First-principles modeling of defects and hydrogen in oxides

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Supported by ONR and SRC

International Workshop on Models and Data for Plasma-Material Interaction in Fusion Devices (MoD -PMI 2019)
National Institute for Fusion Science, Tajimi, Japan
June 18-20, 2019
First-principles calculations
Density functional theory, many-body perturbation theory

Oxides
- Transparent conductors
- Dielectrics
- Thermal barriers
- Complex oxides

Hydrogen as a fuel
- Kinetics
- Complex hydrides
- Metal hydrides
- Proton conductors

Quantum computing with defects
- Qubits
- Single photon emitters

Nitrides
- Doping
- Surfaces
- Interfaces
- Efficiency, loss
Computational Approach

• Traditional density functional theory approach
  – Local or semi-local density approximation
• Hard to interpret due to band-gap problem
• Major problem when addressing defects or surface/interface states
• Our approach: Hybrid functional calculations
  – The HSE hybrid functional
• A fraction of screened Hartree-Fock exchange
• Accurate band gaps and defect levels
• 120-atom supercell, 400 eV cutoff energy,
  2x2x1 $k$-point mesh

Defect Formation Energy

Determine defect concentrations: \([D] = N_0 \exp(-E_f/kT)\)

\[
E_f[V_O] = E_{\text{tot}}[V_O] - E_{\text{tot}}[\text{bulk}] + \mu_O
\]
Defect Formation Energy

Determine defect concentrations: \([D] = N_0 \exp(-E^f/kT)\)

\[
E^f[V^+_O] = E^{tot}[V^+_O] - E^{tot}[\text{bulk}] + \mu_O + \varepsilon_F
\]

\(\text{Al}_2\text{O}_3: V_O\) \hspace{1cm} \(\text{Al}_2\text{O}_3\) \hspace{1cm} \(\frac{1}{2} \text{O}_2\) \hspace{1cm} \(e^- @ \varepsilon_F\)

O chemical potential
Defect Formation Energy

Determine defect concentrations: $[D] = N_0 \exp(-E^f/kT)$

$$E^f[V_O^-] = E^{tot}[V_O^-] - E^{tot}[\text{bulk}] + \mu_O - \varepsilon_F$$

"First-principles calculations for point defects in solids",
Defect Formation Energies

example: $V_O$

- Plotted for extreme Al-rich and O-rich limits
  - Very wide range given by $\Delta H_f (\text{Al}_2\text{O}_3) = -17.36 \text{ eV}$
  - Actual chemical potential is somewhere in between
- Slope indicates charge
- Kinks: charge transition levels
- Information used to study fixed charge and defect levels
Native point defects in $\alpha$-Al$_2$O$_3$

![Graph showing formation energy as a function of Fermi level for O-Rich and Al-Rich conditions.](image)
Defect level positions in $\alpha$-Al$_2$O$_3$

Energy (eV)

Conduction band

- $V_{\text{Al}}$
- $V_{\text{O}}$
- $Al_i$
- $O_i$

Valence band

- $V_{\text{Al}}$
- $V_{\text{O}}$
- $Al_i$
- $O_i$

Energy levels:
- $(0/-)$
- $(+/-)$
- $(+/0)$
- $(+/+)$
- $(0/2-)$
- $(2/-3-)$
- $(0/-)$
- $(0/2-)$
Local geometry and charge densities

$V_O$  

$V_{Al}$  

$Al_i$  

$O_i$  

$V_{O}^0$  

$Al_{i}^0$  

$O_{i}^0$  

$h^+$  

$e^-$
Defect levels in $\kappa$- and $\alpha$-Al$_2$O$_3$

Hydrogen in Al$_2$O$_3$

Formation Energy (eV)

$\mu_0 = -0.65$ eV

$O_2$ gas @ 270 °C and 1 Torr
Hydrogen in $\text{Al}_2\text{O}_3$

- Hydrogen can easily incorporate into $\text{Al}_2\text{O}_3$
- Hydrogen occupies the interstitial site ($H_i$)
  - (+/-) impurity level near mid-gap
- Low migration energy
- $H_i$ can interact with native defects or impurities in $\text{Al}_2\text{O}_3$

$\alpha$-$\text{Al}_2\text{O}_3$

\[ \mu_0 = -0.65 \text{ eV} \]

$O_2$ gas @ 270 °C and 1 Torr
H complexes with Al vacancy in Al$_2$O$_3$

- Al vacancy:
  - 3 charge state over most of Al$_2$O$_3$ band gap
  - negative fixed-charge center

- H captured by Al vacancy:
  - $V_{Al}+nH$ ($n=1,3$) complexes lower the electrical charge of $V_{Al}$
  - $V_{Al}+3H$ complex is electrically inactive
Local geometry and charge density

$\text{Ga}_{\text{Al}}^0$

$\text{N}_0^0$

$\text{C}_{\text{Al}}^0$

$\text{H}_1^0$
Gallium in Al₂O₃

Formation Energy (eV)

Ga-rich

Gaₐ

Ga₀

Gaₐ₂Al

O-rich

μ₀ = -0.65 eV

O₂ gas @ 270 °C and 1 Torr
Nitrogen in Al$_2$O$_3$

![Graphs showing formation energy vs. Fermi level for Al-rich and O-rich conditions.]

- $N_{Al}$
- $N_i$
- $N_O$

Formation Energy (eV) vs. Fermi level (eV)

- $\mu_O = -0.65$ eV
- $O_2$ gas @ 270 °C and 1 Torr
Carbon in Al$_2$O$_3$

Formation Energy (eV)

Al-rich

O-rich

$\mu_0 = -0.65$ eV

$\text{O}_2$ gas @ 270°C and 1 Torr
Impurity Levels in Al$_2$O$_3$
Diffusion of point defects

- Relevant for ...
  - growth
    » Defects ‘frozen in’ or not
  - Ion implantation
    » Anneal damage
  - Degradation
  - Irradiation

- Zinc interstitial:
  - $E_m=0.57$ eV
Annealing temperature of point defects

\[ \Gamma = \Gamma_0 \exp \left( -\frac{E_b}{kT} \right) \]

\[ \Gamma_0 \approx 10^{13} \text{s}^{-1} \]

\[ \Gamma \approx 1 \text{s}^{-1} \]

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<thead>
<tr>
<th></th>
<th>(E_b) (eV)</th>
<th>T annealing (K)</th>
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<tbody>
<tr>
<td>(\text{Zn}_i^{2+})</td>
<td>0.57</td>
<td>219</td>
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<tr>
<td>(V_{\text{Zn}}^{2-})</td>
<td>1.40</td>
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<td>(V_{\text{O}}^{2+})</td>
<td>1.70</td>
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<td>(V_{\text{O}}^{0})</td>
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<td>(O_i^{0})(split)</td>
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<td>(O_i^{2-})(oct)</td>
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Summary

• First-principles calculations provide qualitative insights and quantitative details for point defects
• Native defects and impurities in Al_2O_3

References