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 (\(\text{HfO}_2\)) and Zirconia (\(\text{ZrO}_2\)) demonstrate good thermal stability in contact with silicon, and a good balance between band gap and dielectric constant.
- Avoid instability with Si to form \(\text{SiO}_2\)

\[
\text{Si} + \text{MO}_x \rightarrow \text{M} + \text{SiO}_2
\]
- Avoid silicide formation

\[
\text{Si} + \text{MO}_x \rightarrow \text{MSi} + \text{SiO}_2
\]

Oxygen Vacancies

- Creation of oxygen vacancy causes very small displacements of surrounding \(\text{Hf}\) ions – two electrons remain in the vacancy.
- Vacancy formation energy for 3- to 4-coordinated sites is similar to \(\sim 9.3\) eV
- Neutral Frenkel pair formation energy is \(8.0\) eV
- Ionization leaves one electron localized in the vacancy. Relaxation of \(\text{Hf}\) ions is an order of magnitude larger.
- Ionization of \(2^+\) leads to further relaxation to compensate the absence of electrons at the oxygen site.

Defect Processes

- In cubic crystals, \(\text{O}\) 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 \(\text{O}^+\) diffusion.

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 \(\text{O}^+\) via an exchange mechanism.
- Defect levels predict the possibility of electron transfer from cation to defects in the oxide.