Theory of Hydrogen-Related Levels in Semiconductors and Oxides

Chris G. Van de Walle

Materials Department
University of California, Santa Barbara
Acknowledgments

• Computations
  J. Neugebauer (Max-Planck-Institut, Düsseldorf)
  A. Janotti (UCSB)
  S. Limpijumnumong (Suranaree U. Tech., Thailand)
  B. Tuttle (Penn State University)

• Support
  AFOSR; ONR
  Palo Alto Research Center
  Alexander von Humboldt Foundation
  Fritz-Haber-Institut & Paul-Drude-Institut, Berlin
Motivation for studying hydrogen

• Omnipresent impurity
  – Growth
    • vapor-phase transport, hydrothermal growth, MOCVD, MBE, sputtering (H\textsubscript{2} atmosphere), …
  – Processing: forming gas anneal, …

• Beneficial effects & applications
  – Passivation of defects
    • Si/SiO\textsubscript{2}
    • Reliability? (deuterium)
    • High-k dielectrics?
Motivation for studying hydrogen

• Unintended / detrimental effects
  – Passivation of dopant impurities
    • DRAM variable retention time
    • Nanoscale MOSFETs

Source: Intel
Motivation for studying hydrogen

- Unintended / detrimental effects
  - Passivation of dopant impurities
    - DRAM variable retention time
    - Nanoscale MOSFETs
  - Trapping of hydrogen in oxide
    - Stress-induced leakage currents
  - Charging of interface
Hydrogen impurities

- Understanding “interstitial” hydrogen
  ⇒ interactions with defects and impurities

- Hydrogen is **electrically active!**
  - $H^0$: rarely important
  - $H^+$ → donor
  - $H^- → acceptor$

- Amphoteric impurity
  - relative stability of $H^+/H^-$
    depends on Fermi level
Example: interstitial H in GaN

Amphoteric impurity:
- $H^+$ in $p$-type / $H^-$ in $n$-type
  ➔ Always counteracts prevailing conductivity

- **First-principles calculations**
  - Density-functional theory
  - Pseudopotentials / Atomic relaxations

- **Applies to**: Si, …; GaAs, AlAs, GaN, AlN, …; ZnSe, …

- **What about ZnO?**
Zinc oxide devices

- Applications in optoelectronics
- Zinc oxide: typically $n$-type
  - Conductivity due to electrons
  - Cause: heavily debated
  - Traditionally attributed to oxygen vacancies
- First-principles calculations:
  - Oxygen vacancies are not shallow donors!
  - So what is the cause?…
Hydrogen in ZnO

$H^+$ is the only stable charge state


Confirmed by more than 20 experiments to date
Why is ZnO different?

• Position of $\varepsilon(+/\text{-})$ in the band gap

**Question:** Why is $\varepsilon(+/\text{-})$ so much higher in energy in ZnO?
Why is ZnO different?

Band lineups!

GaN

ZnO

$\epsilon (+/-)$

CB

VB
Why is ZnO different?

Band lineups!

GaN                ZnO

\[ \varepsilon(+/-) \]

CB                  VB
Use natural band lineups to align band structures

Band lineups

E (eV)

Si  Ge  SiC  AlN  GaN  InN  GaAs  GaSb  ZnSe  ZnO  SiO$_2$

hydrogen $\varepsilon(+/−)$ level

Band lineups


Band lineups

E (eV)

Si, Ge, SiC, AIN, GaN, InN, GaAs, GaSb, ZnSe, ZnO

hydrogen $\varepsilon(+/-) level$


Band lineups

H exclusively a donor

Hydrogen $\epsilon(\pm)$ level


Band lineups

H exclusively an acceptor

Band lineups

E (eV)

0
-2
-4
-6
-8
-10

Si Ge SiC AlN GaN InN GaAs GaSb ZnSe ZnO SiO$_2$

hydrogen $\varepsilon(+/−)$ level

Band lineups

<table>
<thead>
<tr>
<th>Material</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>-10</td>
</tr>
<tr>
<td>Ge</td>
<td>-8</td>
</tr>
<tr>
<td>SiC</td>
<td>-6</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-4</td>
</tr>
<tr>
<td>SnO₂</td>
<td>-2</td>
</tr>
<tr>
<td>HfO₂</td>
<td>0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>4</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>6</td>
</tr>
<tr>
<td>ZnO</td>
<td>8</td>
</tr>
<tr>
<td>AlN</td>
<td>10</td>
</tr>
</tbody>
</table>

SnO₂
H exclusively a donor

Transparent conductors
Band lineups

E (eV)

Si Ge SiC AlN ZnO In$_2$O$_3$ TiO$_2$ HfO$_2$ ZrO$_2$

High-k dielectrics
Conclusions

• Hydrogen strongly interacts with defects and impurities
• Understanding this behavior:
  – First-principles calculations
• Interstitial hydrogen:
  – basis for understanding complex interactions
• Towards general understanding:
  – Universal alignment
  – Predictive model
• Connection with band lineups