Germanium oxidation occurs by diffusion of oxygen network interstitials

H Li and J Robertson
Engineering Dept, Cambridge University, Cambridge CB2 1PZ, UK

Abstract Density functional modeling is used to show that germanium oxidation occurs by the diffusion of network oxygens across the film as peroxyl bridges, not by molecular O₂ interstitials (O₂*). The smaller O bond angle of GeO₂ leads to lower order rings in the amorphous GeO₂ network than in SiO₂. This leads to narrower interstitial diffusion channels, and less dilation of the interstitial volume around the transition state. This raises the migration barrier of O₂* in GeO₂, so that the overall diffusion energy of O₂* in GeO₂ is now higher than that of a network O interstitial. The low formation energy of the O vacancy in GeO₂ leads to GeO₂ being O-poor very near the Ge/GeO₂ interface, but the lower overall diffusion energy of the O network interstitial than the vacancy leads to the network interstitial dominating diffusion.

Silicon has been the dominant semiconductor for many years largely because SiO₂ is such a well-behaved oxide. However, to continue Moore’s law scaling, it is becoming necessary to replace Si with a higher mobility semiconductor. Ge has higher electron and hole mobilities than Si and would be a reasonable choice. However, Ge has a poor native oxide GeO₂ with a poorer interface with its parent Ge for reasons that are not fully understood [1-3].

Historically, one of the notable features of silicon was its well-understood oxidation process. Silicon oxidation follows the linear/quadratic Deal-Grove model [4], in which the O₂ molecule diffuses along interstitial channels of the amorphous (a-) SiO₂ network [4,5], to react exothermically with Si at the Si/SiO₂ interface [6-9]. This occurs because of the remarkably open network of a-SiO₂. This model was verified by the lack of O isotopic exchange with the existing network oxygens [10,11]. Ge oxidation somehow differs, it creates Ge/GeO₂ interfaces with more interfacial defects [1,2], molecular GeO is volatile [12], the oxidation kinetics follow an unusual pressure dependence [13], but the Ge/GeO₂ interface can be flat [14]. Here, we analyze the Ge oxidation mechanism in terms of atomic transport processes across the GeO₂ layer, and conclude that it occurs mainly by transport of oxygen network interstitials (also known as peroxyl bridges) rather than by molecular oxygen interstitials [15]. A hint of this is already seen by comparing the experimental oxidation rates of Si and Ge [5,12,13], and the kinematic viscosities of SiO₂ and GeO₂ [16-19] in Fig 1(a).

There are three possible transport paths for the oxidation of Si or Ge, see Fig 1(b); diffusion of molecular O₂ interstitials along channels in the oxide, diffusion of interstitial network oxygens, or diffusion of oxygen vacancies across the oxide network. The immobility of the cation in SiO₂ and GeO₂ was confirmed by isotope tracer studies [10,12]. The mechanism for the oxidation is as follows. If Si or Ge is pre-oxidized in ¹⁶O and then further oxidized in ¹⁸O, if molecular O₂ transport dominates, then an ¹⁸O peak will be found at the Si/SiO₂ interface, as indeed occurs for Si [8,9]. If oxidation occurs by transport of O lattice interstitials or vacancies, there is ¹⁸O exchange with the network, and a broad peak of ¹⁸O will be found across the oxide layer, as is seen for GeO₂ by Xu et al [20] and da Silva et al [21].

Here, we use density-functional supercell calculations to find out which species control the oxidation mechanism in a-GeO₂ by calculating the defect formation energies and the migration
energies. The overall diffusion energy is then the sum of these two energies. The calculations are carried out using the CASTEP plane-wave density-functional code [22] and ultra-soft pseudopotentials. The plane-wave cut-off energy is 500 eV. Energies are relaxed until residual forces are below $10^{-5}$ eV/Å. Some 144 atom and 216 atom GeO$_2$ network models were made by molecular dynamics, equilibrating at 3000K for 10 ps, then quenching in 10 ps, followed by an energy minimization. Similar a-SiO$_2$ networks were created with the same procedure. In addition, supercells of quartz-like SiO$_2$ and GeO$_2$ are used. The defect formation energy is the energy cost to form the defect, with the O atom going to form an O$_2$ molecule outside the SiO$_2$. The migration energy is the energy barrier of the transition state over which the defect atoms must pass to get to its next site. The total diffusion energy is the sum of these two energies. The migration energies for network defects are derived by the nudged elastic band method [23].

Of the three possible diffusing species (Fig. 1b), let us first consider the competition between the O$_2$ molecular interstitial O$_2^*$ and the O lattice interstitial O$_i$. The defect formation energies of O$_i$ and the oxygen vacancy V$_o$ are relatively independent of network, as they depend on the forming or breaking of specific covalent bonds. In contrast, the formation energy of the O$_2^*$ arises from the closed-shell repulsions of the O$_2$ molecule and the surrounding oxide network, and thus it depends on the size of the network interstice. The O$_2^*$ molecule is surrounded by lattice oxygens. In quartz SiO$_2$ of density 2.66 gm/cm$^3$, there is one main interstice configuration, and the defect formation energy at this site is $\sim$2.04 eV, Fig 2(a), similar to found by Bongiorno [6] but larger than in Hamann [24].

A-SiO$_2$ (silica) is less dense than quartz at 2.25 gm/cm$^3$ and it contains a range of interstices and channels mostly of larger size [25,26]. The lower density means that the Si-O-Si bond angle increases from 144$^0$ in quartz towards 150$^0$ in silica. Fig 2(a) plots the O$_2^*$ formation energy vs the relaxed interstice volume. This energy varies inversely with volume and follows a $V^{-3.5}$ dependence. The interstice volume is calculated from the distance between the O$_2$ bond center to the six nearest network O sites, averaged, and then approximated as a sphere. A similar calculation is carried out for quartz-like GeO$_2$ and for a-GeO$_2$ random networks whose density is 3.55 gm/cm$^3$ [27]. Fig 2(a) shows that the O$_2^*$ defect formation energy follows the same line as in SiO$_2$, confirming that the energy depends mainly on O-O repulsions in both cases.

We studied many interstices in a-SiO$_2$ and a-GeO$_2$ in both their initial unrelaxed and relaxed state (ie before and after the O$_2$ molecule is added). Fig 2(b) shows the relaxation ratio (relaxed volume/unrelaxed volume) vs. interstitial volume for each oxide. A major difference between a-SiO$_2$ and a-GeO$_2$ is that a-SiO$_2$ has a longer tail of large interstitial volumes. This arises from the larger O bond angle and different network topology of silica giving more low-order rings. This allows a greater interstice relaxation for the SiO$_2$ case.

Fig 2(c) plots the probability distribution of relaxed interstitial volumes for both a-SiO$_2$ and a-GeO$_2$. Interestingly, the average volume is rather similar, around 110 Å$^3$, and slightly larger for the SiO$_2$ case. Thus from Fig 2(c), the O$_2^*$ defect formation energy is slightly lower in a-SiO$_2$, but not by much. But it is notably smaller in a-SiO$_2$ than in quartz.

The O$_2$ or O diffusion energy is the sum of the defect formation energy and the migration (barrier) energy. For the O$_2^*$ in an interstice site in quartz, there are two diffusion paths, along the O$_z$ channel or along the O$_{xy}$ channels with quite different diffusion barriers. In silica or a-GeO$_2$, there are a range of diffusion paths. As in Bongiorno and Pasquarello [6,7], there are roughly six adjacent interstitial sites around each O$_2^*$ site for it to hop to. Thus, diffusion can be simplified to
a percolation problem on a simple cubic mesh, for which the percolation threshold is 0.55 as previously used [6]. Thus, the overall diffusion energy is the energy at 55% of its cumulative distribution, as in Fig 2(d).

This leads to the O$_2^*$ migration energy being larger in a-GeO$_2$ than in a-SiO$_2$, see Table 1. This is because the migration channels between interstices can dilate more in a-SiO$_2$ during the passage of O$_2^*$ giving it a lower migration barrier, Fig 3(a,b). This gives a total diffusion energy of ~1.4 eV for a-SiO$_2$ and ~2.0 eV for a-GeO$_2$ for O$_2^*$ as in Table 1. The key difference for a-GeO$_2$ is its smaller O bond angle, which raises its O$_2^*$ migration barrier, due to its reduced channel relaxation. (We also note the greater interstitial volume in silica than quartz because of its lower mass density, which increases the O$_2^*$ diffusion rate by five orders magnitude at 600$^0$C [26].)

We now consider the neutral O lattice interstitial O$_i$ or ‘peroxyl bridge’. Its configuration is shown in Fig 3(c). The oxygen bond angles are typically 100-110$^0$. We see in Table 1 that the formation energy of O$_i$ changes from 2.0 eV in quartz to 1.4 eV in a-SiO$_2$ to ~0.4 eV in a-GeO$_2$, for O-rich chemical potentials. In a-GeO$_2$, the defect formation energy has a distribution. It depends somewhat on the Ge-Ge separation of the initial Ge-O-Ge unit, as this determines the two bond angles at the oxygens. The O$_i$ migrates from one SiO$_2$ or GeOGe bridge to an adjacent bridge site via a 5-fold coordinated Si or Ge transition state in both oxides, as shown in Fig 3(c). A similar transition state was seen by Hamann [24].

The overall effect is that the lowest energy diffusion path for oxygen in silica is the O$_2^*$ route because of its open channels, whereas the lowest path in a-GeO$_2$ is by the network interstitial O$_i$. Thus, O diffuses by the O$_2^*$ route in a-SiO$_2$, giving an experimental activation of oxidation of 1.23 eV similar to the O$_2^*$ diffusion energy 1.4 eV, while in a-GeO$_2$ the O$_2^*$ diffusion energy is increased, and the process shifts to the O$_i$ path which has an diffusion energy of ~1.8 eV.

These values are compared to experiment in Table 1 (in bold). The O$_2^*$ diffusion energy of 1.4 eV in a-SiO$_2$ is consistent with the experimental activation energy of 1.23 eV for Si oxidation in Fig 1(a), and the O$_i$ diffusion energy of 1.79 eV for a-GeO$_2$ is consistent with the experimental activation energy of 2.0 eV for Ge oxidation.

We finally consider competition between V$_O$ and O interstitials. The O vacancy is a very costly defect in SiO$_2$, so this is not involved in Si oxidation (except in any reactive layer next to the interface [28]). On the other hand, the O vacancy is thought to be important in a-GeO$_2$, and has been considered to be a key diffusing species [9,16]. This is because the O vacancy has a low cost in GeO$_2$ in the O-poor condition, as occurs at the Ge/GeO$_2$ interface. However, the O-rich condition dominates across most of the film under oxidation conditions.

To understand the relevance of the interstitials and vacancies for diffusion in detail, we note that defect formation energies depend on the oxygen chemical potential, $\mu(O)$. $\mu(O)$ varies from $\mu(O) = 0$ eV at atmospheric pressure at the film’s surface to $\mu(O) = -4.85$ eV at the Si/SiO$_2$ interface, where -4.85 eV is the bulk heat of formation of SiO$_2$ per O atom. Or, in GeO$_2$, $\mu(O)$ varies from 0 eV at the external surface to $\mu(O) = -3.02$ eV at the Ge/GeO$_2$ interface, where -3.02 eV is the bulk heat of formation of GeO$_2$ per O. The defect formation energy $E_{form}$ at an arbitrary O chemical potential $\mu_1$ is given by

$$E_{form}(\mu_1) = E_{form}(\mu_0) + n\mu_1$$

where $E_{form}(\mu_0)$ is $E_{form}(\mu_0)$ at $\mu(O) = 0$ eV, and $n = +1$ for vacancies and $n = -1$ for interstitials.
At the SiO$_2$ surface where $\mu(O)=0$ eV, O$_i$ has a fairly low formation energy and V$_O$ has a very large formation energy of 6.05 eV. At the Si/SiO$_2$ interface, V$_O$ is now a lower cost defect, but it still costs 1.4 eV. GeO$_2$ is different. At the GeO$_2$ surface, O$_i$ is low cost, at ~0.5 eV and V$_O$ costs 3.16 eV, but at the Ge/GeO$_2$ interface V$_O$ is very low cost at only 0.14 eV, much lower than at Si/SiO$_2$.

Under diffusing conditions, the oxygen flux $J$ across a layer is given by

$$J = -\sum_i D_i \frac{\partial c_i}{\partial x} = -\sum_i D_i \frac{\partial c_i}{\partial \mu} \frac{\partial \mu}{\partial x}$$

where the concentration of species $i$ $c_i = c_0 \exp (-E_{\text{form},i}/kT)$. The flux must be the same across the whole film. This equation can describe two situations for GeO$_2$. In condition 1, the quiescent state, the low cost of V$_O$ at the Ge/GeO$_2$ interface dominates, and the $\mu(O)$ of O-poor condition spreads across most of the film to near the surface, and then changes quickly to the O-rich condition very close to the surface, Fig. 4(a). $\mu(O)$ changes from fully O-rich to O-poor across the film thickness, and the main change occurs over a fraction ($kT/\Delta \mu$) of this thickness below the surface.

In condition 2, corresponding to oxidation, the O-rich condition spreads from the GeO$_2$ surface down through most of the film to the Ge/GeO$_2$ interface. This causes the O flux to be carried by the O interstitial. $\mu(O)$ then rapidly falls very close to the interface, Fig 4(a), V$_O$ then becomes the flux carrier, formally across the last atomic layer, and the sharp decrease in $\mu(O)$ occurs to create a large concentration gradient to force the same flux to be carried by V$_O$.

The difference of V$_O$ between SiO$_2$ and GeO$_2$ arises as follows. Making a V$_O$ leaves two dangling bonds on the adjacent Si or Ge sites. These sites rebind into Si-Si or Ge-Ge bonds. The formation energy of a O vacancy is very large in SiO$_2$ even after the rebonding (6.05 eV) in the O rich condition, because of the large cost of breaking Si-O bonds. It is less in GeO$_2$ (3.16 eV) because the Ge-O bond is weaker. (Table 1). Furthermore, the migration barrier for the O vacancy is very high in SiO$_2$, at 4.28 eV, and is much less in GeO$_2$, at 1.71 eV. The migration energy largely consists of undoing the reconstruction of the vacancy into a Si-Si or Ge-Ge bond.

A final detail about defects is the valence alternation pair (VAP). This consists of a positively charged 3-fold O site, and a negatively charged 3-fold Ge site. These sites have been seen in simulations of a-GeO$_2$ and a-SiO$_2$ [29,30]. Briefly, they are O-deficiency defects created from O vacancies. Their formation energy is greater than the vacancy, but their migration energy is much lower than for the vacancy, Table 1. They are relevant to other processes in these oxides.

Thus, in summary, the main diffusing species changes from the interstitial O$_2^*$ molecule in SiO$_2$ to the lattice O interstitial in a-GeO$_2$. This is largely due to the smaller O bond angle in GeO$_2$, meaning fewer high order rings, and this less ability for its network to dilate around the O$_2^*$ to allow it to lower its migration energy, unlike in a-SiO$_2$. This is consistent with isotopic tracer results. The O lattice interstitial dominates O O vacancy diffusion in a-GeO$_2$ because this becomes O-poor only very close to the Ge/GeO$_2$ interface under oxidizing conditions.

The authors thank EPSRC grant EP/M009297 for funding.

References
19. W Xu, T Nishimura, T Yajima, A Toriumi, presented at JSAP meeting (March 2017, Yokohama, 16p-413-4)
21. H Li, J Robertson, IEEE-SISC (San Diego, Dec 2016) p7.2
29. H Li, J Robertson, App Phys Lett 110 032903 (2017);
<table>
<thead>
<tr>
<th></th>
<th>a-GeO$_2$</th>
<th>a-SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond angle</td>
<td>130°</td>
<td>144-150°</td>
</tr>
<tr>
<td>Bulk heat of</td>
<td></td>
<td></td>
</tr>
<tr>
<td>formation/O</td>
<td><strong>3.02</strong></td>
<td><strong>4.85</strong></td>
</tr>
<tr>
<td>Heat of formation</td>
<td>3.06</td>
<td>4.78</td>
</tr>
<tr>
<td>(exp) [31]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Formation energy (eV)</th>
<th>Migration barrier (eV)</th>
<th>Diffusion energy (eV)</th>
<th>Formation energy (eV)</th>
<th>Migration barrier (eV)</th>
<th>Diffusion energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ interstitial / O$_2$</td>
<td>0.97</td>
<td>0.95</td>
<td>1.92</td>
<td>0.7</td>
<td>0.7</td>
<td><strong>1.40</strong></td>
</tr>
<tr>
<td>O interstitial$^&lt;$</td>
<td>0.42</td>
<td>1.37</td>
<td><strong>1.79</strong></td>
<td>1.40</td>
<td>1.39</td>
<td>2.79</td>
</tr>
<tr>
<td>O vacancy$^&lt;$</td>
<td>3.16</td>
<td>2.54</td>
<td>5.7</td>
<td>6.05</td>
<td>4.28</td>
<td>10.33</td>
</tr>
<tr>
<td>O vacancy$^&gt;$</td>
<td>0.14</td>
<td>2.54</td>
<td>2.68</td>
<td>1.20</td>
<td>4.28</td>
<td>5.48</td>
</tr>
<tr>
<td>VAP$^&gt;$</td>
<td>0.82</td>
<td>1.71</td>
<td>2.53</td>
<td>2.2</td>
<td>3.5</td>
<td>5.7</td>
</tr>
<tr>
<td>Experiment [12,5]</td>
<td></td>
<td></td>
<td><strong>2.00</strong></td>
<td></td>
<td></td>
<td><strong>1.23</strong></td>
</tr>
</tbody>
</table>

Table 1 Calculated defect formation energies and migration barrier energies in GeO$_2$ and SiO$_2$. $^<$ in O rich-limit, $^>$ in O-poor limit. The experimental diffusion energies in the last row are to be compared with the specific calculated values in bold above.
Figure Captions

1. (a) Oxidation rates of Ge and Si vs temperature [5,12,13], compared to kinematic viscosity of amorphous GeO$_2$ and SiO$_2$ [15-18]. We note that the activation energies for oxidation and viscosity are fairly close for the case of Ge (2.00 eV and 2.74 eV), but quite different for Si (1.23 eV and 5.99 eV), indicating that similar processes may be involved in the case of Ge whereas this is not so for Si. (b) Schematic of alternative oxygen transport paths through SiO$_2$ and GeO$_2$ to the semiconductor interface. The open circle in the right hand diagram signifies a vacancy.

2. (a) Formation energy vs relaxed interstitial volume of O$_2^*$ in SiO$_2$ and GeO$_2$. (b) Relaxation ratio vs initial unrelaxed interstitial volume for a-SiO$_2$ and a-GeO$_2$, noting larger relaxation for the a-SiO$_2$ case. (c) Probability distribution of relaxed interstitial volumes of O$_2^*$ in a-SiO$_2$ and a-GeO$_2$ network models, gaussian broadened by 5Å$^3$. (d) Probability distribution of diffusion barrier energies for a-GeO$_2$ models.

3. (a) Migration paths of various species in SiO$_2$ or GeO$_2$. Migrating species is in orange. (a) O$_2^*$ in quartz SiO$_2$, (b) O$_2^*$ in quartz-like GeO$_2$ showing slight bonding to channel O in the transition state. (c) Migration path of oxygen network interstitial in SiO$_2$ and GeO$_2$ via 5-fold intermediate Si/Ge site. (d) Migration path of the O vacancy (equivalent to a Ge-Ge bond) to adjacent site. Si=yellow, Ge=green, O = red.

4. (a) O chemical potential vs depth across a GeO$_2$ film while in contact with Ge substrate and while being oxidised from surface. The length scale is the fractional depth between surface and interface. (b) Summary of diffusion barrier energies of O$_2^*$, O$_i$ and V$_O$ at high $\mu$(O) (at surface) and at low $\mu$(O) (near interface), for GeO$_2$, and their relevance to transport mechanisms in different regions of the GeO$_2$ film (right).
(a) Rate (m²/s)

\[
\begin{align*}
\text{Rate (m}^2\text{/s)} & \quad 10^{-24} & \quad 10^{-22} & \quad 10^{-20} & \quad 10^{-18} & \quad 10^{-16} & \quad 10^{-14} & \quad 10^{-12} \\
1/T & \quad 0.0000 & \quad 0.0004 & \quad 0.0008 & \quad 0.0012 & \quad 0.00 \\
\text{SiO}_2 \text{ visc} & \quad \text{GeO}_2 \text{ visc} & \quad \text{SiO}_2 & \quad \text{GeO}_2
\end{align*}
\]

(b) interstitial O\_2  interstitial lattice O  O vacancy

oxide

semiconductor
(a) Formation Energy vs Interstitial Volume
(b) Relaxation Ratio vs Unrelaxed Interstitial Volume
(c) Distribution of $O_2$ Formation Energy for SiO$_2$ and GeO$_2$
(d) Distribution of Saddle Point Energy for SiO$_2$ and GeO$_2$