

Ge Oxidation does not follow the Deal-Grove Mechanism

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1. Introduction

The dominance of silicon as a semiconductor is partly based on the well-behaved dielectric properties of its native oxide SiO_2 . Ge is a possible high mobility channel to replace Si, but its native oxide is much less well behaved. One of the benefits of Si was its well-understood oxidation mechanism that followed the Deal-Grove[1] mechanism. The oxidation of Ge somehow differs, it creates Ge/GeO₂ interfaces with more interface defects, molecular GeO is volatile [2] and the oxidation kinetics have a strange pressure dependence [3], but the Ge/GeO₂ interface can be flat.

There are three possible processes for the oxidation of Si or Ge, diffusion of O₂ molecular interstitials (denoted O₂^{*}) along channels in the SiO₂, diffusion of interstitial lattice oxygens (O_i), or diffusion of oxygen vacancies (V_O) along the SiO₂ lattice, Fig. 1. Silicon follows the Deal-Grove model [1], in which O₂^{*} diffuses along the interstitial channels of the SiO₂ network to react exothermically with Si at the Si/SiO₂ interface [4]. This is possible because of the remarkably open lattice of SiO₂. This is verified by the lack of O¹⁸ exchange with network oxygens [5]. On the other hand, O exchange with the network is seen during Ge oxidation [6,7]. This suggests that Ge oxidation follows a different mechanism. This is also seen by the different temperature dependence of Ge oxidation [7,8,2,3], Fig. 2.

2. Method

Here, we use density functional supercell models to calculate defect formation and migration energies [9], as in Table 1. The total diffusion barrier is the sum of these two energies. The O chemical potential (p_{O_2}) changes across the film, and this greatly changes the defect formation energies.

3. Results.

The energy of O₂^{*} in the interstitial channels depends on O-O closed shell repulsions. Fig 3 shows that this energy decreases rapidly with interstitial volume V as $V^{-3.5}$, and follows the same dependence in both SiO₂ and GeO₂. The larger O bond angle in α -SiO₂ allows it to have large order rings of bonds, and so the interstices can expand more easily as the O₂^{*} passes. This lowers the diffusion energy, Fig. 4. GeO₂ has a smaller O bond angle, which makes the channels narrower, the network stiffer, and this raises the diffusion energy to ~ 2.79 eV, Table 1.

The alternative path is by network interstitial oxygens,

O_i or ‘peroxyls’. The energy of the peroxy is relatively constant but depends slightly on the Si-Si separation. The diffusion transition state is the same for SiO₂ and GeO₂ and consists of a 5-fold Gs or Ge site. In GeO₂, this process costs slightly less than in SiO₂ and it becomes the lowest energy pathway in α -GeO₂, Fig. 5.

At high p_{O_2} , the interstitial oxygen of either O₂^{*} or O_i form dominates. But at low p_{O_2} , near the interface, it crosses over to diffusion by oxygen vacancies, Fig. 8. O vacancies are a costly defect in SiO₂, even at the Si/SiO₂ interface, because it involves breaking two Si-O bonds, Table 1. But the vacancies have a low cost at the Ge/GeO₂ interface at this equilibrium, and this allows off-stoichiometry. Nevertheless, the diffusion barrier is high, and so overall interstitials dominate except very close to the interface. In Table 1, we compare the energy barriers of the dominant process in bold to the experimental activation energies of oxidation.

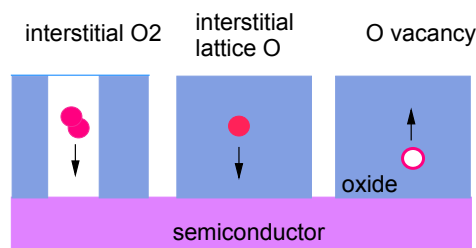


Fig 1. Diffusion processes, molecular O interstitial (O₂^{*}), network O interstitial, O vacancy.

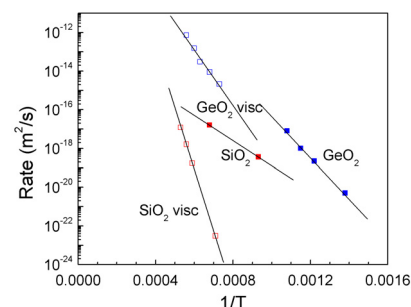


Fig. 2. Experimental oxidation rates of Si and Ge and kinematic viscosities of SiO₂, GeO₂

References

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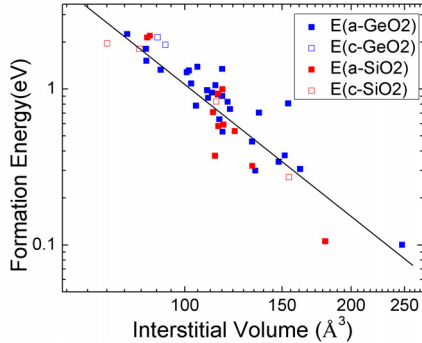


Fig. 3. O₂* defect formation energy vs. relaxed interstitial volume.

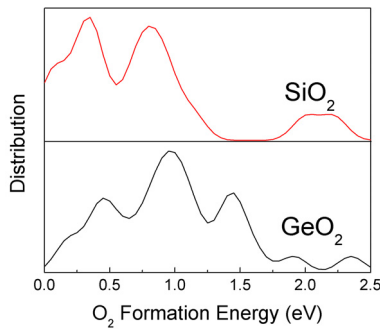


Fig. 4. Probability distribution of O₂* formation energy in SiO₂ and GeO₂.

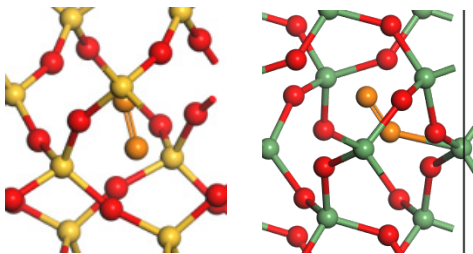


Fig. 5. O₂* migration path in SiO₂ and GeO₂. green = Ge,

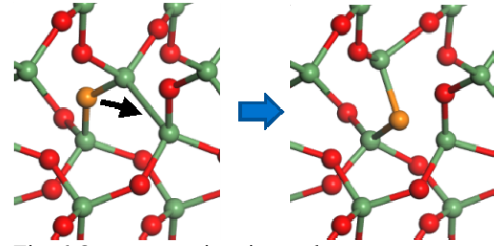


Fig. 6. O vacancy migration path.

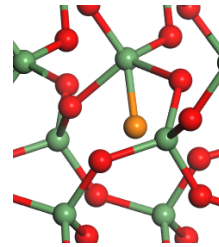


Fig. 7. O_i migration path.

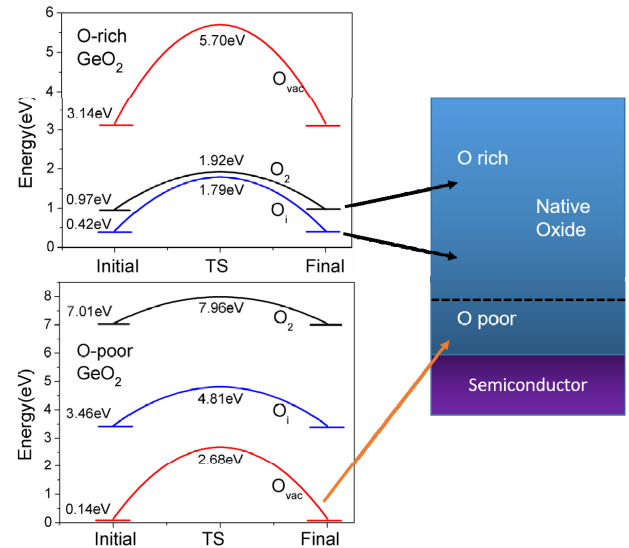


Fig. 8. Summary of diffusion mechanisms and energy barriers in different parts of the GeO₂ film.

	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)	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	1.92	2.89	0.7	0.7	1.40
O interstitial ⁵	0.42	1.37	1.79	1.40	1.39	2.79
O vacancy (O-rich)	3.16	2.54	5.7	6.05	4.28	10.33
O vacancy (O-poor)	0.14	2.54	2.68	1.20	4.28	5.48
Experiment [1,3]			2.00			1.23

Table 1. Calculated defect formation energies and diffusion energies for a-SiO₂ and a-GeO₂, compared to experiment.