

Effect of Metal-oxide Addition on GeO_2 and Ge/GeO_2 interfaces: DFT Calculations

Hongfei Li¹, John Robertson¹

¹ Dept Engineering, Cambridge University
Cambridge CB21 1PZ, UK

Phone: +44-1223-748331 E-mail: jr@eng.cam.ac.uk

Abstract

Y_2O_3 alloying is found experimentally to improve certain electrical and physical properties of GeO_2 gate stacks. Density functional calculations here show this is due to high formation energy of oxygen vacancies. However, metal-Ge bonds at vacancies must be avoided.

1. Introduction

Ge should be the most favored high mobility channel material for CMOS devices because of its high electron and hole mobility. However, it is let down by the poor performance of its oxide, GeO_2 . Recently, Toriumi et al [1-4] noted that alloying GeO_2 with Y_2O_3 reduces its water etch rate, decreases the GeO evolution rate, decreases the interfacial trap density and improves the reliability of Ge/GeO_2 interfaces. They also compared the effects of Sc, Y, La, Al and Hf oxide additions, in terms of the metal reactivity with Ge. The effects were explained using semi-empirical models. Here, we use ab-initio electronic structure calculations on supercell models to understand the underlying behavior.

2. Methods

The calculations are carried out using the plane wave density functional code CASTEP, with ultra-soft pseudo-potentials and the PBE exchange correlation functional. The band gap error of PBE is corrected using the screened exchange (SX) or HSE hybrid functional where necessary. The supercells are amorphized by a molecular dynamics routine, and then quenched and energy minimized.

We created 144 atom supercells of the amorphous GeO_2 structure and ~ 72 atom supercells of amorphous Y_xGeO_2 networks. The amorphous alloys were created by substituting Y atoms for Ge in the GeO_2 networks. To maintain electron counting, we must remove one oxygen for every two Y atoms inserted. For the Hf alloys, we simply substitute Hf at Ge sites. However, a short MD run is useful to avoid the structure being trapped in a local energy minimum due to the very different coordination of Hf than Ge. Fig. 1 shows typical atomic structures.

3. Results and discussions

We first plot the atomic volume per oxygen versus composition. Fig 2 shows that the pseudo-lattice constants fall below the linear dependence expected for Vegard's law, showing that alloying is exothermic and Y_2O_3 is a base [5]. The effect of metal additions is to create additional Y-O bonds to the oxygen vertices. The coordination numbers of the metal sites are given in Table 1 for 8% metal addition,

increasing with atomic radius along Sc, Y, La.

We calculated the bulk modulus (rigidity) versus metal content. Fig. 3 shows that the rigidity increases with alloying up to 50% Y content. However, it lies well below the rigidity of Y_2O_3 itself or that of crystalline $\text{Y}_2\text{Ge}_2\text{O}_7$. This increased rigidity arises from the extra Y-O bonding, and could explain the reduction of water etch rate.

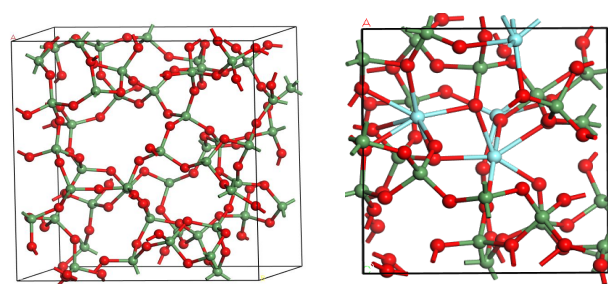


Fig. 1 (a) a- GeO_2 network. (b). a- Y_xGeO_2 network with 16% Y.

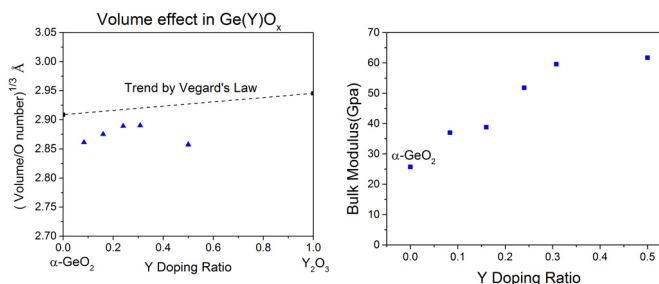


Fig. 2. Atomic volume per O atom vs. composition.

Fig. 3. Bulk modulus vs composition.

We then calculated the formation energies of oxygen vacancies. These will affect O diffusion through the network. There are three basic types of oxygen vacancy (Fig 4), with 2 Ge neighbors, 1 Ge and 2 Y neighbors, and 1 Ge and 1 Y neighbor, 8% Y addition changes the formation energy from 3.33 eV of pure a- GeO_2 to 4.27 eV, 4.67 eV and 3.04 eV respectively, an average increase to 3.97 eV. Y also increases the second neighbor vacancy cost to 3.48 eV.

The evolution of molecular GeO is known to occur by diffusion of O vacancies from the Ge/GeO_2 interface through the Ge-O-Ge network to the GeO_2 surface [6]. The diffusion of O vacancies across the GeO_2 network is impeded by any increase in vacancy formation energy around each Y, so the diffusion pathway is gradually blocked off. This explains the decrease of GeO evolution rate.

The increased cost of O vacancies will reduce the concentration of O vacancies, improving the reliability of $Y_x\text{GeO}_2$ alloys. In bulk GeO_2 , the O vacancy reconstructs to form a Ge-Ge bond [7], shown as yellow in Fig 5. If the vacancy is at the interface between an Ge site on the Ge side and a metal site in the GeO_2 , the vacancy may rebond across the vacancy. If a Me-Ge bond does form, this will create a gap state, and thus an interface trap state at ~ 1 eV (Fig 8), increasing D_{it} . This is undesirable. This is equivalent to ‘reactive metal’ in the classification of Lu et al [3].

Figs. 6,7 show the relaxed interfaces for the cases of Sc,Y, La, Al and Hf alloying. We find that Sc, Y, and Al do not create a Me-Ge bond, whereas Hf and La do. Thus Y and Sc are suitable additives. Interestingly Y and La behave slightly differently, in both experiment and theory. This is consistent with the behavior found by Lu et al [3] in Fig 9.

3. Conclusions

Density functional simulations explain the effect of different trivalent metal oxide additions to GeO_2 , increasing the cost of O vacancies in the GeO_2 and at the Ge/ GeO_2 interface and increasing the network rigidity. The increased cost of O vacancies reduces GeO volatility.

Acknowledgements

We thank EPSRC-JSPS core to core program for funding.

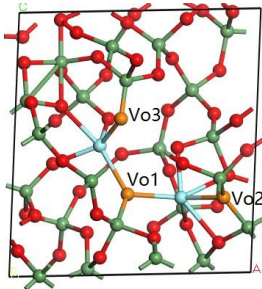


Fig. 4(a). The 3 different vacancy sites in 8% Y network

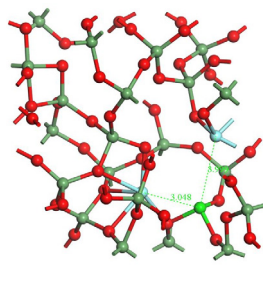


Fig 4(b) No rebonding at type 1 vacancy

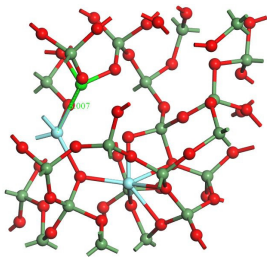


Fig 4(c). Rebonding at type 3 vacancy. (bright green)

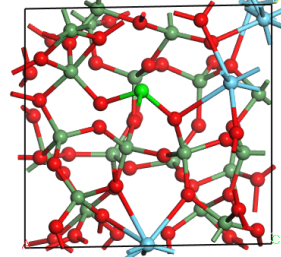


Fig. 4(d) O vacancy in 8% La network,

References

- [1] C. Lu, C H Lee, W Zhang, T Nishimura, K Nagashio, A Toriumi, Extended Abstracts of SSDM (2013) B5-1.
- [2] C. Lu, C H Lee, W Zhang, T Nishimura, K Nagashio, A Toriumi, Appl Phys Lett 104 092909 (2014)

- [3] C. Lu, C H Lee, W Zhang, T Nishimura, K Nagashio, A Toriumi, J Appl Phys 116 174103 (2014)
- [4] C Lu, A Toriumi, IEDM (2015) p14.6
- [5] M Copel et al, App Phys Lett 97 182901 (2010).
- [6] S K Wang, K Kita, T Nishimura, K Nagashio, A Toriumi, Jpn J Appl Phys 50 04DA01 (2011)
- [7] E P O'Reilly, J Robertson, Phys Rev B 27 3780 (1983)

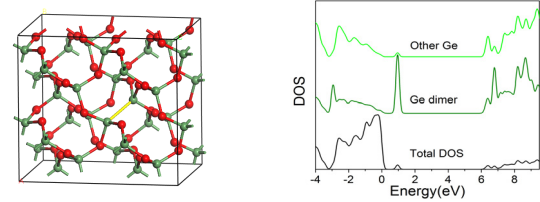


Fig. 5. The reconstructed O vacancy in GeO_2 as a Ge-Ge bond, and its local density of states from sX.

Table I. Metal coordination numbers

Sc	Y	La
5.25	6.25	6.75

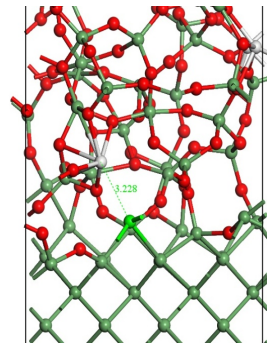


Fig. 6. O interface vacancy in $Y_x\text{GeO}_2$

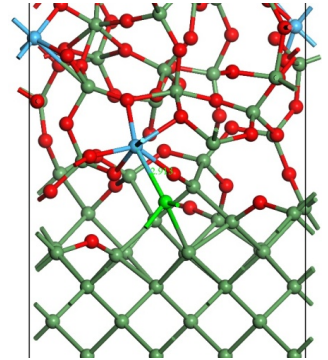


Fig. 7. O interface vacancy in $Hf_x\text{GeO}_2$, showing formation of Ge-Hf bond.

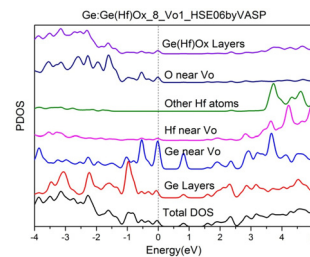


Fig. 8. Partial density of states, for $Hf_x\text{GeO}_2/\text{Ge}$ system showing gap state at +1 eV due to Hf-Ge bond.

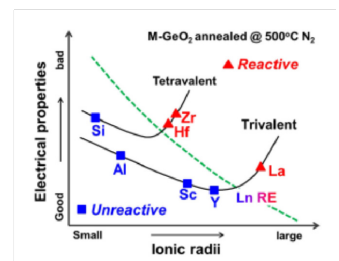


Fig. 9. Schematic of behaviors (Lu/Toriumi [3]), also supported by theory.