Vacancies and Interstitials in High−k Oxides

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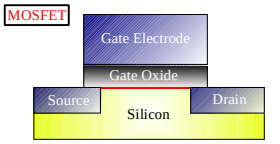
High−k Oxides − Motivation

- Wide applications in areas such as optics, protective coatings, fuel cells and oxygen sensors.



- Recent interest due to potential for replacement of silica as gate oxide in MOSFET, allowing continued device scaling.
- Performance of oxide films as gate dielectrics will be affected by defects and experiments suggest that as−grown films are non−stoichiometric.

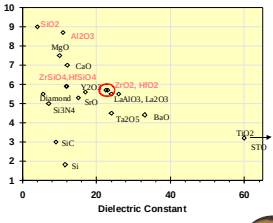
Hafnia and Zirconia

- Hafnia (HfO_2) and Zirconia (ZrO_2) demonstrate good thermal stability in contact with silicon, and a good balance between band gap and dielectric constant.
- Avoid instability with Si to form SiO_2

$$Si + MO_x \rightarrow M + SiO_2$$

- Avoid silicide formation

$$Si + MO_x \rightarrow MSi_z + SiO_2$$



Dr Hsing−Huang Tseng, Digital DNA Labs, Motorola

Method

- Spin Polarized DFT with GGA (VASP).
- Ultrasoft pseudopotentials − Zr/Hf (s1d3), O(s2p4).
- 2 kpoints,cutoff 500 eV − Converged total energy to meV.
- Supercell − 2x2x2 monoclinic primitive unit cell with 96±1 atoms. Defect images separated by greater than 10 Å.
- Forces on atoms relaxed to less than 0.05 eV/Å.

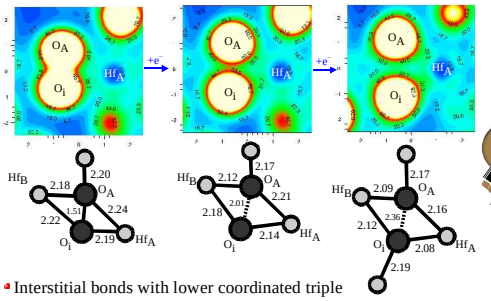
Calculations on the three bulk phases gave excellent agreement with experimental structure and energy hierarchy. [1,2]

- Incorporation energy calculated as:

$$E_{inc} = E_{defected} - (E_{ideal} \pm 0.5E_{O_2})$$

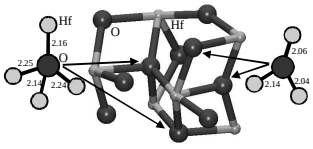
where E_{O_2} is the energy of an oxygen molecule in the triplet state.

Atomic Oxygen Interstitials



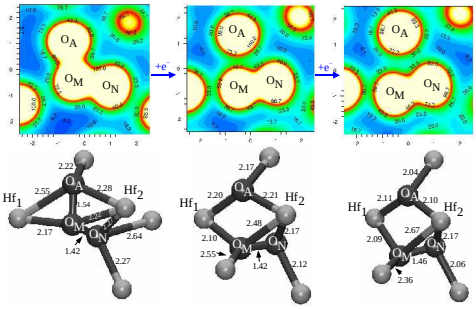
- Interstitial bonds with lower coordinated triple bonded lattice oxygen. Incorporation energy from O_2 source is +1.6 eV (−1.3 eV for atomic oxygen source). Incorporation at more cramped tetragonal lattice oxygen costs +2.3 eV (−0.6 eV).
- After a strong defect and lattice relaxation charge localizes on defect pair, increasing distance and ionicity.

Structure



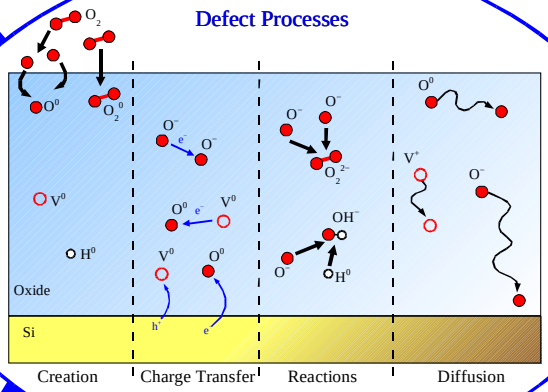
- Monoclinic hafnia/zirconia characterized by 3− and 4−coordinated oxygen sites, and significant co−valent bonding between Hf/Zr and O.

Molecular Oxygen Interstitials



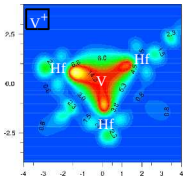
- Incorporation at triple site costs +4.2 eV (+5.8 eV at tetragonal site). This is double the value for silica [3].

Defect Processes



Oxygen Vacancies

- Creation of oxygen vacancy causes very small diplacements of surrounding 4 Hf ions − two electrons remain in the vacancy.



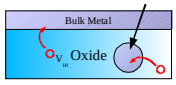
- Vacancy formation energy for 3−/ 4−coord. sites is similar ~ 9.3 eV.
- Neutral Frenkel pair formation energy is 8.0 eV.
- Ionization leaves one electron localized in the vacancy. Relaxation of Hf ions is an order of magnitude larger.
- Ionization of 2nd e^- leads to further relaxation to compensate the absence of electrons at the oxygen site.

Cation Vacancies

- Formation energy of metal vacancy in the oxide depends strongly on the reference state:

$$E_{for}(V_{Hf}) = E_V + E_{Hf} - E_0^0$$

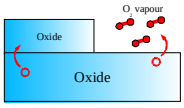
- Metal Reference Metal Cluster



- E_{Hf} from bulk metal

$E_{for}(V_{Hf})$ = 16.9 eV

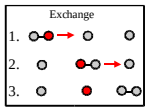
- Oxide Reference



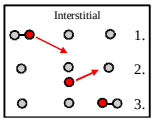
$E_{Hf} = E_{HfO_2} - E_{O_2}$

$E_{for}(V_{Hf})$ = 5.7 eV

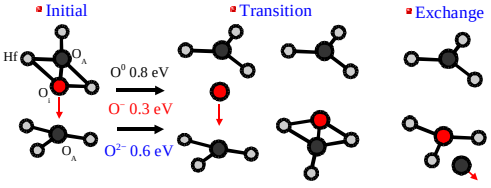
Oxygen Diffusion



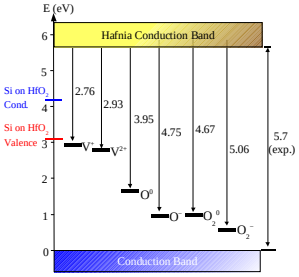
- In cubic crystals, ions diffuse via an exchange rather than via an interstitial mechanism.



- In hafnia/zirconia calculations suggest an exchange diffusion mechanism is energetically favoured, and predict that the smallest barrier is for O^- diffusion.



Defect Levels



- Electron Affinity

$$E_{aff} = E^q_{defect} - E^{q-1}_{defect} + k$$

- V^+ and V^{2+} are deep traps with large cross−section.
- V^0 is a potential shallow trap (DFT delocalization).
- O^0, O^-, O_2 and O_2^- are deep traps with small cross−section.

Reactions − Hafnia and Zirconia

Charge Transfer

$$O^0 + V^0 \xrightarrow{+0.7/+0.5} O^- + V^+$$

$$O^- + V^+ \xrightarrow{+1.5/+1.4} O^{2-} + V^{2+}$$

$$O^{2-} + O^0 \xrightarrow{-0.8/-0.9} 2O^-$$

$$V^{2+} + V^0 \xrightarrow{+0.0/+0.2} 2V^+$$

Recombination/Annihilation

$$2O^0 \xrightarrow{-1.0} O_2^0 + E_0^0$$

$$2O^- \xrightarrow{+0.8} O_2^{2-} + E_0^0$$

$$O_2^- + V^+ \xrightarrow{+7.6} O^0 + E_0^0$$

$$O_2^{2-} + V^{2+} \xrightarrow{+5.7} O^0 + E_0^0$$

Summary

- Qualitatively identical results for hafnia and zirconia.
- Reactions demonstrate clearly the preference of oxygen to exist in an atomic charged state, which is supported by isotope exchange observed in experiments.
- Barriers predict that atomic oxygen would diffuse as O^- via an exchange mechanism.
- Defect levels predict the possibility of electron transfer from silicon to defects in the oxide.

[1] A. S. Foster, V. B. Sulimov, F. Lopez Gejo, A. L. Shluger and R. M. Nieminen, *Structure and electrical levels of point defects in monoclinic zirconia*, Phys. Rev. B **64** (2001) 224108

[2] A. S. Foster, F. Lopez Gejo, A. L. Shluger and R. M. Nieminen, *Vacancy and interstitial defects in hafnia*, Phys. Rev. B (2001) submitted − obtain from www.fyslab.hut.fi/~asf/physics/Articles.html

[3] M. A. Szymanski, A. M. Stoneham and A. L. Shluger, *The different roles of charged and neutral atomic and molecular oxidising species in silicon oxidation from ab initio calculations*, Sol. State Elec. **45** (2001) 1233