Germanium oxidation occurs by diffusion of oxygen network interstitials

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Abstract Density functional modeling is used to show that germanium oxidation occurs by the diffusion of network oxygens across the film as peroxy bridges, not by molecular O_2 interstitials (O_2^*). The smaller O bond angle of GeO_2 leads to lower order rings in the amorphous GeO_2 network than in SiO_2 . This leads to narrower interstitial diffusion channels, and less dilation of the interstitial volume around the transition state. This raises the migration barrier of O_2^* in GeO_2 , so that the overall diffusion energy of O_2^* in GeO_2 is now higher than that of a network O interstitial. The low formation energy of the O vacancy in GeO_2 leads to GeO_2 being O-poor very near the Ge/ GeO_2 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 SiO_2 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 GeO_2 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 O_2 molecule diffuses along interstitial channels of the amorphous (a-) SiO_2 network [4,5], to react exothermically with Si at the Si/ SiO_2 interface [6-9]. This occurs because of the remarkably open network of a- SiO_2 . 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/ GeO_2 interfaces with more interfacial defects [1,2], molecular GeO is volatile [12], the oxidation kinetics follow an unusual pressure dependence [13], but the Ge/ GeO_2 interface can be flat [14]. Here, we analyze the Ge oxidation mechanism in terms of atomic transport processes across the GeO_2 layer, and conclude that it occurs mainly by transport of oxygen network interstitials (also known as peroxy 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 SiO_2 and GeO_2 [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 O_2 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 SiO_2 and GeO_2 was confirmed by isotope tracer studies [10,12]. The mechanism for the oxidation is as follows. If Si or Ge is pre-oxidized in ^{16}O and then further oxidized in ^{18}O , if molecular O_2 transport dominates, then an ^{18}O peak will be found at the Si/ SiO_2 interface, as indeed occurs for Si [8,9]. If oxidation occurs by transport of O lattice interstitials or vacancies, there is ^{18}O exchange with the network, and a broad peak of ^{18}O will be found across the oxide layer, as is seen for GeO_2 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- GeO_2 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 Vo 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 $\sim 2.04 \text{ eV}$, 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° in quartz towards 150° 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 $\text{O}_{x,y}$ 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-GeO₂ than in a-SiO₂, see Table 1. This is because the migration channels between interstices can dilate more in a-SiO₂ 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-SiO₂ and ~2.0 eV for a-GeO₂ for O_2^* as in Table 1. The key difference for a-GeO₂ 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°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°. 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-SiO₂ to ~0.4 eV in a-GeO₂, for O-rich chemical potentials. In a-GeO₂, 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 SiOSi 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-GeO₂ is by the network interstitial O_i . Thus, O diffuses by the O_2^* route in a-SiO₂, giving an experimental activation of oxidation of 1.23 eV similar to the O_2^* diffusion energy 1.4 eV, while in a-GeO₂ 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-SiO₂ 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-GeO₂ 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 SiO₂, 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-GeO₂, and has been considered to be a key diffusing species [9,16]. This is because the O vacancy has a low cost in GeO₂ in the O-poor condition, as occurs at the Ge/GeO₂ 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/SiO₂ interface, where -4.85 eV is the bulk heat of formation of SiO₂ per O atom. Or, in GeO₂, $\mu(O)$ varies from 0 eV at the external surface to $\mu(O) = -3.02$ eV at the Ge/GeO₂ interface, where -3.02 eV is the bulk heat of formation of GeO₂ per O. The defect formation energy E_{form} at an arbitrary O chemical potential μ_1 is given by

$$E_{\text{form}}(\mu_1) = E_{\text{form}}(\mu_0) + n \cdot \mu_1 \quad (1)$$

where $E_{\text{form}}(\mu_0)$ is $E_{\text{form}}(\mu_0)$ at $\mu(O) = 0$ eV, and $n = +1$ for vacancies and $n = -1$ for interstitials.

At the SiO₂ surface where $\mu(\text{O})=0$ 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/SiO₂ interface, V_O is now a lower cost defect, but it still costs 1.4 eV. GeO₂ is different. At the GeO₂ surface, O_i is low cost, at ~0.5 eV and V_O costs 3.16 eV, but at the Ge/GeO₂ interface V_O is very low cost at only 0.14 eV, much lower than at Si/SiO₂.

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

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

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 GeO₂. In condition 1, the quiescent state, the low cost of V_O at the Ge/GeO₂ interface dominates, and the $\mu(\text{O})$ 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). $\mu(\text{O})$ 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 GeO₂ surface down through most of the film to the Ge/GeO₂ interface. This causes the O flux to be carried by the O interstitial. $\mu(\text{O})$ 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 $\mu(\text{O})$ occurs to create a large concentration gradient to force the same flux to be carried by V_O.

The difference of V_O between SiO₂ and GeO₂ arises as follows. Making a V_O leaves two dangling bonds on the adjacent Si or Ge sites. These sites rebond into Si-Si or Ge-Ge bonds. The formation energy of a O vacancy is very large in SiO₂ 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 GeO₂ (3.16 eV) because the Ge-O bond is weaker. (Table 1). Furthermore, the migration barrier for the O vacancy is very high in SiO₂, at 4.28 eV, and is much less in GeO₂, 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-GeO₂ and a-SiO₂ [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 O₂* molecule in SiO₂ to the lattice O interstitial in a-GeO₂. This is largely due to the smaller O bond angle in GeO₂, meaning fewer high order rings, and this less ability for its network to dilate around the O₂* to allow it to lower its migration energy, unlike in a-SiO₂. This is consistent with isotopic tracer results. The O lattice interstitial dominates O O vacancy diffusion in a-GeO₂ because this becomes O-poor only very close to the Ge/GeO₂ interface under oxidizing conditions.

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References

1. Y Kamata, Materials Today **11** 30 (2008)

2. A Delabie, F Bellenger, M Houssa, T Conard, S VanElshocht, M Caymax, M Heyns, M Meuris, *App Phys Lett* **91** 082904 (2007)
3. J Robertson, R M Wallace, *Mat Sci Eng R* **88** 1 (2015)
4. B E Deal, A S Grove, *J Appl Phys* **36** 3770 (1965)
5. J D Plummer, M D Deal, P B Griffin, 'Silicon VLSI Microelectronics', Prentice Hall (2000) p319
6. A Bongiorno, A Pasquarello, *Phys Rev Lett* **88** 125901 (2002)
7. A Bongiorno, A Pasquarello, *Phys Rev B* **70** 195312 (2004)
8. A Bongiorno, A Pasquarello, *Phys Rev Lett* **93** 086102 (2004); *J Phys Condens Mat* **17** S2051 (2005)
9. L Tsetseris, S T Pantelides, *Phys Rev Lett* **97** 116101 (2006)
10. F Rochet, S Rigo, M Froment, C D'Anterrosches, C Maillot, H Roulet, G Dufour, *Adv Phys* **35** 237 (1986)
11. E P Gusev, H C Lu, T Gustafsson, E Garfunkel, *Phys Rev B* **52** 1759 (1995)
12. S K Wang, K Kita, T Nishimura, K Nagashio, A Toriumi, *Jpn J App Phys* **50** 04DA01 (2011)
13. C H Lee, T Tabata, T Nishimura, K Nagashio, A Toriumi, *App Phys Exp* **5** 114001 (2012)
14. T Sasada, Y Nakakita, M Takenaka, S Takagi, *J App Phys* **106** 073716 (2009)
15. G Hetherington, K H Jack, J C Kennedy, *Phys Chem Glasses* **5** 130 (1964)
16. G Urbain, Y Bottinga, P Richelt, *Geochim. Cosmochim. Acta* **46** 1061 (1982)
17. E F Riebling, *J Chem Phys* **39** 1889 (1963)
18. S K Sharma, D Virgo, I Kushiro, *J Non-Cryst Solids* **33** 235 (1979)
19. W Xu, T Nishimura, T Yajima, A Toriumi, presented at JSAP meeting (March 2017, Yokohama, 16p-413-4)
20. S R M daSilva, G K Rolm, G V Soares, I J R Baumvol, C Krug, L Miotti, F L Freire, M E H M daCosta, C Radike, *App Phys Lett* **100** 191907 (2012)
21. H Li, J Robertson, *IEEE-SISC* (San Diego, Dec 2016) p7.2
22. S J Clark, M D Segall, C J Pickard, P J Hasnip, M J Probert, K Refson, M C Payne, Z Krist **220**, 567 (2005); S. J. Clark and J. Robertson, *Phys. Rev. B* **82**, 085208 (2010)
23. G Henkelman, H Jónsson, *J. Chem. Phys.* **113**, 9901 (2000)
24. D R Hamann, *Phys Rev Lett* **81** 3447 (1998)
25. S L Chan, S R Elliott, *Phys Rev B* **43** 4423 (1991)
26. R A B Devine, J Capponi, J Arndt, *Phys Rev B* **35** 770 (1987)
27. M Micoulaut, L Cormier, G S Henderson, *J Phys Condens Mat* **18** R753 (2006)
28. R M C deAlmeida, S Goncalves, I J R Baumvol, F C Stedile, *Phys Rev B* **61** 12992 (2000)
29. H Li, J Robertson, *App Phys Lett* **110** 032903 (2017);
30. A Pasquarello, M S Hybertsen, R Car, *Nature* **396** 58 (1994)
31. O Kubaschewski, C B Alcock, 'Metallurgical Thermochemistry', (Pergamon, Oxford, UK, 1979)

	a-GeO ₂			a-SiO ₂		
Bond angle	130 ⁰			144-150 ⁰		
Bulk heat of formation/O	3.02			4.85		
Heat of formation (exp) [31]	3.06			4.78		
	Formation energy (eV)	Migration barrier (eV)	Diffusion energy (eV)	Formation energy (eV)	Migration barrier (eV)	Diffusion energy (eV)
O ₂ interstitial / O ₂	0.97	0.95	1.92	0.7	0.7	1.40
O interstitial ^{\$}	0.42	1.37	1.79	1.40	1.39	2.79
O vacancy ^{\$}	3.16	2.54	5.7	6.05	4.28	10.33
O vacancy [#]	0.14	2.54	2.68	1.20	4.28	5.48
VAP [#]	0.82	1.71	2.53	2.2	3.5	5.7
Experiment [12,5]			2.00			1.23

Table 1 Calculated defect formation energies and migration barrier energies in GeO₂ and SiO₂. \$ 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 GeO₂ and SiO₂ [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 SiO₂ and GeO₂ to the semiconductor interface. The open circle in the right hand diagram signifies a vacancy.
2. (a) Formation energy vs relaxed interstitial volume of O₂* in SiO₂ and GeO₂. (b) Relaxation ratio vs initial unrelaxed interstitial volume for a-SiO₂ and a-GeO₂, noting larger relaxation for the a-SiO₂ case. (c) probability distribution of relaxed interstitial volumes of O₂* in a-SiO₂ and a-GeO₂ network models, gaussian broadened by 5Å³. (d) probability distribution of diffusion barrier energies for a-GeO₂ models.
3. (a) migration paths of various species in SiO₂ or GeO₂. Migrating species is in *orange*. (a) O₂* in quartz SiO₂, (b) O₂* in quartz-like GeO₂ showing slight bonding to channel O in the transition state. (c) migration path of oxygen network interstitial in SiO₂ and GeO₂ 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 GeO₂ 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 O₂*, O_i and V_O at high μ(O) (at surface) and at low μ(O) (near interface), for GeO₂, and their relevance to transport mechanisms in different regions of the GeO₂ film (right).

(a)

(b)