Defects and doping in oxides: What we have learned so far

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Oxide semiconductors

Variety of crystal structures and band gaps

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>wurtzite</td>
<td>3.4</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Anatase, rutile</td>
<td>3.0 - 3.4</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>rutile</td>
<td>3.6</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>bixbyte</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Possible applications
- light emitting diodes and laser diodes
- transparent electronics
- electronic “noses” (gas sensors)
- photocatalysis, water splitting
- transparent electrodes, smart windows

Available as large single crystals

ZnO-based “Invisible” electronics


ZnO transparent electrode: Mega cone

Vision

• **Multifunctional materials**
  – Novel high-k dielectrics/Nonlinear optics
  – Ferroelectricity/Chemical sensors/Nanotechnology

• **Reach new levels of performance**
  – Conventional preparation methods (sputtering, laser ablation):
    » levels of stoichiometry and purity on the order of 0.1 – 1% (~ $10^{20}$ cm$^{-3}$)
    » Still: high mobility, low resistivity!
  – Semiconductor standards of purity and crystalline quality:
    » impurity and point defect concentrations in ppm range (< $10^{17}$ cm$^{-3}$)

• **Semiconducting binary oxides**
  – ZnO, SnO$_2$, In$_2$O$_3$ (and ITO), Ga$_2$O$_3$, TiO$_2$, ...

• **Vision:**
  – Enhanced control over impurities and defects will enable unprecedented performance and new science, leading to new applications
Controlling the conductivity is a major problem

• High levels of unintentional $n$-type conductivity
  – traditionally attributed to native point defects: oxygen vacancies and/or cation interstitials
  – conductivity varies inversely with oxygen partial pressure

• Difficult to make $p$-type
  – valence band is low in energy in an absolute scale
  – stability and reproducibility are main issues ($p$-ZnO)

Goal: understand the effects of native defects and impurities by performing first-principles calculations (DFT-LDA and beyond)

Hartnagel and Dawar, Semiconducting Transparent Thin Films, (IOP, Bristol, 1995)
### First-principles formalism

#### Formation energies

Determine concentrations/solubility

\[
c = N_0 e^{-\beta E_f}
\]

Ex.: Oxygen vacancy in ZnO

\[
E_f^f (V_O^q) = E_t (V_O^q) - E_t (\text{ZnO}) + \frac{1}{2} E_t (\text{O}_2) + \mu_O + q\epsilon_F
\]

\[
\mu_{\text{Zn}} + \mu_O = \Delta H_f (\text{ZnO}) \quad \text{O-rich, Zn-rich conditions}
\]

\[
\epsilon_{\text{VBM}} \leq \epsilon_F \leq \epsilon_{\text{CBM}} \quad \text{p-type, n-type}
\]

#### Transition levels (shallow/deep donor/acceptor)

#### Migration barriers (stability)

#### Optical transitions - configuration coordinate diagrams

#### Frequencies of local vibration modes

VASP: periodic boundary conditions, plane-wave basis set, special k points, projector augmented potentials (PAW)
Oxygen vacancy in ZnO cannot be described by DFT-LDA

- Electrically active - introduces levels in the gap
- Possible charge states: 0, +1, +2,
- Optically active - sub band-gap transitions
- Cannot be described in DFT-LDA/GGA?

The band gap is drastically underestimated in DFT-LDA/GGA
0.8 eV (LDA/GGA) vs. 3.4 eV (Expt.)
Approaches to overcome the band gap problem

**LDA+U**
- \( U \) applied to semicore \( d \) states \( \rightarrow \) partial correction of band gaps
  - extrapolation from LDA and LDA+\( U \) calculations
  - ex: ZnO, InN, GaN, SnO\(_2\), In\(_2\)O\(_3\)

**Screened hybrid functional (Heyd, Scuseria, Einzernhof)**
- mix of Hartree-Fock and GGA/LDA exchange \( \rightarrow \) removes self-interaction
- band gaps in agreement with experiments (by tuning mixing parameter)
  - more general, can be applied to any semiconductor/material
  - ex: ZnO, InN, TiO\(_2\), SrTiO\(_3\)

**GW**
- correct band gaps
- combined with LDA \( \rightarrow \) correct formation energies and transition levels
- ex: Si, MgO

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Combining LDA and LDA+$U$ to overcome the band gap problem

**LDA+$U$**

- $U$ applied to semicore $d$ states $\rightarrow$ partial correction of band gaps
  - extrapolation from LDA and LDA+$U$ calculations
  - ex: ZnO, InN, GaN, SnO$_2$, In$_2$O$_3$

**LDA+$U$:** $d$ bands are lowered with respect to VBM
The band gap is partially corrected: LDA: 0.8; LDA+$U$ 1.5; Exp. 3.4 eV
Combining LDA and LDA+\(U\) to overcome the band gap problem

LDA+\(U\)
- \(U\) applied to semicore \(d\) states \(\Rightarrow\) partial correction of band gaps
  - extrapolation from LDA and LDA+\(U\) calculations
  - ex: ZnO, InN, GaN, SnO\(_2\), In\(_2\)O\(_3\)

\(p-d\) repulsion

\(d\) states

VBM (O \(p\) states)

CBM (Zn \(s\) states)

LDA+\(U\): affects both valence band and conduction band

\(E_c\)

\(E_v\)

\(ZnO(\text{LDA})\)

\(ZnO(\text{LDA+U})\)

\(E_c\)

\(E_v\)

\(Zn\) 3\(d\)-band

\(\text{VBM (O } p\text{ states)}\)

\(\text{CBM (Zn } s\text{ states)}\)

\(\text{\(p-d\) repulsion}\)

\(\text{\(d\) states}\)

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\(\text{\(d\) states}\)

\(\text{\(p-d\) repulsion}\)

\(\text{\(d\) states}\)
Correcting transition levels and formation energies based on LDA/LDA+U calculations

\[ \varepsilon(q/q') = \varepsilon(q/q')^{\text{LDA}+U} - \varepsilon(q/q')^{\text{LDA}} \left( E_g^{\text{exp}} - E_g^{\text{LDA}+U} \right) + \varepsilon(q/q')^{\text{LDA}+U} \]

Take into account valence vs. conduction band character of the defect state in the gap

Oxygen vacancy in ZnO

- Deep donor (2+/0) at 1 eV below CBM cannot cause conductivity
- +1 charge state unstable
  - EPR active, need light excitation to see +1
- High formation energy in $n$-type
  - Low concentrations in equilibrium conditions
  - In agreement with Watkins & Vlasenko, Phys. Rev. B 71, 125210 (2005): +1 only observed after irradiation

![Diagram showing formation energy vs. Fermi level (eV)](image)
Oxygen vacancy in ZnO

Electronic properties strongly coupled with local lattice relaxations
$V_0$ in ZnO: comparison with experiment


$V_0$ created by irradiation

2.1 eV threshold for $V_0^0 \rightarrow V_0^+ + e$

Need to **create** $V_0$ by irradiation!
No $V_0$ observed in as-grown material.
Consistent with high formation energy.

**FIG. 4.** Wavelength dependence of changes in charge state while illuminating at 30 K. The monitored EPR signals are (a) Fe$^{3+}$ ions, (b) singly ionized oxygen vacancies ($V_0^+$), and (c) zinc vacancies with a OH$^-$ ion at an adjacent oxygen site, i.e., ($V_{Zn}^{2-}$H$^+$)$^{3+}$ centers.
Native point defects in ZnO

- $V_{O}$, $V_{Zn}$: dominant defects

- $V_{O}$: deep donor
  - Also high formation energy in $n$-type ZnO

- $V_{Zn}$: deep acceptor
  - Cause of green luminescence

- $Zn_{i}$: high formation energy
  - unstable, migration barrier 0.57 eV
Native defects vs. impurities

- Native defects cannot explain $n$-type doping
- Impurities: donors?
Interstitial hydrogen in ZnO

\[ \text{Formation energy (eV)} \]

\[ E_F (\text{eV}) \]

\[ \text{H}^+ \]

\[ \text{H}^+ \text{ is the only stable charge state} \Rightarrow \text{hydrogen acts as shallow donor} \]

Unexpected! In other semiconductors hydrogen reduces the conductivity


Hydrogen is a likely candidate for unintentional incorporation

• But: highly mobile


\( \Rightarrow \) unstable at temperatures where \( n \)-type conductivity is known to persist (>500°C)

Also cannot explain dependence of conductivity on oxygen partial pressure…
Substitutional hydrogen in ZnO

- Forced to reconsider the role of hydrogen...
  - ... and in the process some interesting new physics/chemistry emerged!

- Substitutional hydrogen
  - Hydrogen on a substitutional oxygen site
  - Formation energy: **low**
  - Ionization energy: small; **shallow donor**

- Consistently explains dependence of *n*-type conductivity on oxygen partial pressure
Diffusion of substitutional hydrogen

How does H₀ move?

► Dissociation:
H₀⁺ → Hᵢ⁺ + V₀⁰ costs 3.8 eV!
Diffusion of substitutional hydrogen

How does $H_0$ move?

- **Dissociation:**
  
  $H_0^+ \rightarrow H_i^+ + V_0^0$ costs 3.8 eV!

- **Migration:**
  - Concerted exchange of H and neighboring O
  - Barrier: 2.5 eV
  - $\Rightarrow$ becomes mobile above 500 ºC

- Consistent with experimental observations
  
Hydrogen multicenter bonds

- Hydrogen equally bonds to four atoms
- Truly multicoordinated configuration

Nitrogen doping in ZnO

- In principle, the most promising p-type dopant in ZnO
- Experimental results are highly controversial
- Stability and reproducibility are main issues
ZnO: Hybrid functional calculations

ZnO band structure
No in ZnO

- Deep acceptor
- Will not lead to p-type conductivity

Lyons, Janotti, and Van de Walle,
Appl. Phys. Lett. 95, 252105 (2009)
\( N_0 \) in ZnO – theory vs. experiment

Lyons, Janotti, and Van de Walle,
Appl. Phys. Lett. 95, 252105 (2009)

Garces et al.,
No in ZnO: theory vs. experiment

Lyons, Janotti, and Van de Walle, Appl. Phys. Lett. 95, 252105 (2009)

Anisotropy in the spin density
Oxygen vacancy in TiO$_2$

- **Is DFT-LDA/GGA enough?**
- **LDA/GGA functionals can describe only +2 charge state**
- **Electrons from 0 and +1 charge states go to the conduction band**

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TiO$_2$: Hybrid functional calculations

<table>
<thead>
<tr>
<th>functional</th>
<th>$a$ (Å)</th>
<th>$c/a$</th>
<th>$u/a$</th>
<th>$E_g$</th>
<th>$\Delta H_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>4.65</td>
<td>0.639</td>
<td>0.305</td>
<td>1.77</td>
<td>-9.33</td>
</tr>
<tr>
<td>HSE</td>
<td>4.59</td>
<td>0.642</td>
<td>0.305</td>
<td>3.05</td>
<td>-9.73</td>
</tr>
<tr>
<td>Exp.</td>
<td>4.59</td>
<td>0.644</td>
<td></td>
<td>3.1</td>
<td>-9.74</td>
</tr>
</tbody>
</table>
TiO$_2$: GGA vs. Hybrid functional (HSE)

$V_O$ in TiO$_2$: GGA vs. HSE

relaxed $V_O^0$ and $V_O^+$ can be described in HSE

$V_0^0$ and $V_0^+$ charge distributions

gap states have strong contributions from the two out-of-plane Ti atoms

$V_O$ in TiO$_2$: HSE results

- shallow donor - can cause conductivity
- low formation energy only in extreme O-poor conditions

Summary

LDA/LDA+$U$ scheme
- Limited to systems with semicore $d$ states
- Computationally inexpensive, large systems (>200 atoms)

Hybrid functionals (HSE)
- Mixing parameter and screening length
- Can be applied to any semiconductor
- Computationally demanding (~100 atoms, few k-points)
Summary

ZnO

- Native defects are not the cause of unintentional $n$-type conductivity
- Impurities are the likely cause (hydrogen)
- Nitrogen doping not lead to $p$-type ZnO

TiO$_2$

- Oxygen vacancy is a shallow donor
- Low formation energy only in extreme O-poor
- Need to relate $\mu_O$ to realistic conditions
LDA/LDA+\(U\) vs. HSE

Janotti & Van de Walle
PRB 76, 165202 (2007)

Oba et al.,
PRB 77, 245202 (2008)
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

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

- \( \Gamma_0 \approx 10^{13} \text{s}^{-1} \)
- \( \Gamma \approx 1 \text{s}^{-1} \)

<table>
<thead>
<tr>
<th>Defect</th>
<th>( E_b ) (eV)</th>
<th>( T ) annealing (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Zn}_i^{2+} )</td>
<td>0.57</td>
<td>219</td>
</tr>
<tr>
<td>( V_{\text{Zn}}^{2-} )</td>
<td>1.40</td>
<td>539</td>
</tr>
<tr>
<td>( V_{\text{O}}^{2+} )</td>
<td>1.70</td>
<td>655</td>
</tr>
<tr>
<td>( V_{\text{O}}^0 )</td>
<td>2.36</td>
<td>909</td>
</tr>
<tr>
<td>( O_{i}^0\text{(split)} )</td>
<td>0.87</td>
<td>335</td>
</tr>
<tr>
<td>( O_{i}^{2-}\text{(oct)} )</td>
<td>1.14</td>
<td>439</td>
</tr>
</tbody>
</table>

Si and Ge in ZnO

- Si and Ge are shallow donors
- [Si] of up to 10E17 cm-3 observed in as grown single crystals

Phys. Rev. B 80, 205113 (2009)