FORMATION AND DIFFUSIVITY OF SMALL OXYGEN AGGREGATES IN SI AND GE

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ABSTRACT

Ab initio total energy calculations are carried out on small oxygen clusters in supercells of Si and Ge. The migration energies of the oxygen dimer and trimers are found. These energies are much lower than the migration energy of oxygen interstitials. The dimers in Si and Ge diffuse with barriers of 1.4 and 1.1 eV, while the trimer diffuses with barriers of 1.3 and 1.1 eV respectively. These results imply that kinetic models for oxygen aggregation cannot rely on O_i or O_{2i} as the only oxygen carriers. It is also shown that the reaction $O_{ni} \rightarrow VO_n$ is endothermic for $n \leq 3$ and exothermic for $n = 4$.

INTRODUCTION

There have been suggestions based on studies of the loss of interstitial oxygen O_i from solution in annealed CZ–Si, that oxygen dimers diffuse faster than O_i.[1, 2, 3] This hypothesis can then explain why thermal donors evolve at rates faster than the diffusion of O_i. Recently the oxygen dimer has been unabambiguously identified in annealed CZ–Si by combined infrared absorption experiments and theoretical modelling studies.[4] Early calculations also support the idea that the dimer (O_{2i}) can diffuse through Si with a lower barrier than O_i.[5] Such dimers would be expected to be trapped mainly by single oxygen interstitials and form trimers. If the trimer were stable and immobile, then their concentration would gradually build up and larger oxygen aggregates would not easily form. The trimer bottleneck can be removed in two ways. Either the binding energy of the trimer is negligible so that they dissociate into dimers and O_i, and further growth is based on dimer association, or the trimer is stable but mobile and O_{4i} defects are rapidly formed. The first hypothesis requires that the trimer is unstable but previous calculations suggest that this is not the case.[6] However, the other proposal leaves unresolved the rate at which larger aggregates can form. One suggestion is that these aggregates along with thermal donors are all mobile.[7] To this end, we show here that the trimer is a stable mobile entity.

Another important question concerns the critical size of an oxygen aggregate which is thermodynamically unstable against VO_n formation. As oxygen clusters grow, there is a an increase in strain energy which will be relieved at a critical size by the ejection of a self-interstitial (I). We will show here that VO_n formation becomes exothermic only for $n = 4$ but the activation barrier probably prevents this happening around 450°C.

To address these questions we use local density functional theory with 64 and 128 atom supercells[8] containing oxygen aggregates. The barriers for diffusion are investigated by relaxing supercells either with a fixed symmetry appropriate to a saddle point, or with a constraint preventing the saddle point structure from relaxing back into the stable aggregate. These constraints fix the relative lengths of different bonds. Details of the method are discussed elsewhere.[9]

OXYGEN FAST DIFFUSING SPECIES

Interstitial oxygen is known to migrate with barriers of 2.5 and 2.0 eV in Si and Ge respectively.[10] There have been several attempts to calculate this barrier and it is in general underestimated when supercell methods are used. Values between 1.8 and 2.2 eV have been reported [11, 12]. Our calculations give similar results. Specifically, the barrier for oxygen diffusion is found to be $E_a = 2.2$ eV in Si and 1.7 eV in Ge. The saddle point for oxygen diffusion is the Y-lid configuration shown in Figure 1(b) and the high barrier is attributed to the dangling bonds in this structure.

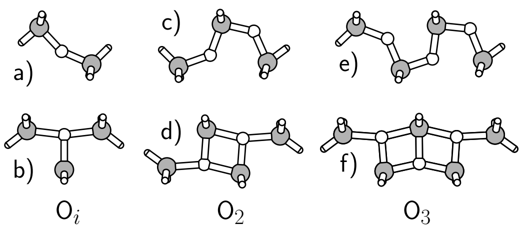

Figure 1: Schematic structure of the ground state of interstitial oxygen centres [a), c) and e)], and respective saddle–point configurations [b), d) and f)]. Gray and white spheres represent Si and O atoms respectively.

We now consider the oxygen dimer. The structure of the dimer is found to be a staggered form as shown in Figure 1(c).[11] The binding energy of the two O atoms is 0.5 and 0.6 eV in Si and Ge. The former is comparable with 0.3 eV estimated experimentally.[4] The activation energy for its movement was investigated using three different diffusion paths: (i) a correlated jump of both oxygen atoms from the staggered configuration through the asymmetric double-Y-lid structure in the left side of Figure 2(i) , (ii) a partial dissociation involving an asymmetric Y-lid as in Figure 2(ii), and a transition between the staggered and skewed dimers as proposed by Pesola *et al.*[6] and shown in Figure 2(iii).

Path (i) leads to a migration energy of 1.4 eV, (ii) leads to a similar barrier of 1.6 eV, although the complete diffusion event requires the oxygen atom at the left side to make a similar jump to reform the dimer. However, symmetry considerations require this second step to be equivalent to the first. Path (iii) is activated by a barrier of 2.2 eV, and resembles the diffusion of isolated interstitial oxygen.

One can rationalize these results by noting that in (i) both three-fold coordinated Si atoms labeled 1 in Fig. 1(c) are now bonded to the other O–atoms. Similarly, in (ii) the tensile strain along [110] in the Y-lid is off-set by the presence of the second O atom. The effect of both these processes is to transport the dimer along [110] but both lead to a staggered dimer which tilts in the opposite direction. Before long range migration can occur, the dimer must reorientate and point in the opposite direction. The energy barrier for this is found to be low: 0.38 eV in Si and 0.65 eV in Ge. Thus we conclude that the diffusion path probably occurs by the staggered dimer migrating along its [110] axis with a correlated jump of both oxygen atoms.

The structure of the oxygen trimer is shown in Fig. 1(e) and consists of a staggered arrangement of oxygen atoms in agreement with earlier studies.[6] The binding energy of the dimer to the third oxygen atom is 0.9 eV in Si and 1.0 eV Ge. These high binding energies suggest that the trimer is stable around 450°C.

The diffusion energy for O_{3i} is also found to be low. Its diffusion barrier is 1.3 and 1.1 eV in Si and Ge respectively. The mechanism for migration corresponds to a correlated jump of all O atoms towards the nearest bond centred site along the $\langle 110 \rangle$ chain of host atoms. The saddle point corresponds to the structure shown in Figure 1(f). Note that in this configuration the Si or Ge atoms are all fully coordinated in contrast with the Y-lid configuration of O_i where the saddle point [Figure 1(b)] possess one undercoordinated Si atom. This is the principal reason why the dimer and trimer are able to diffuse rapidly and suggests that larger aggregates may also be mobile.

FORMATION ENERGIES OF O_{ni} AND VO_n DEFECTS

Simple geometric considerations suggests that oxygen clusters beyond a certain size are unstable and release a Si self-interstitial forming a VO_n defect. We investigate in detail the thermodynamics of such reactions and conclude that they only can occur for n equal or greater than 4. The energy of the reaction $O_{ni} \rightarrow VO_n$ is found by moving the abstracted Si atom to a reservoir of bulk Si. Thus for neutral defects, ΔE_f is simply $E_f(VO_n) + \mu - E_f(O_{ni})$ where μ is the energy of a Si atom in bulk material. Figure 2 (right) gives these formation energies found from supercells of 128 atoms and demonstrates that the threshold for the reaction is around $n = 4$,

The activation barrier to the process must include the formation energy of the self–interstitial near the vacancy aggregate. It is not clear what this barrrier is but when the interstitial is far from VO_n, then the energy difference includes the formation energy of the interstitial which is found to be around 3.9 and 3.3 eV in Si and Ge respectively. It is unlikely that this barrier can be reduced significantly by the formation of an I–O defect as such complexes are not thought to be stable above room temperature. As the formation rates of thermal donors are activated with much smaller barriers, we conclude that VO_4 defects will not be formed around the temperatures where thermal double donors are stable.

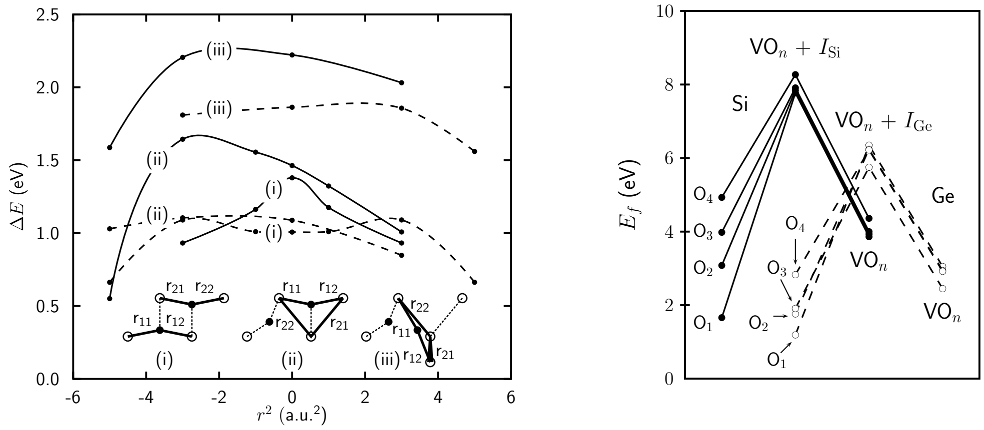

Figure 2: Left – Reaction paths for O_{2i} migration in Si and Ge. Right – Formation energies (eV) for O_{ni} and VO_n defects in Si (solid curves) and Ge (dashed curves). The necessary energy to form VO_n plus a I_{Si} (or I_{Ge}) are also plotted.

CONCLUSION

The *ab–initio* calculations demonstrate that oxygen dimers can migrate with barriers lower than those of O_i by 0.8 eV in Si and 0.6 eV in Ge. It is demonstrated for the first time, that the oxygen trimer can also migrate through a similar activation energies. Thus O_{4i} defects can be formed rapidly once dimers have been created.

A comparison between the formation energies of O_{ni} and VO_n defects, leads us to conclude that the ejection of a self–interstitial from O_{ni} aggregates does not occur for $n \leq 4$. The reaction is exothermic for O_{4i} defects in Si but the activation barrier prevents this happening at temperatures as low as 450°C.

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