxygen chemical potential is half the energy of the oxygen molecule in the gas: $\mu_O = \frac{1}{2}E(O_2)$. If, conversely, the sample cannot exchange oxygen atoms with the gas—for example because capped as in the experiment by Mikkelsen [2]—then oxygen defects can be formed only as stoichiometric defect complexes, like Frenkel pairs or Schottky triplets. If the oxide sample is in contact with bulk silicon, then additional formation modes are available—again, provided that there are no permeation/diffusion limiting factors. Let us take as an example the formation of an oxygen vacancy in the oxide in contact with bulk silicon (but not with gaseous O_2); then in order to form a neutral oxygen vacancy at least two reactions have to be considered:



where the upper right label says if the defect is formed in the oxide (x) or in silicon.

The corresponding formation energies for the oxygen vacancy are, respectively:

$$E_f(V_O) = E^{Vo}(nSiO_2) - E(nSiO_2) + E^{Io}(nSi) - E(nSi) \quad (5)$$

$$\begin{aligned} E_f(V_O) &= E^{Vo}(nSiO_2) - E(nSiO_2) + \frac{1}{2} [E(SiO_2) - E(Si)] \\ &= E^{Vo}(nSiO_2) - E(nSiO_2) + \frac{1}{2} [E(O_2) - E_f(SiO_2)] \end{aligned} \quad (6)$$

where $E_f(SiO_2)$ is the positive formation energy of SiO_2 : $E_f(SiO_2) = E(Si) + E(O_2) - E(SiO_2)$ and n and m are the sizes of the reference supercells for the calculation of defect energies in the oxide and bulk silicon, respectively. We indicate with $E^{Io}(mSi)$ the energy of a silicon supercell containing m silicon atoms and an oxygen interstitial and with $E^{Vo}(nSiO_2)$ the energy of an oxide supercell containing an oxygen vacancy in a supercell of n stoichiometric units.

The formation energy of an oxygen interstitial in bulk silicon has been calculated to be around 1.5 eV [21] with respect to $\mu_O = \frac{1}{2} [E(O_2) - E_f(SiO_2)]$, which means that the second reaction is the most favourable one. Using equation n.6 and the results for the formation energy obtained in ref. [20] we obtain $E_f(V_O) = 1$ eV. As a comparison, we remind that the formation reaction (and energy) for the same defect, the neutral oxygen vacancy, in equilibrium with an atmosphere of gaseous oxygen are:



$$E_f(V_O) = E^{Vo}(nSiO_2) - E(nSiO_2) + \frac{1}{2}E(O_2) \quad (8)$$

giving $E_f(V_O) = 5.6$ eV.

In the following, we show in figure 1, the formation energy of several defects as a function of the electron chemical potential in the two experimental situations previously described: equilibrium with gaseous oxygen and equilibrium with bulk silicon (left and right respectively).

In the case of equilibrium with gaseous oxygen, an important term in the Boltzmann exponential of the concentrations, is the entropic term of the oxygen molecule, as discussed in ref. [11]: $\exp \left[\frac{S_{O_2}(p_{O_2})}{2K_B} \right]$, where p_{O_2} is oxygen partial pressure and K_B is the Boltzmann constant. This contribution is far from being negligible it can control the change of regimes, as shown in [11]; for $p_{O_2} = 1$ bar and $T = 1000$ K then $TS_{O_2}(p_{O_2}) = 2.3$ eV, and $TS_{O_2}(p_{O_2}) \propto p_{O_2}^{-1}$. As

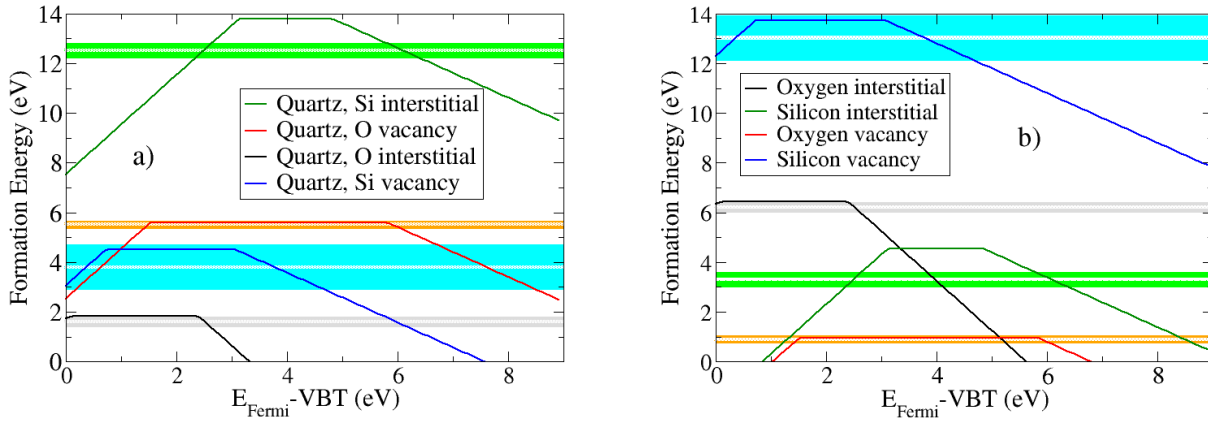


Fig. 1: We show the formation energy of neutral and charged defects in quartz as a function of the electron chemical potential (or Fermi Energy) referred to the valence band top. The shaded areas represents the corresponding neutral defects in amorphous silica; the width of the shaded area is the standard deviation of the formation energy distribution [15]. The two plots refer to formation energies calculated for an oxide in equilibrium with: a) gaseous oxygen, b) bulk silicon.

already discussed [11] the variation of the oxygen pressure is expected to lead to changes in the diffusion mechanism. In the region where the dominant diffusion mechanism is the displacement of network oxygen in the form of oxygen interstitials, it is still not clear if the oxygen is charged (with charge $Q = -2$) or not [20], as the role of impurities can be crucial in this respect. As a complement to figure 1 we show in table 1 the simplest formation reactions within the two open modes (equilibrium with O_2 and bulk silicon) and in closed mode. We omit the x superscript as all the defects are formed in the oxide. In the reactions, *Si* alone means always bulk silicon and O_2 means the oxygen molecule in the gas. As one can see the value of formation energies are quite different and so will be the equilibrium concentrations, even if the entropic contribution can partly act as a compensation.

Closed Mode Let us consider now a piece of silicon dioxide which cannot exchange atoms with the environment. Some experiments, where samples are capped by a layer of a material which is meant to be a diffusion barrier, are approaching that ideal theoretical case. In this case defects in the oxide can be formed only by stoichiometric complexes, the simplest of which are Frenkel pairs and Schottky triplets. In the following we refer to Schottky defects as triplets of vacancies and we call anti-Schottky the complex made by three interstitials, one silicon and two oxygen. The reaction leading to the formation of these defect complexes are shown in table 1, where it is understood that one stoichiometric unit of oxide is missing on one of the two sides of the reaction, in order to keep the number of atoms unchanged.

The contribution to diffusion coming from Frenkel pairs has an activation energy $E_{act}^{FP} = \frac{E_f^{FP}}{2} + E_{mig}$ while for the triplets the activation energy is:

$E_{act}^{S3} = \frac{E_f^{S3}}{3} + E_{mig}$. In both cases E_{mig} refers to the lowest migration energy between those of the defects involved in the defect complex, and E_f is the formation energy of the defect complex as shown in table 1.

Closed Mode stoichiometric defects	Open Mode equilibrium with bulk <i>Si</i>				Open Mode equilibrium with <i>O</i> ₂			
	oxygen Frenkel pair	silicon Frenkel pair	anti-Schottky triplet	Schottky triplet	oxygen interstitial	oxygen vacancy	silicon interstitial	silicon vacancy
$SiO_2 \rightleftharpoons V_O + I_O$ 7.2 eV		$SiO_2 \rightleftharpoons V_{Si} + I_{Si}$ 18.3 eV	$SiO_2 \rightleftharpoons 2I_O + I_{Si}$ 17.4 eV	$SiO_2 \rightleftharpoons 2V_O + V_{Si}$ 15.7 eV		$SiO_2 + O_2 \rightleftharpoons 2I_O$ 1.8 eV	$SiO_2 \rightleftharpoons I_{Si} + O_2$ 13.8 eV	$O_2 \rightleftharpoons V_{Si} + SiO_2$ 4.5 eV
					oxygen interstitial	oxygen vacancy	silicon interstitial	silicon vacancy
$SiO_2 \rightleftharpoons 2I_O + Si_i$ 6.4 eV		$Si_i \rightleftharpoons 2V_O + SiO_2$ 1.0 eV	$Si_i + SiO_2 \rightleftharpoons I_{Si_i}$ 4.5 eV	$SiO_2 \rightleftharpoons V_{Si_i} + Si_i$ 13.7 eV				

Table 1: Formation Modes, reactions and corresponding formation energies for neutral defects in α -quartz

Self-Diffusion

The calculation of migration energies The second ingredient which is necessary in order to be able to evaluate the contribution of each defect to the diffusion constant, on the basis of equation 1, is the jump frequency Γ of a given defect. The jump frequency is given by the knowledge of the free enthalpy of migration. In the following we will neglect the effect of the migration entropy which, similarly to the vibrational part of the formation one, is a solid state term and so should be small, although not completely negligible [11]. Indeed it will have a much smaller effect than the gas part of the formation entropy in open mode.

Then at a given temperature, one can approximate the jump frequency by $\exp(-\frac{E_{mig}}{k_B T})$ where E_{mig} is the minimum energy barrier that the system has to overcome during a defect jump. The search for minimum energy barrier in 3N-dimensional space (N=number of atoms) is still a hard task especially when the calculation of the energy is very time-consuming, as for first principles calculations. This is particularly relevant in polymeric systems like SiO_2 , in which jumps involve displacements of many atoms, not only of the jumping one, and switching of several bonds. In the framework of the transition state theory, two methods are routinely used, and have been used here, to locate the saddle point, the Bennett's one [22] and the Nudged Elastic Band [23]. In the first method one defines a reaction coordinate corresponding to a guessed jump path and one pursues a series of energy relaxation of all atomic coordinates under the constraint of a fixed reaction coordinate, in the second method a series of configurations interpolated between the initial configuration and the final one, are simultaneously relaxed with respect to atomic positions under the constraint of a mutual distance in the configuration space not becoming too large. So in this NEB method both final and initial positions should be known, contrarily to the first which can, to some extent, be used to discover one of them.

In figure 2 a) and b) we show the energy variation during the migration paths respectively of an oxygen interstitial and of an oxygen vacancy in quartz, both obtained using Bennett's method. The figure 3 displays the equivalent path of an interstitial in a model of amorphous silica resulting from NEB calculations [24, 25], and the figure 4 the migration path of a silicon interstitial in quartz also obtained with Bennett's method [26]. The paths displayed in figures 2 a) and 4 have both been discovered without any knowledge of the final configuration. The NEB technique was unable to find a relevant migration path for the silicon interstitial in silica and work is still in progress. The migration energies of the oxygen defects studied there amount then to 1.2 eV for the zero charge interstitial and 3.2 eV for the vacancy in quartz. The values in silica are a bit larger by ~ 0.5 eV. According to Jin and Chang's calculations [27], the migration energy in quartz of the charged interstitials is lowered to .27 eV and .11 eV in the -1 and -2 cases respectively. The activation energy of the neutral silicon interstitial amounts to 1.2 eV, and doesn't show such large variations with the charge state [26].

Oxygen self-diffusion Two kinds of experimental results are available here to compare with the calculated ones, obtained, as already said, in the open or the closed configuration. Two kinds of methods also are used for measuring diffusions coefficients. In the first the sample is kept in contact with gaseous oxygen, generally enriched in the isotope 18 in order to allow an analysis of the in-diffusion using mass spectrometry either of the isotope level decreasing in the gas or increasing in the sample during the diffusion annealing. In the second a thin layer of silica built from the isotope 18 is deposited on a natural sample and true isotope diffusion can occur in the solid state. The first method however involves at least four steps all of which are thermally activated and unknown: the surface dissolution reaction, the permeation

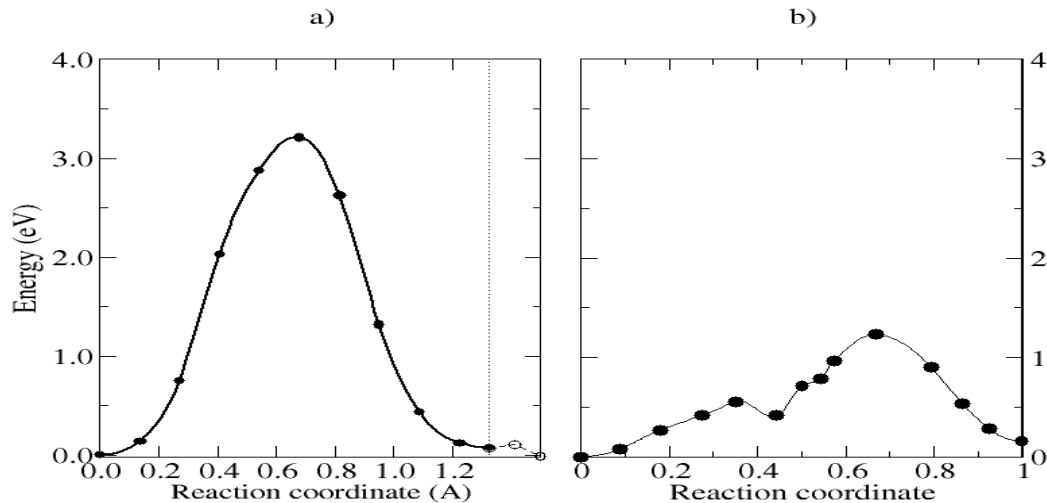


Fig. 2: The migration paths for the oxygen vacancy (left) and interstitial (right) in the neutral state. The points were obtained by constrained relaxations using the Bennett window constraint (see text for more details). The line is a guide for the eye

of the oxygen molecules, the atomic exchange between molecules and lattice and, eventually, the lattice diffusion, goal of the investigation. It is generally supposed that one or the other of these steps is limiting—hopefully the diffusion one!— and diffusion coefficients are extracted using a model built on this hypothesis.

Insofar, as results exhibit generally for these four steps activation energies of the same order of magnitude, the validity of the coefficients obtained along this way is dubious [28]. This is probably the main reason for the huge dispersion of the results quoted above, beside the unavoidable contribution of hydroxyl at the high gas pressure involved in these experiments. It is indeed well established that even tiny levels of OH can greatly enhance lattice oxygen diffusion, which displays then activation energies of the order of 1 eV in silica [29].

The thin layer method is therefore the most suitable for determining true lattice diffusion. It has been used in silica only and in the closed regime of defect formation [2], but could also be used in open one. No information is available in quartz. In this experiment the hydroxyl content is maintained very low, probably at a ppm level at most [30]. Solving the neutrality equation [20] for these conditions in a pure silica gives a self-consistent Fermi level lying 2.3 eV above the valence band edge. At this level the oxygen interstitial defects are charged both in the -1 and -2 states, and then the oxygen lattice self-diffusion is controlled by the migration of the interstitial part of the Frenkel pair [24, 25]. The activation energy amounts then to 3.8 eV, in clear disagreement with Mikkelsen's result, 4.7 eV, even more if the large decrease of the migration energy quoted by Jin in quartz is present in silica. Supposing conversely that the Fermi level is such that neutral defects are dominant, corresponding to a Fermi level below approximately 2 eV, one gets an activation energy ranging from 4.6 to 5.3 eV according to the diffusion model used in the amorphous solid [24, 25]. These figures are now in good agreement with Mikkelsen's result. One has therefore to conclude that given the low defect concentration level at experimental temperatures, around 0.1 ppm, some undetected impurity at a ppm level, hydroxyl but possibly also aluminium, lowers the Fermi level by 0.3 eV or a bit more. Work in this direction is in progress. The availability of oxygen self-diffusion in quartz in various experimental conditions, closed mode but also in the open one under varying oxygen partial

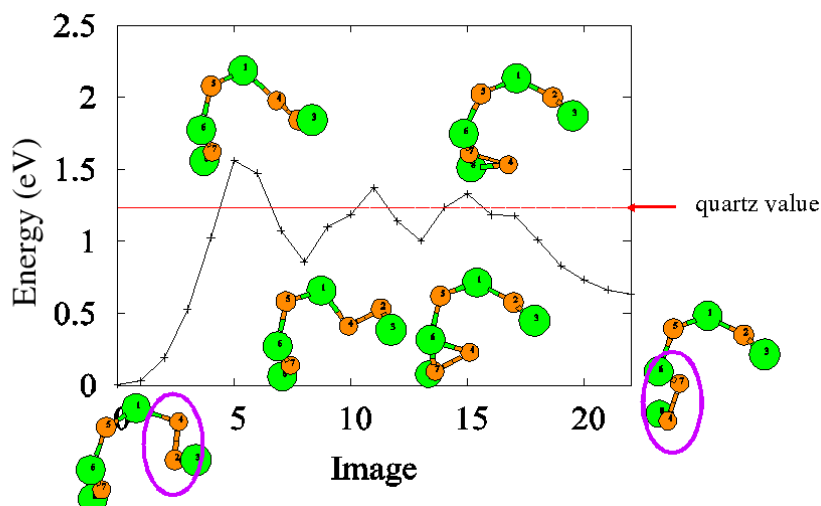


Fig. 3: The migration paths for the neutral oxygen interstitial in silica. The points are images of a NEB calculation. The line is a guide for the eye. The atomic configuration along the path show the rotations and bond breaking/reforming of the dumb-bell structure of the neutral oxygen interstitial

pressure as well as total external pressure, could help in solving this point [31, 25]. Indeed the same effect has been determined in this crystalline form of SiO_2 , for which the complexity involved in handling diffusion in amorphous matter could be avoided [32].

Silicon self-diffusion Limiting our discussion to experiments where the conditions are well controlled [3, 4, 9, 10, 33], three kinds of experiments can be distinguished. Jaoul's results, 7.6 ± 1 eV in quartz, has been obtained in conditions which are presumably closed [4]. All the others pertain to open conditions in silica. Brebec's results pertain to massive silica sample in equilibrium with oxygen at a partial pressure of the order of 10^{-9} atm [3]. The others report on silica thins films grown on silicon wafers in conditions which vary in a loosely controlled manner from more or less the equilibrium with oxygen and the equilibrium with silicon [6, 7, 8, 9, 33], depending on the thickness of the silica layer. The activations energies then are in the range of 4.5–5.5 eV, with an error of the order of 0.8 eV, given the large scatter of the data. An important point is that in the thickest layers [9], where the tracer diffuses far from the silicon substrate, the diffusivity agrees well with Brebec's result and the activation energy also, taking due account of the lower precision on thin film measurements. The thinner the oxide the higher the diffusivity and the lower the activation energy when going from 5.2 eV [9] to 4.7 eV [7]. The trend for absolute values (but not for activation energies) seems to be contradicted by some of the results presented in [33]; here the same diffusivity was measured for three uncapped samples of varying thickness at $T=1250$ C.

A sample capped with a silicon nitride film, isolating it from the oxygen atmosphere, shows enhanced diffusivity [8], close to the values observed in the uncapped thinnest films [7]. It is not clear if this effect has to be attributed to the the thickness of the sample or to the capping, especially in comparison to results by [33], where the thickness effect seems to be present also for capped samples.

These results can be partly understood in the following scheme. In closed conditions the figure of the table 1 show that the silicon self-diffusion mechanism should be the migration

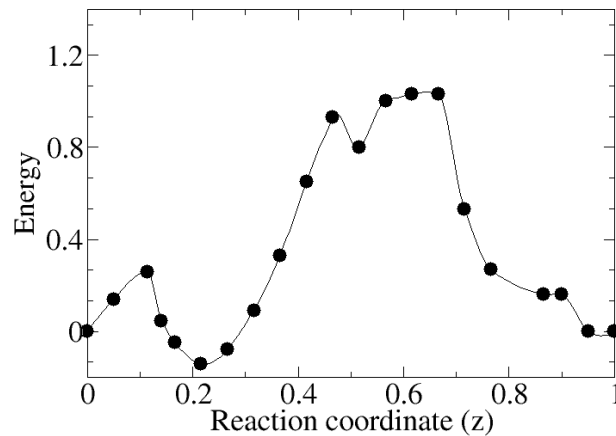


Fig. 4: Migration path of a silicon interstitial in quartz, obtained using Bennett's method. As in figure 2 and 3, intermediate metastable positions are found.

of silicon interstitials from anti-Schottky triplets, with an activation energy amounting to 7 eV, whatever the position of the Fermi level, in quite good agreement with Jaoul's figure. The contribution of vacancies can be excluded from the very high migration energy [26].

In very thin films the activation energy decreases and the diffusivity increases greatly, the chemical potential conditions becoming closer to equilibrium with the silicon substrate, the thinner the film. This lowers the interstitial formation energy down to 4.5 eV, which corresponds to 5.7 eV for the activation energy for diffusion. Turning progressively to oxygen equilibrium conditions in thick films one should observe either the interstitial mechanism, with an unrealistic energy of 15 eV, or the vacancy one, with an energy amounting to at least 9 eV. Moreover, one expects a strong oxygen partial pressure effect, which is not observed [3]. However the values pertaining to the closed mode in silica would fit perfectly the figures since the formation energy of the silicon interstitial lowers by 1 eV for a similar migration one between quartz and silica [26]. This point remains then to be investigated.

The frequently quoted SiO interstitial [5, 10] is certainly not involved in diffusion since its formation free energy is high *in the solid*, although the molecule concentration can be relatively high with respect to the silicon one *in the gas phase* at very high temperatures if oxygen is available.

Conclusions

Using up to date ab-initio calculations in a quantum mechanical frame, we have determined the contributions of the usual simple points defects, vacancies and interstitials, to self-diffusion, in all possible experimental conditions in quartz and silica. The experimental results available can be partially interpreted using our results by underlying the dominant role of interstitials in all cases, either for oxygen or silicon.

The oxygen self-diffusion observed in closed conditions is probably not an intrinsic effect, since position of the Fermi level that controls the diffusivity is probably fixed by some impurity present with a very low concentration. In this case the dominant defect switches from charge $Q = -2$ to neutral. Experiments are still needed, especially under varying oxygen partial pressure

in open mode. The choice of quartz is particularly interesting due to its greater simplicity as compared to silica.

In the silicon self-diffusion case our results are in good agreements with the sole available experiment in quartz. They allow also to rationalise the measurements on thin films, almost all performed in open conditions. Indeed the increase of the diffusivity and the decrease of the activation energy observed in very thin films is due to a progressive switching from a regime of oxygen equilibrium conditions to silicon ones, for which the agreement with our figures is very good. Anyhow, the regime of oxygen equilibrium is not yet fully understood, which could also imply to perform new experiments both on quartz and massive silica.

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