

Chapter 3

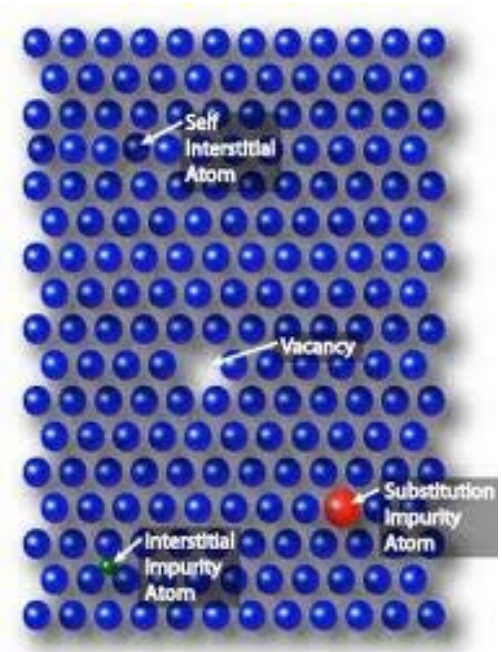
Lecture 11: Doping Engineering of Semiconductors

First-principles simulations of defects in oxides and nitrides

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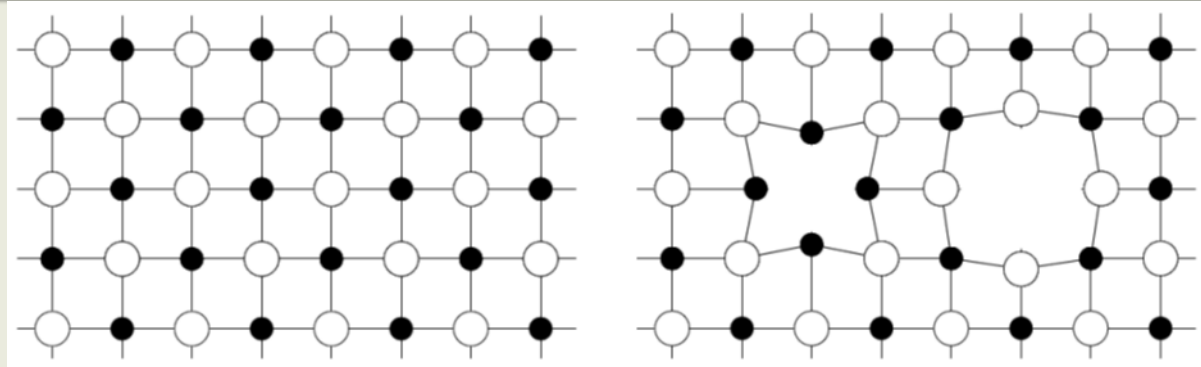
Acknowledgments:

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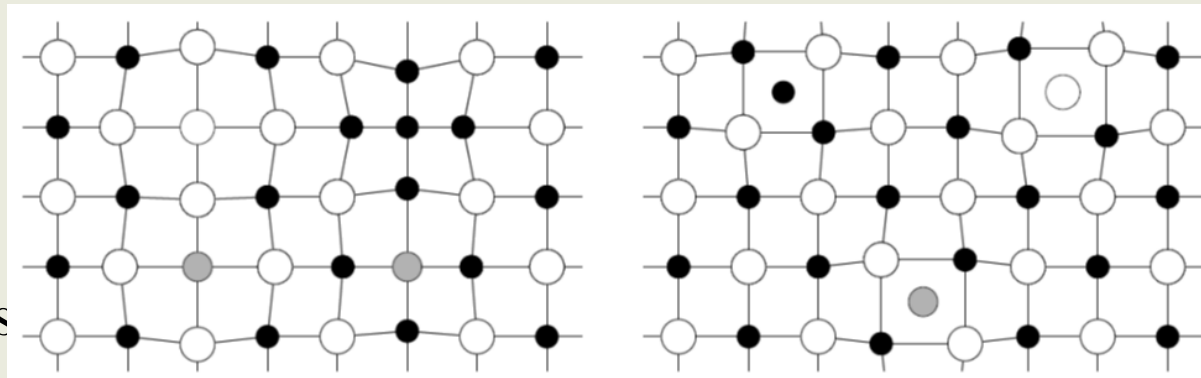


Why study defects?

- **“Defects”**
- ✓ Extended defects
 - dislocations
- ✓ Point defects
 - Native defects
 - Impurities



- **Defects often determine the properties of materials**
- ✓ Doping and its limitations
- ✓ Device degradation
- ✓ Diffusion
 - Mediated by point defects



antisite

interstitial

Technological Significance

- **Semiconductors**

- Achieve higher doping levels
 - » *p*-type doping of AlN would allow UV lasers
- Controllably dope materials *p*-type and *n*-type
 - » Oxides

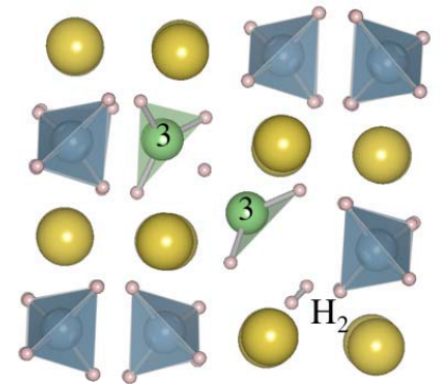
- **Photovoltaics**

- $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$

- **Hydrogen storage materials**

- Kinetics of hydrogen release in NaAlH_4

- **Embrittlement of structural metals**



Useful Experimental Techniques

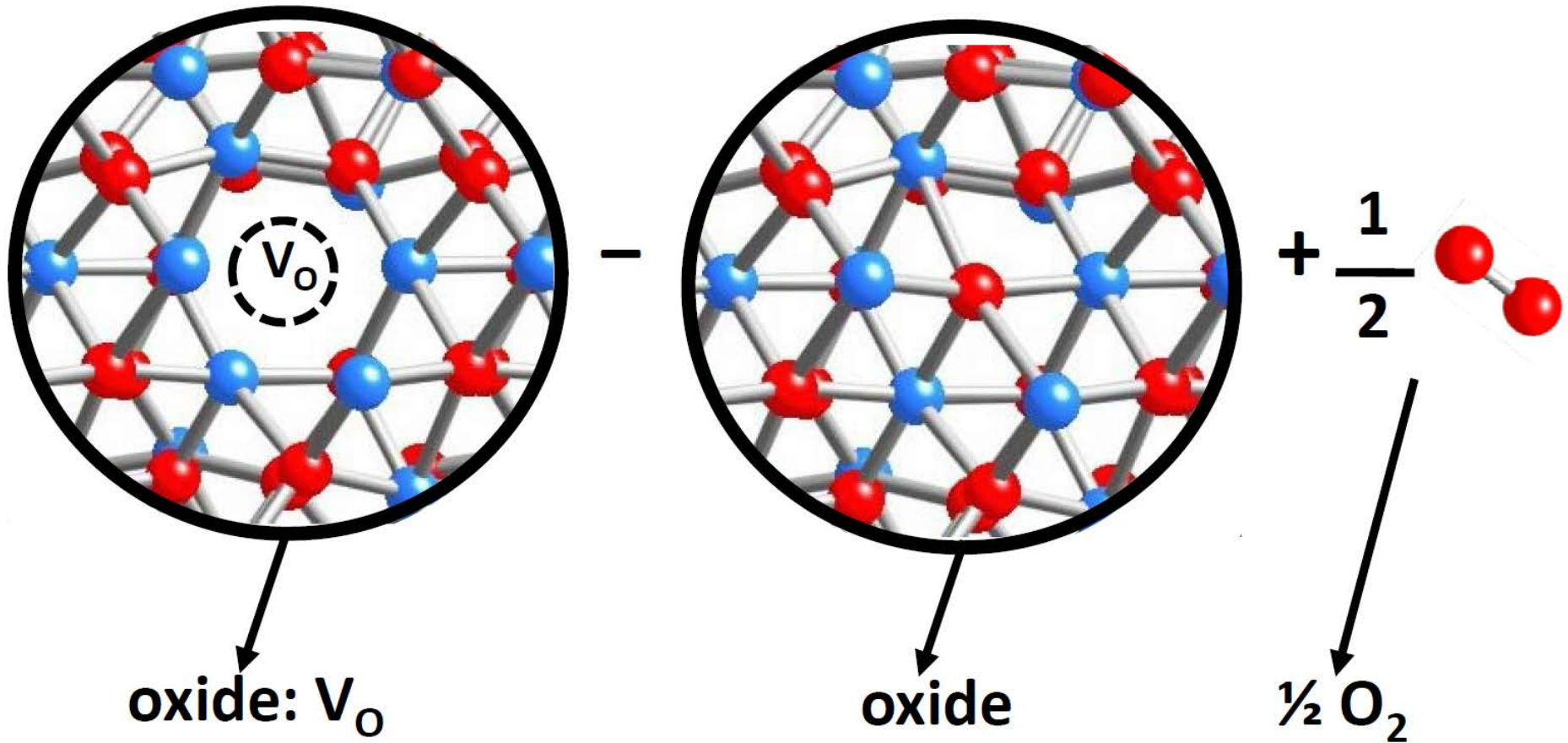
- **Secondary Ion Mass Spectrometry (SIMS)**
 - Impurity concentrations (to within factor of 2)
- **Positron annihilation spectroscopy**
 - Most sensitive to negatively charged vacancy(-like) defects
- **EXAFS (extended x-ray absorption fine structure)**
 - Microscopic structure, atomic relaxations
- **Electron paramagnetic resonance + ENDOR**
 - Hyperfine parameters (wave functions, atomic positions)
- **Vibrational spectroscopy (Raman, FTIR)**
 - Local vibrational modes; sensitive to atomic positions
- **Deep level transient spectroscopy**
 - Electronic transition levels
 - » Total-energy differences, not Kohn-Sham levels
- **Photoluminescence (PL), PL excitation**
 - Optical transition levels

Defect Calculations: Geometry

- **Green's functions**
 - Implementation difficult
 - Non-intuitive
- **Clusters**
 - Surface effects
 - Not “bulk” (quantum confinement)
- **Supercells**
 - “Molecular unit cell approach (MUCA)”
 - » R. P. Messmer and G. D. Watkins, in
Radiation Damage and Defects in Semiconductors
(Inst. of Phys. London, 1972), No. 16, p. 255.

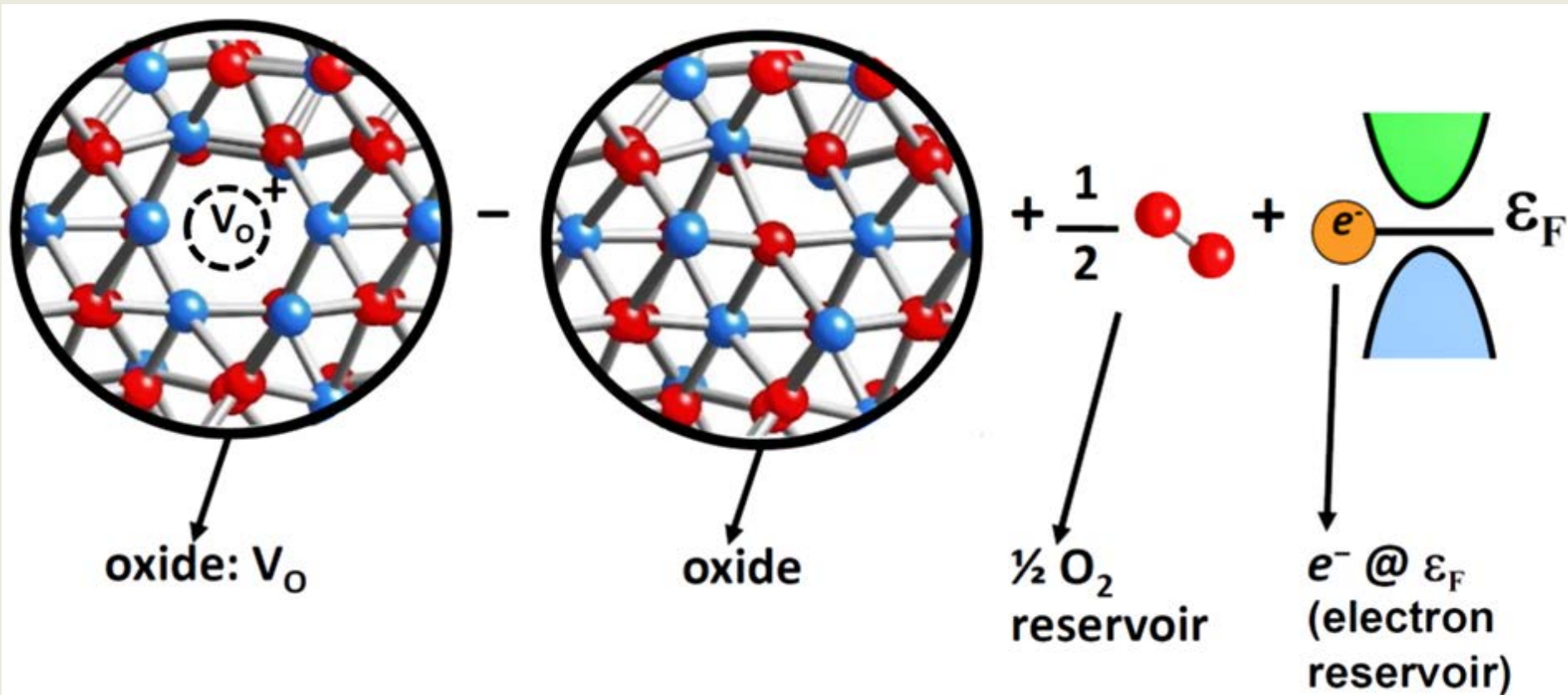
Defect Formation Energies

Example: V_O



Defect Formation Energies

Example: V_O^+



Formalism

- E_{form} : defect formation energy

Concentration of defects or impurities: $C = N_{sites} e^{-(E_{form}/kT)}$

- Example: oxygen vacancy in ZnO

$$E_{form}(V_o^+) = E_{tot}(V_o^+) - E_{tot}(bulk) + \mu_O + E_F$$

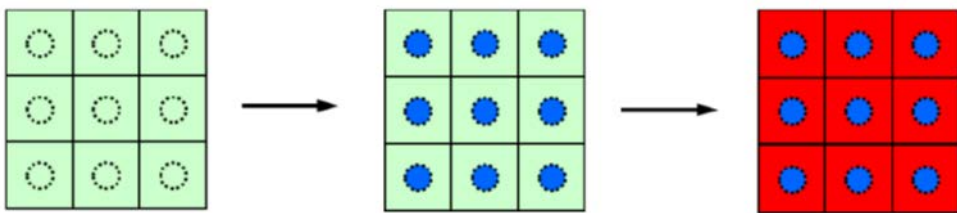
μ_O : energy of oxygen in reservoir, i.e., **chemical potential of oxygen atom.**

E_F : energy of electron in its reservoir, i.e., the Fermi level.

- **General Expression**

$$E_{form}(D^q) = E_{tot}(D^q) - E_{tot}(bulk) + n_i \mu_i + q E_F$$

n_i : number of atoms being exchanged to form the defect.



Modeling charged point defect in DFT: The number of electrons in the supercell is modified corresponding to the effective charge. To avoid diverging Coulomb energy due to interacting supercell images, a neutralizing homogeneous background charge is added.

Chemical Potential Limits

- **Use $A_2B_2O_7$ as an example:** $A_2B_2O_7$ -phase is stable at equilibrium gives $2\mu_{0,A} + 2\mu_{0,B} + 7\mu_{0,O} = \mu_{0,A_2B_2O_7} = E_{tot}[A_2B_2O_7]$.
- In order to determine all three chemical potentials, two more equilibrium equations are needed. Assume for simplicity that **A** has no stable bulk phase, but has one stable binary oxide phase A_2O_3 . **B** has only one stable oxide phase BO_2 , and can also exist as bulk. Oxygen can exist in any of the oxide phases but also in the "bulk" gas phase: $O_2(g)$.

	phase 1	phase 2	equilibrium equation 1	equilibrium equation 2
1	O	A_2O_3	$2\mu_{0,O} = E^{tot}[O_2]$	$2\mu_{0,A} + 3\mu_{0,O} = E^{tot}[A_2O_3]$
2	O	B	$2\mu_{0,O} = E^{tot}[O_2]$	$n\mu_{0,B} = E^{tot}[B_n]$
3	O	BO_2	$2\mu_{0,O} = E^{tot}[O_2]$	$\mu_{0,B} + 2\mu_{0,O} = E^{tot}[BO_2]$
4	A_2O_3	B	$2\mu_{0,A} + 3\mu_{0,O} = E^{tot}[A_2O_3]$	$n\mu_{0,B} = E^{tot}[B_n]$
5	A_2O_3	BO_2	$2\mu_{0,A} + 3\mu_{0,O} = E^{tot}[A_2O_3]$	$\mu_{0,B} + 2\mu_{0,O} = E^{tot}[BO_2]$
6	B	BO_2	$n\mu_{0,B} = E^{tot}[B_n]$	$\mu_{0,B} + 2\mu_{0,O} = E^{tot}[BO_2]$

Chemical Potential Limits

- Synthesis of a material takes place in equilibrium with an atmosphere containing oxygen. The value of $\mu_{0,O}$ is pinned, leaving only points 1–3.
- The values of the metal atoms in an oxygen-rich environment are limited by the formation of binary oxides, A_2O_3 and BO_2 .
- The **A**-rich limit of point 1 is defined by chemical equilibrium with A_2O_3 and corresponds to an upper bound on $\mu_{0,A}$:

$$\mu_{0,A}^{max} = \frac{1}{2} E_{tot}[A_2O_3] - \frac{3}{2} \mu_{0,O}.$$

- Similarly, point 3 corresponds to the **B**-rich limit:

$$\mu_{0,B}^{max} = \frac{1}{2} E_{tot}[BO_2] - 2\mu_{0,O}.$$

- From $2\mu_{0,A} + 2\mu_{0,B} + 7\mu_{0,O} = \mu_{0,A_2B_2O_7} = E_{tot}[A_2B_2O_7]$, only one degree of freedom in the chemical potentials of the native atoms remains, with bounds defined by the **A** and **B**-rich. For example, in **A**-rich condition:

$$\frac{1}{2} E_{tot}[A_2B_2O_7] - \frac{1}{2} E_{tot}[A_2O_3] - 2\mu_{0,O} \leq \mu_{0,B} \leq \frac{1}{2} E_{tot}[BO_2] - 2\mu_{0,O}$$

Defect Formation Energy

- V_O in ZnO

Zn-rich conditions

($\Delta\mu_{Zn} = \mu_{Zn} - \mu_{0,Zn} = 0$):

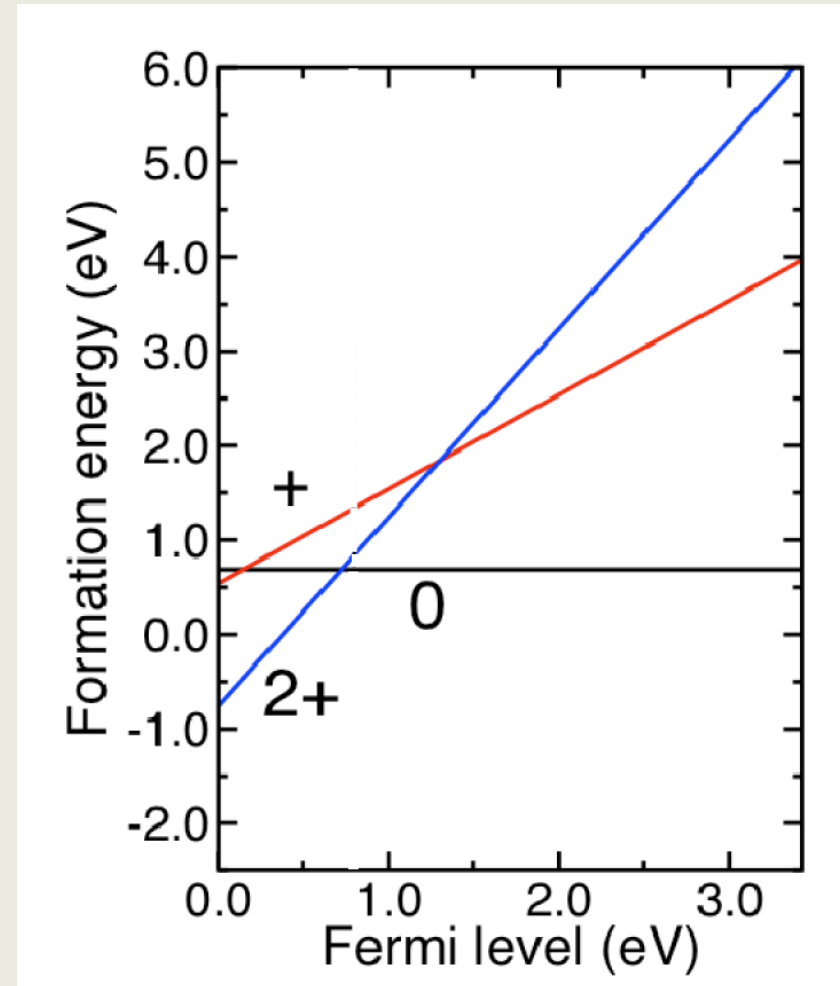


$\Delta\mu_O + \Delta\mu_{Zn} = E_{tot}(ZnO)$ and

$$\begin{aligned} \Delta\mu_O &= \mu_O - \mu_{0,O} = \mu_O - \frac{1}{2} E_{tot}[O_2] \\ &= E_{tot}[ZnO] \end{aligned}$$

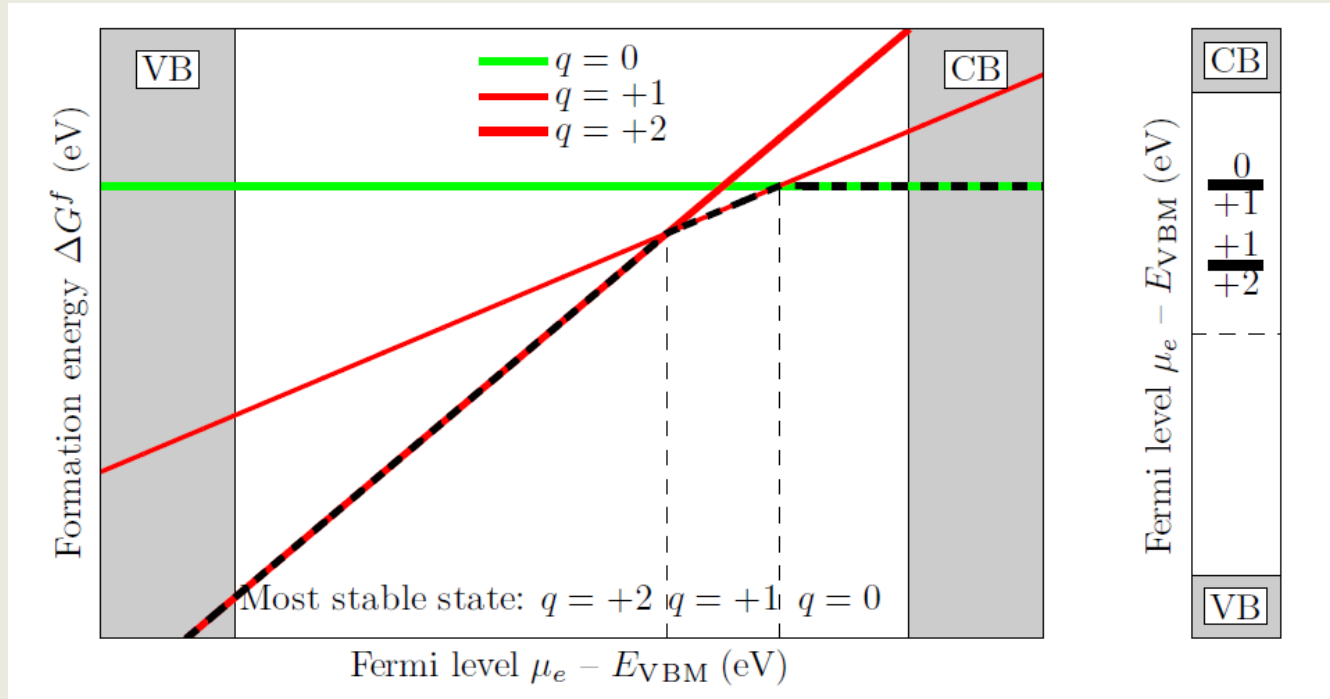
$$\mu_O = \frac{1}{2} E_{tot}(O_2) + E_{tot}(ZnO)$$

$$\begin{aligned} E_{form}(V_O^{+q}) &= E_{tot}(V_O^+) - E_{tot}(bulk) + \mu_O \\ &\quad + qE_F \end{aligned}$$



Transition Level

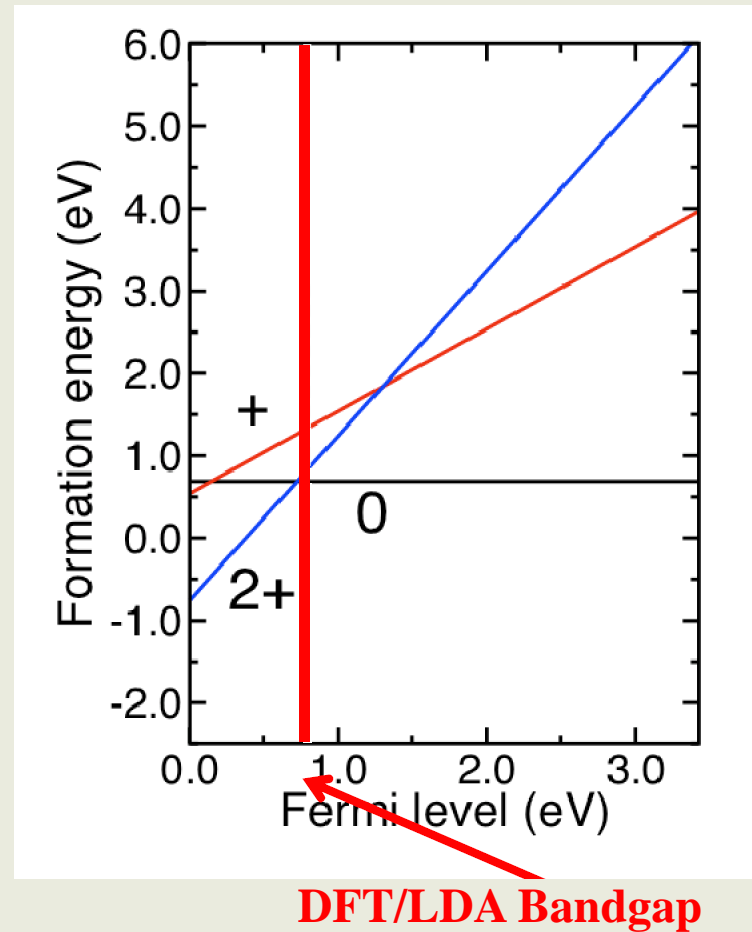
- Charge-state transition



Determination of thermodynamic charge transition levels from formation energies: Plotting the formation energy for three different charge states of the defect, it is found that for low values of μ_e the state with charge +2 is most stable. At $\mu_e - E_{VBM} \approx 2.5$ a transition occurs to the state with charge +1, defining a thermodynamic charge transition level as depicted in the right panel. Increasing μ_e further, another level is found for $\mu_e - E_{VBM}$ just over 3.

Important Issues

- **Band gap problem**
 - DFT (LDA, GGA)
- **Affects formation energies and transition levels**
 - Even for neutral charge states, if defect-induced Kohn-Sham states are occupied with electrons.



Band-gap Corrections: Empirical Correction

- **Ad hoc corrections**

- “Scissors operator”
 - » Shift gap levels based on conduction- vs. valence-band character
- Delta-function(-like) term added to potential, shifts s states
 - » N. E. Christensen, Phys. Rev. B **30**, 5753 (1984).
- “Modified pseudopotentials”
 - » D. Segev, A. Janotti, and C. G. VdW, Phys. Rev. B **75**, 035201 (2007).
- Issues
 - » Hard to control
 - » May have unintended consequences (indirect vs. direct gaps, ...)

- **Extrapolations based on calculations that yield different gaps**

- Different plane-wave cutoffs
- Different exchange-correlation functionals
- ...
 - » S. Zhang, S. Wei, and A. Zunger, Phys. Rev. B **63**, 075 (2001).
- Issue: different choices of parameter not only produce different gap, but also different levels of accuracy for description of defect

Band-gap Corrections: SIC and LDA+ U

- Physically meaningful improvements
- Self-interaction corrections

» J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

- Difficult to implement in self-consistent calculations for solids
- Incorporate in pseudopotentials

» D. Vogel, P. Krueger, and J. Pollmann, Phys. Rev. B **52**, 14316 (1995).

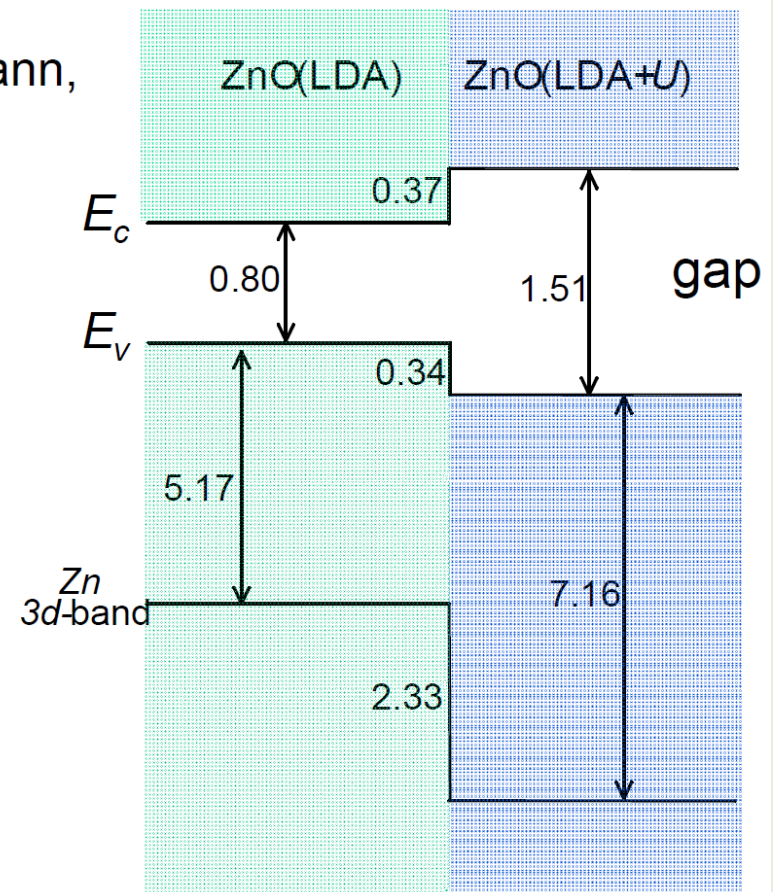
- “LDA+ U ” approach

» A. Janotti and C. G. Van de Walle, Appl. Phys. Lett. **87**, 122102 (2005).

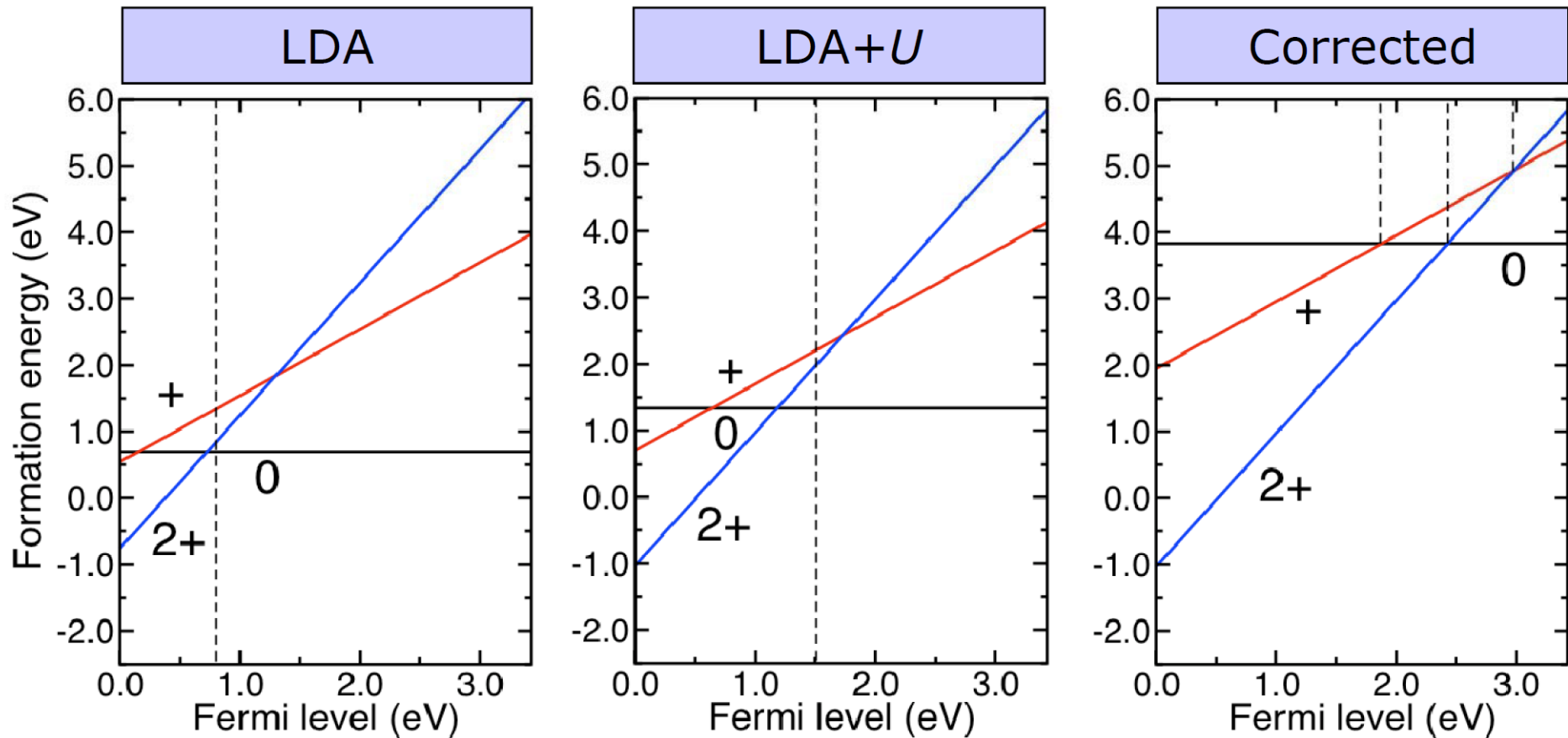
» S. Lany and A. Zunger, Phys. Rev. B **72**, 035215 (2005).

- Issues:

- Determination of U
- Band gap not fully corrected
 - » How to extrapolate to the experimental gap?



Results: Oxygen Vacancy in ZnO



Band-gap Corrections: Hybrid Functionals

Mixing of Hartree-Fock (exact exchange) and DFT

A. D. Becke, J. Chem. Phys. **98**, 1372 (1993)

- **PBE0**: Functionals mix in ~25% of exact exchange
J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).
- • **HSE**: Exact exchange only for short-range interactions
J. Heyd, G. E. Scuseria and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
- ✓ **Obtain very good description of many properties**
 - Band gaps close to experiment
- ✓ **Details of the physics still to be explored/understood**

Band-gap Corrections: Beyond DFT

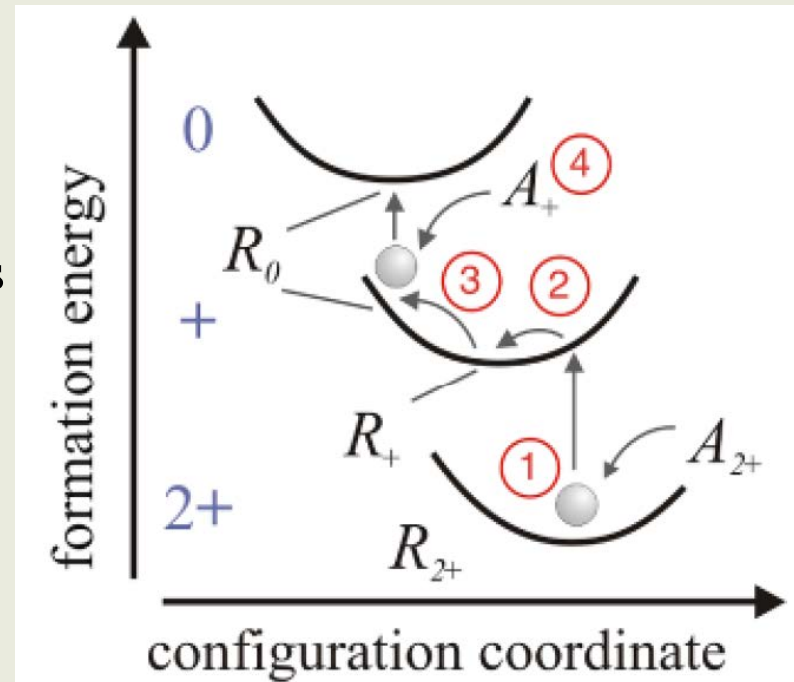
- **Quasiparticle Calculations**

- Combine DFT and G_0W_0
- DFT: good for structural properties
- G_0W_0 (Many-body perturbation theory for defects): accurate electron affinities in solids

P. Rinke, A. Janotti, M. Scheffler, and C. G. Van de Walle, Phys. Rev. Lett. **102**, 026402 (2009).

- **Quantum Monte Carlo**

- Richard Hennig

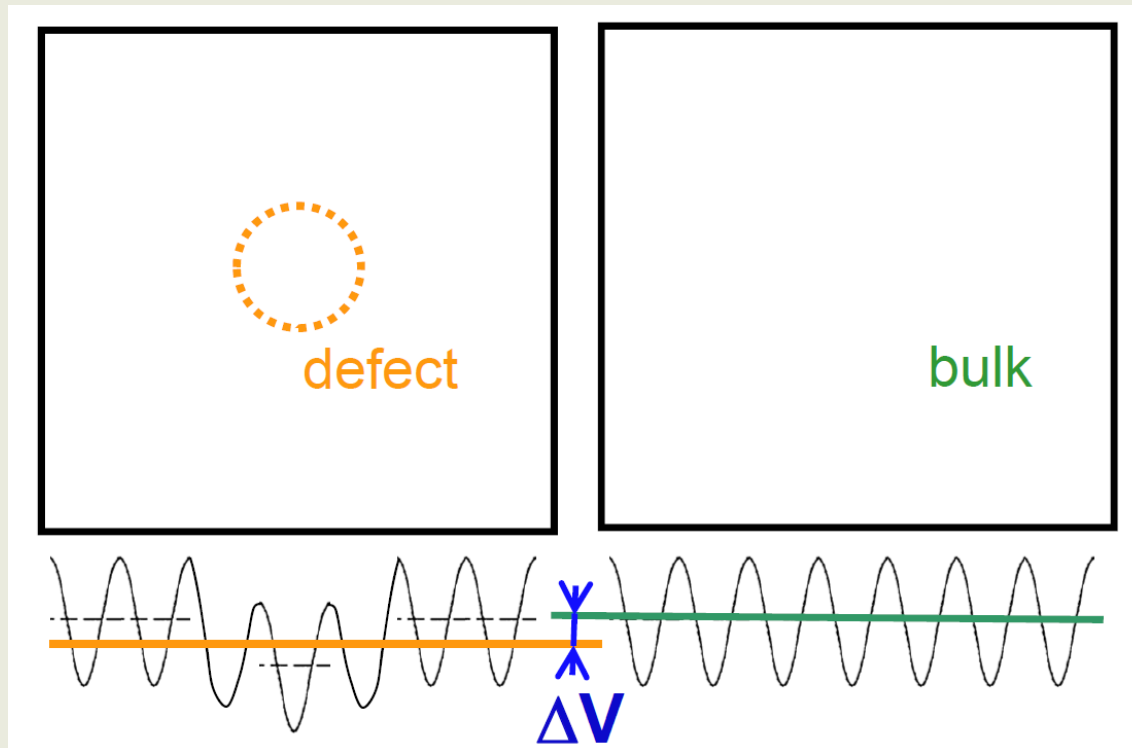


Alignment of Fermi Level

Charges are exchanged with E_F , referenced to E_V

$$E_{form}(D^q) = E_{tot}(D^q) - E_{tot}(bulk) + n_i \mu_i + q E_F$$

– Presence of defect in supercell shifts average electrostatic potential with respect to bulk



Supercell Size Effects

- **Neutral defects:**

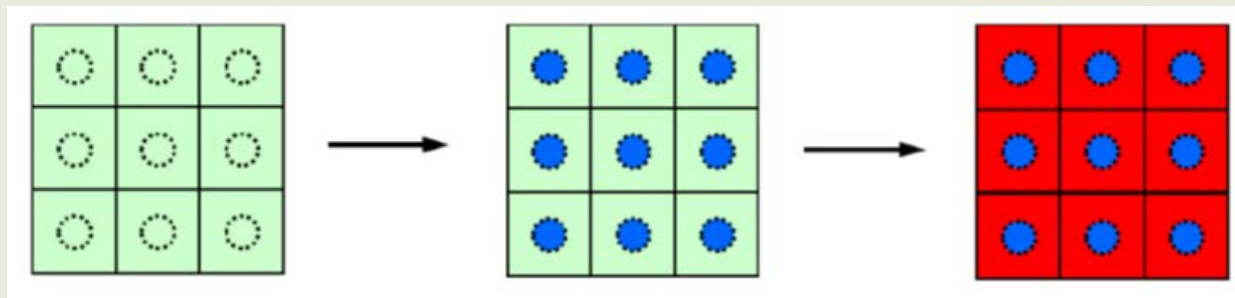
- Supercell should be large enough to ensure atomic relaxations are included, and overlap of wave functions is small enough

- **Charged defects:**

- Imbalance in electronic and ionic charge would lead to Coulomb divergence

- Neutralizing background

No need to explicitly include; $G=0$ term calculated for neutral system



Supercell Size Effects

- **Neutralization leads to unintended terms in total energy**

- Interactions with neutralizing background and between periodic images of defects

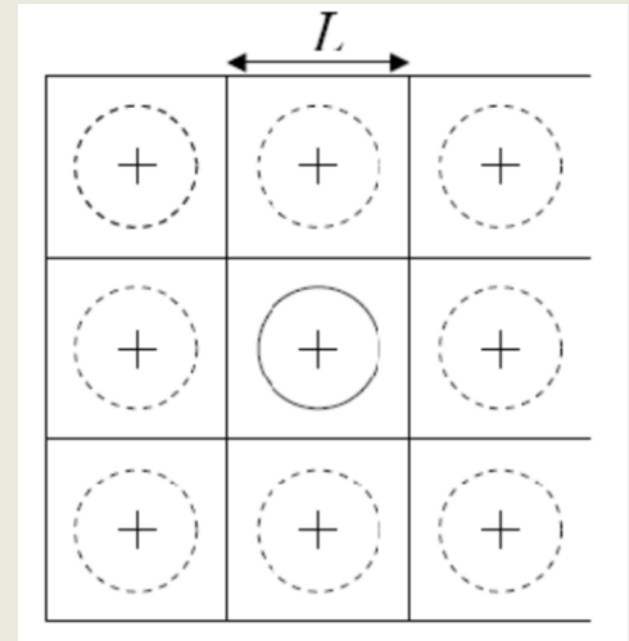
- **Makov-Payne Correction**

$$E(L) = E(\infty) - \alpha q^2 / \epsilon L - C_3 q^2 / L^3 + O(L^{-5})$$

G. Makov and M.C. Payne, Phys. Rev. B **51**, 4014 (1995).

- Correct in vacuum

- Effect of solid: dielectric constant ϵ



Supercell Size Effects

Explicit studies as a function of supercell size have shown complex behavior

- Fits to $1/L$ and $1/L^3$ terms
- In some cases, Makov-Payne correction satisfactory
- In other cases: Makov-Payne correction makes things worse
 - » Example: V^{2+} in diamond
 - » Shim, Lee, Lee, and Nieminen, Phys. Rev. B **71**, 035206 (2005).

Applications with Doping Engineering

Design of Shallow p -type Dopants in ZnO

Su-Huai Wei, J. Li, and Y. Yan

National Renewable Energy Laboratory, U.S.A.

NREL/PR-520-43248

Presented at the 33rd IEEE Photovoltaic Specialist Conference held May 11-16, 2008 in San Diego, California

Introduction

- ZnO is a promising material for short wavelength opto-electronic devices such as UV lasers and LEDs due to its large exciton binding energy and low material cost
- ZnO can be doped easily *n*-type, but the realization of stable *p*-type ZnO is rather difficult

First-principles band structure methods will be used to address

- What causes the *p*-type doping difficulty in ZnO?
- How to overcome the *p*-type doping difficulty?

Method of Calculation

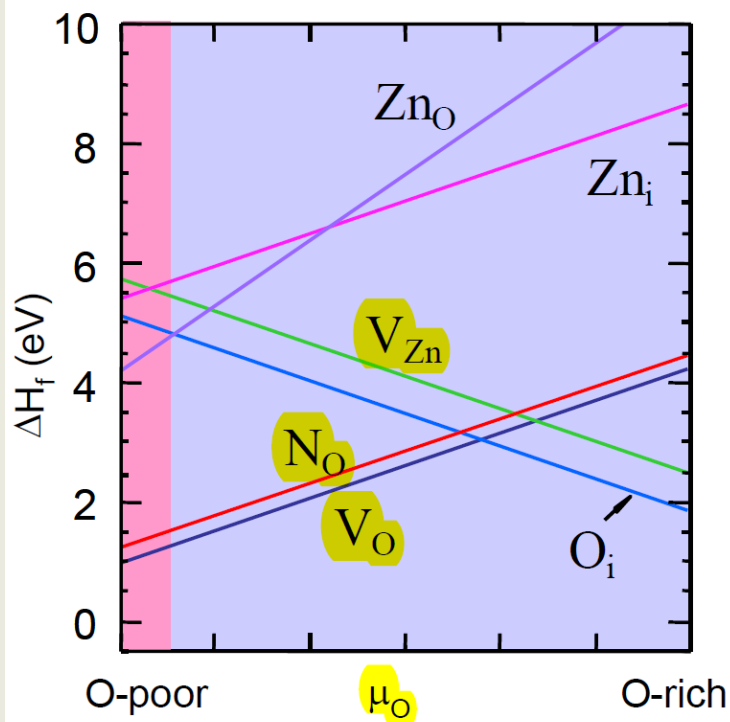
- Band structure and total energy are calculated using the first-principles band structure method as detailed in the previous section.
- Defects are described using the supercell approach. A uniform background charge is added for charged defect calculation
- All the internal structural parameters are optimized by minimizing the quantum mechanical forces.
- Band in different supercell calculations are aligned using atomic core levels or average potentials.

Origin of the p -type Doping Difficulty in ZnO

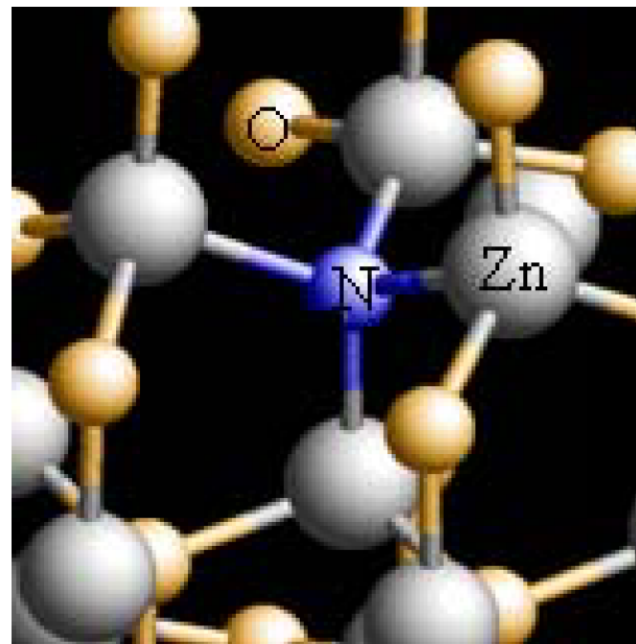
Main reasons of failure-to-dope

- The impurity atom has limited solubility in the host material, so not enough dopants are introduced
- The defect transition energy levels are too deep, so not enough charge carrier are generated at working temperature
- Spontaneous formation of opposite-charged “killer defects” (cation vacancy, anion vacancy, etc.), which pins the Fermi energy

Origin of *p*-type doping difficulty in ZnO: **high acceptor formation energy**



Due to the strong bonding and large formation energy of ZnO, intrinsic defect formation energies are large



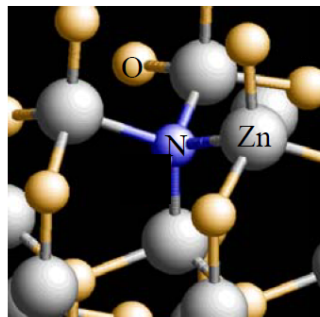
Calculate minimum defect formation energy of neutral N_O

$$H_f(N_O)_{\min} = 1.2 \text{ eV} \quad (N_2)$$

Origin of *p*-type doping difficulty in ZnO: **high acceptor ionization energy**

Acceptor energy levels in ZnO

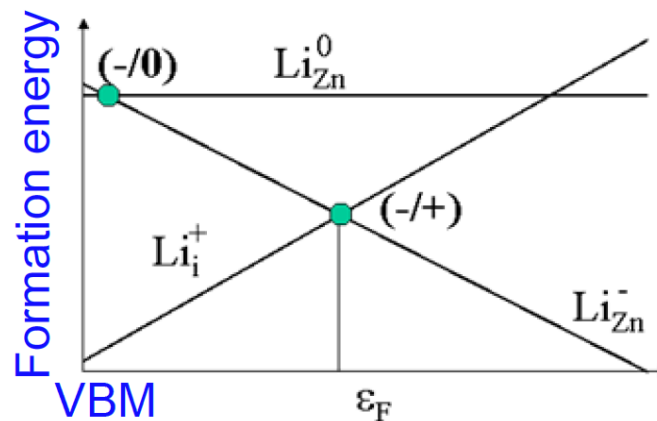
CBM



(0/-)

Sb _O	1.10			
As _O	0.90			
P _O	0.70			
		Cu _{Zn}	0.74	
		Ag _{Zn}	0.40	
		Na _{Zn}	0.17	
		Li _{Zn}	0.09	
				V _{Zn} 0.34 (0/2-)
				0.18 (0/-)

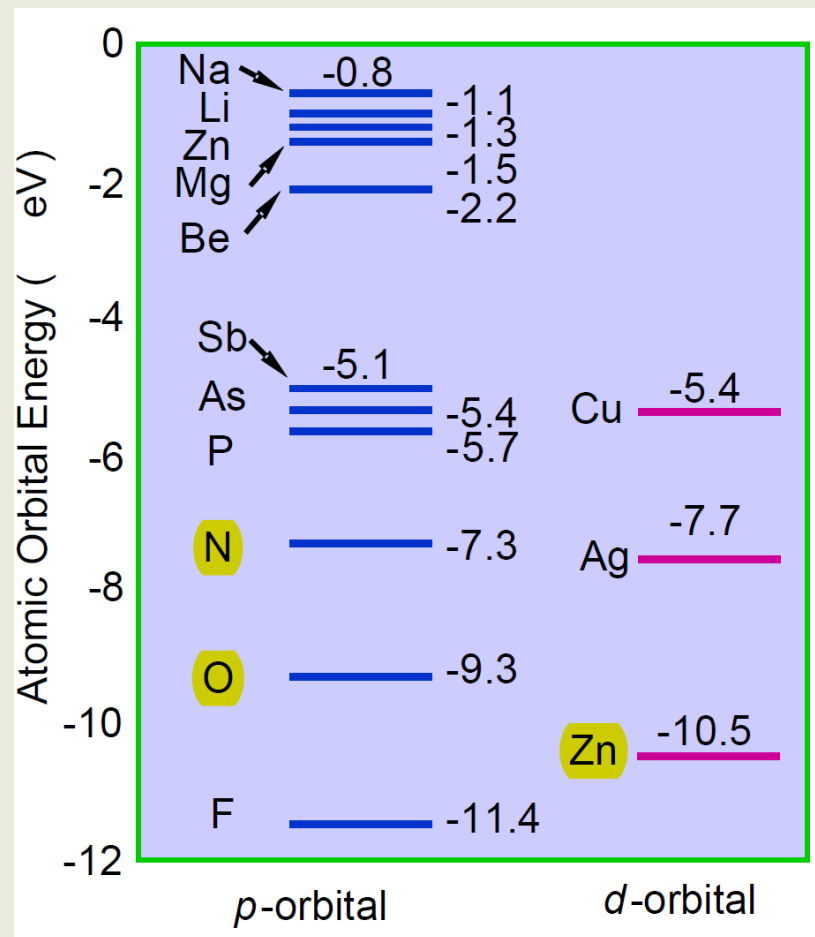
VBM



- For group V on oxygen site acceptor, the lowest transition energy level N_O is 0.35 eV above the VBM
- For group IB on Zn site acceptor, the lowest transition energy level is also deep, at 0.40 eV for Ag_{Zn}
- Group IA on Zn site has relatively shallow defect level, but self compensation limits their use as effective acceptor

Origin of p -type doping difficulty in ZnO: **high acceptor ionization energy**

- An acceptor level above VBM has a wavefunction character similar to the VBM, *i.e.*, it has an anion p and cation d orbital characters.
- Oxygen p orbital energy is very low, there are no group-V elements that are more electronegative than O.
- p - d coupling between host elements and dopants (*e.g.*, N_O with Zn or Cu_{Zn} with O) is large



Strategies to Overcome the Doping Limit

- Increase defect solubility by “defeating” bulk defect thermodynamics
- Reduce defect ionization level through proper co-doping techniques
- Reduce defect compensation and ionization level by modifying the band edge states

Strategies to Overcome the Doping Limit

- Increase defect solubility by “defeating” bulk defect thermodynamics
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- Reduce defect compensation and ionization level by modifying the band edge states

**Improve the Dopant Solubility by
Adjusting Dopant Chemical
Potentials**

Increase defect solubility using non-equilibrium thermodynamics

- What controls the dopant solubility is the dopant chemical potential, μ_A . Therefore, the key to enhance the solubility of the dopant is to raise the chemical potential and avoid the formation of the precipitates of the dopants

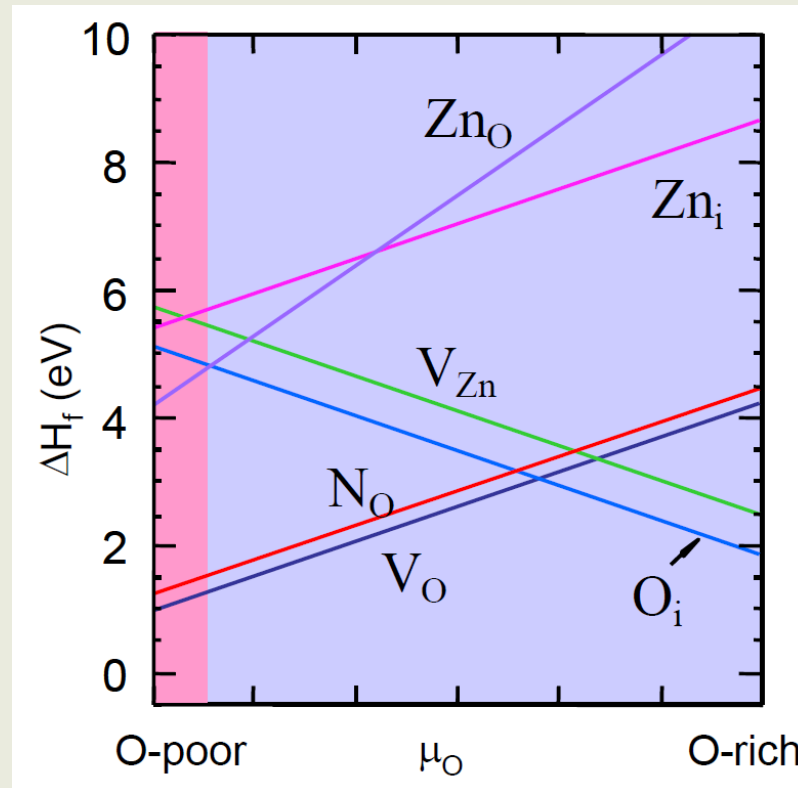
$$\Delta H^{(\alpha,q)}(E_F, \mu) = \Delta E^{(\alpha,q)}(E_F = 0, \mu = 0) + \sum_i n_i \mu_i + qE_F$$

- Choose the optimal host element chemical potentials.
- Enhance solubility by metastable molecular doping.
- Enhance solubility by epi-growth (e.g., MBE).

Choose the optimal host element chemical potentials

- The formation energy of N_O is the lowest under O-poor condition, whereas V_{Zn} is the lowest under the O-rich condition:
condition: $\Delta H_f = E(\text{ZnO}:N) - E(\text{ZnO}) + \mu_O - \mu_N$

$$\Delta H_f = E(\text{ZnO}:V_{Zn}) - E(\text{ZnO}) + \mu_{Zn}$$



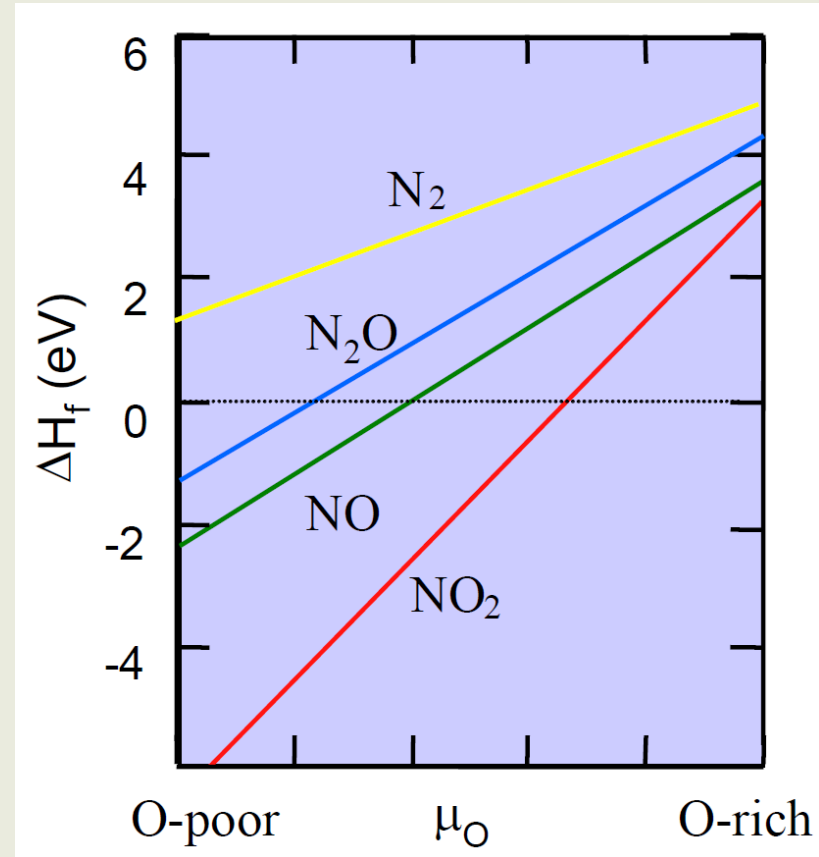
Enhanced solubility by molecular doping: ZnO:N

- N chemical potential depends on the doping sources (N_2 , N_2O , NO , NO_2)
- N solubility in ZnO is much higher if NO or NO_2 is used as dopant
- NO or NO_2 doping also avoids the formation of $(N_2)_O$, which is a compensation donor in ZnO.

$$\Delta H_f = E(\text{ZnO:N}) - E(\text{ZnO}) + \mu_O - \mu_N$$

$$\Delta H_f = E(\text{ZnO:N}) - E(\text{ZnO}) + 2\mu_O - \mu_{NO}$$

$$\mu_N(N_2) < \mu_N(N_2O) < \mu_N(NO) < \mu_N(NO_2)$$



Single N atom in ZnO

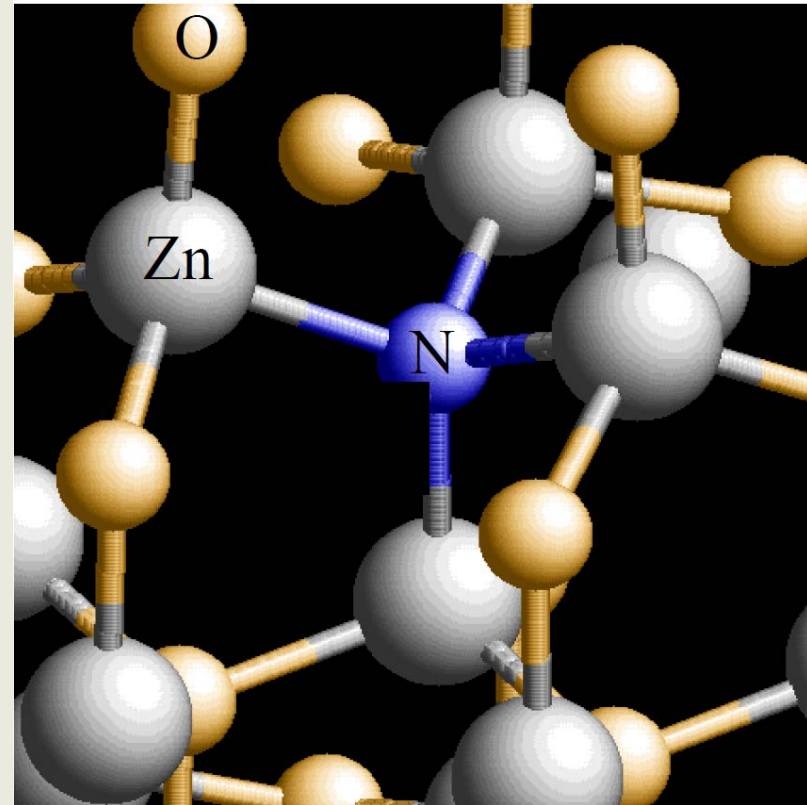
- Transition energy level of N_0

$$E(0/-) = \text{VBM} + 0.35 \text{ eV}$$

- Calculate minimum defect formation energy N_0

$$H_f(N_0)_{min} = 1.2 \text{ eV} (N_2)$$

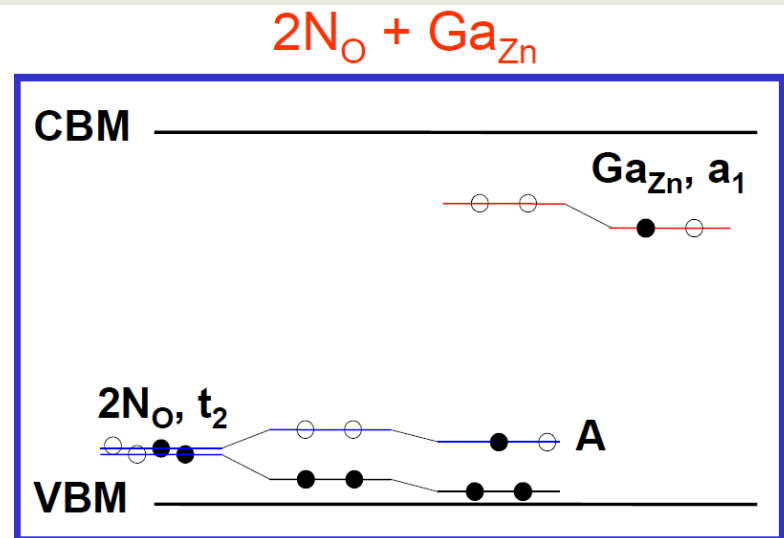
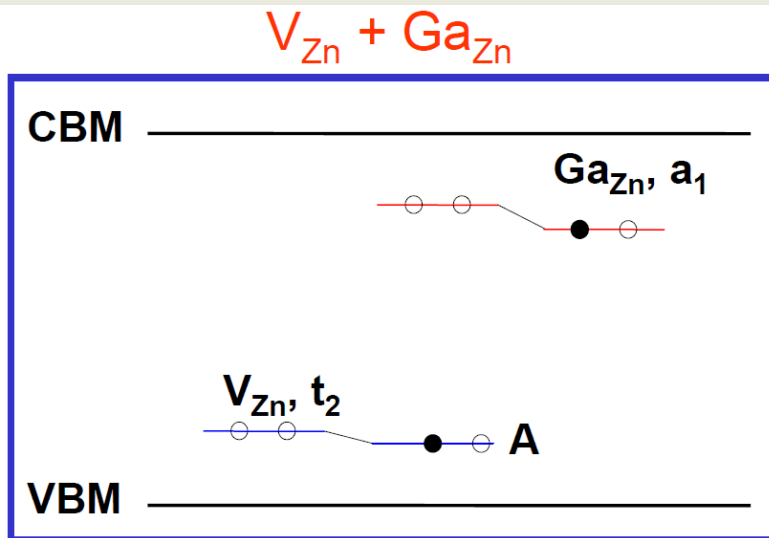
$$H_f(N_0)_{min} = 0.4 \text{ eV} (NO, Zn_3N_2)$$



Design Shallow Defect Levels in ZnO using Band Structure Calculation Method

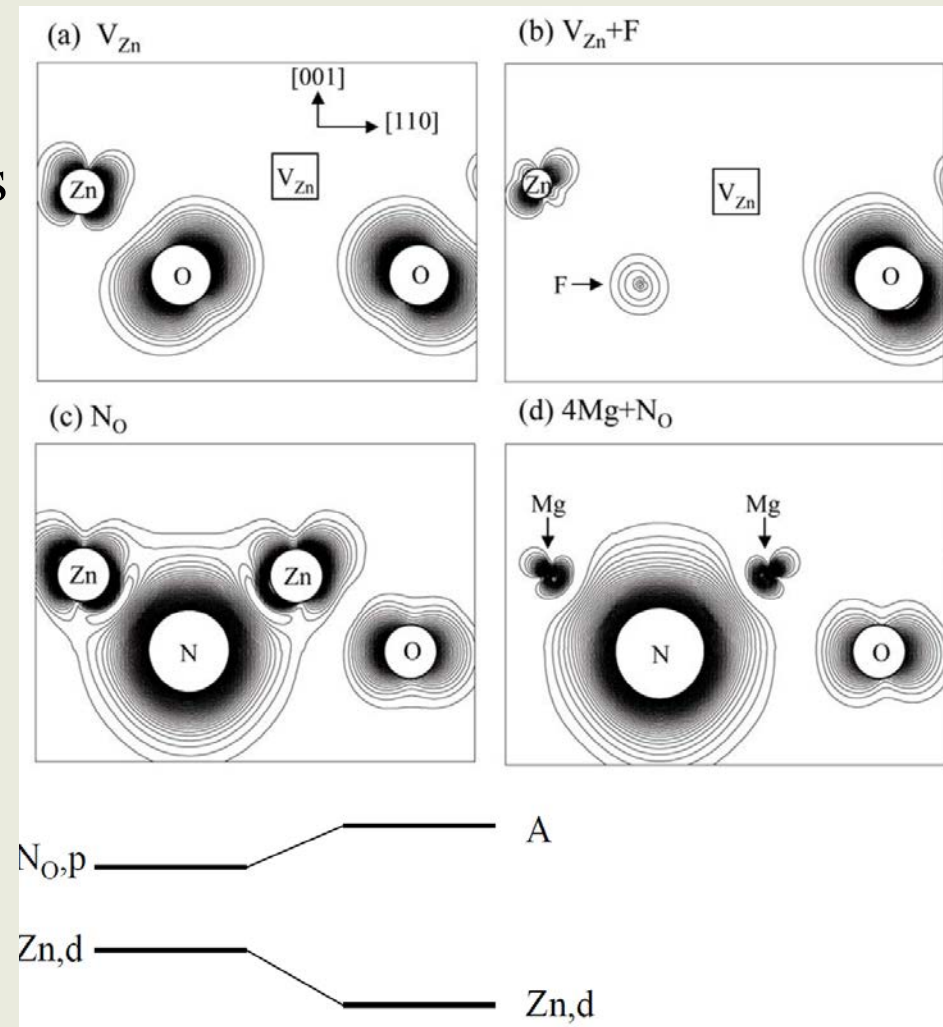
Effects of Conventional Co-doping

- Can co-doping lower the defect transition energy levels?
- The level repulsion effect is rather small because the donor state and the acceptor states have different symmetry
- The defect transition energy level may be lower only if the defect complex consists a single donor and a single acceptor



Design Shallow *p*-type Dopants in ZnO

- Defect wavefunction has large weight on its neighboring atoms
- Replace O by the more electronegative F is expected to lower V_{Zn} energy level
- Remove *p-d* coupling between N_O and cation by replacing Zn with Mg or Be is also expected to reduce the acceptor energy level



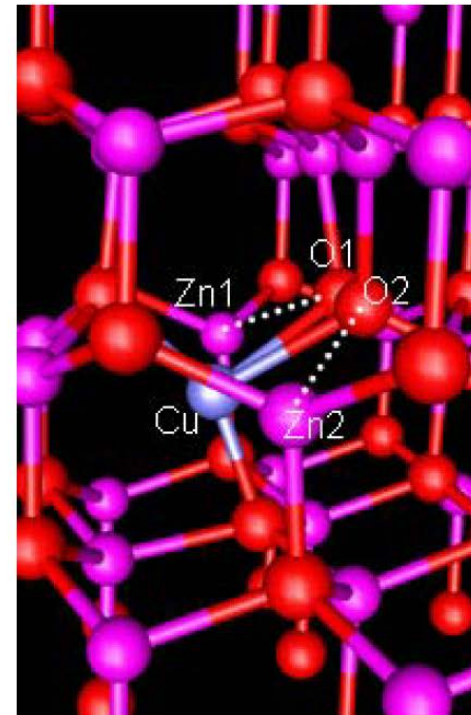
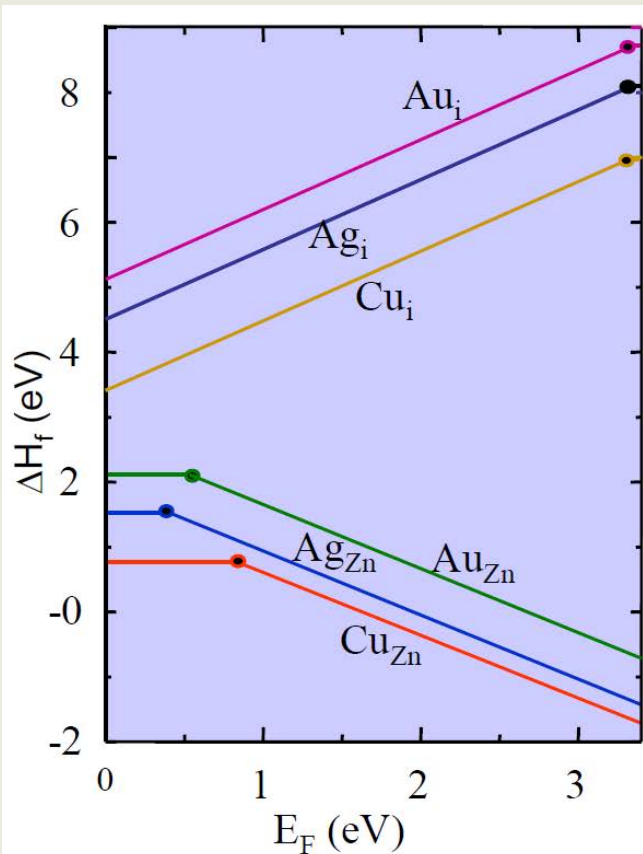
Design Shallow *p*-type Dopants in ZnO

- The calculated defect ionization energy levels suggest that F and Be could be good *p*-type co-dopant for ZnO

Defect	E_b	(0/-)	(-/2-)
N_O		0.31	—
$N_O\text{-Mg}_{Zn}$	0.3	0.29	—
$N_O\text{-4Mg}_{Zn}$	1.6	0.23	—
$N_O\text{-Be}_{Zn}$	0.1	0.22	—
$N_O\text{-4Be}_{Zn}$	1.9	0.12	—
V_{Zn}		0.18	0.34
$V_{Zn}\text{-F}_O$	-2.3	0.16	—

Reduce self-compensation by introducing Group-IB acceptors in ZnO

- Cu_{Zn} has very deep acceptor level because of the large $p-d$ coupling, but Ag_{Zn} has relatively shallower levels
- IB_i is highly unstable, so self-compensation for IB dopants is low



Large Size Mismatched p -type Doping in ZnO:As

Background:

- p -type conductivity in As and P-doped ZnO have been observed and conventional doping model attributed the dopants to As_O and P_O
- We have show that As_O and P_O are unlikely to be the measured acceptor because
 - The formation energy is high (As and P is much larger than O)
 - The ionization energy of As_O and PO are very high ~ 0.8 eV

Acceptor energy levels in ZnO

CBM

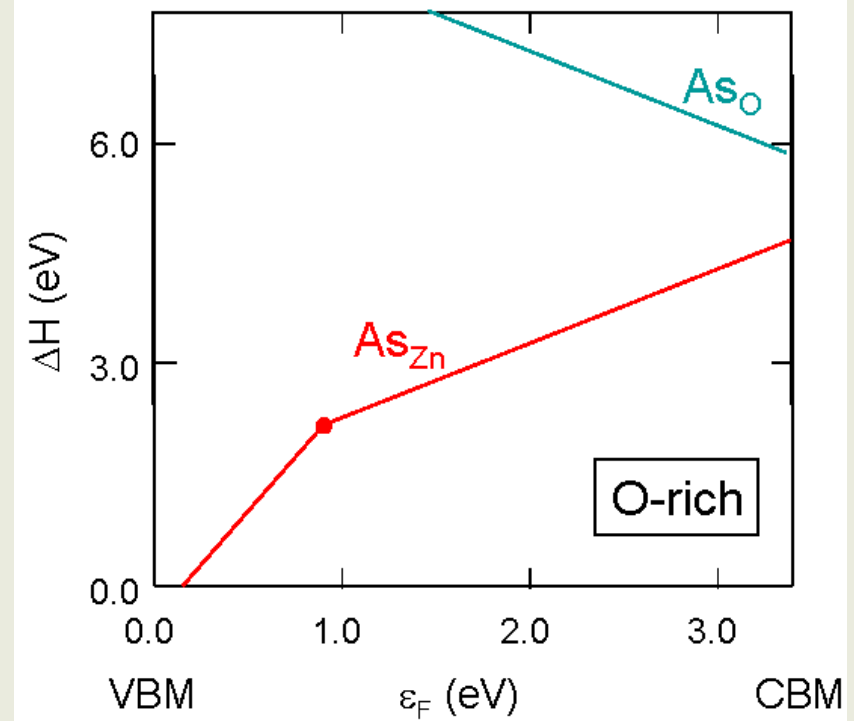
Sb_O	<u>1.10</u>	
As_O	<u>0.90</u>	
P_O	<u>0.70</u>	(0/-)
N_O	<u>0.40</u>	

VBM

Large Size Mismatched p -type Doping in ZnO:As

Limpijumnong, et al., PRL **92**, 155504 (2004)

- In terms of electronegativity, P (2.19), As (2.18), and Sb (2.05) are more similar to Zn (1.65) than to O (3.44)
- In terms of atomic size, P (1.06 Å), As (1.20 Å), and Sb (1.40 Å) are more similar to Zn (1.25 Å) than to O (0.73 Å)



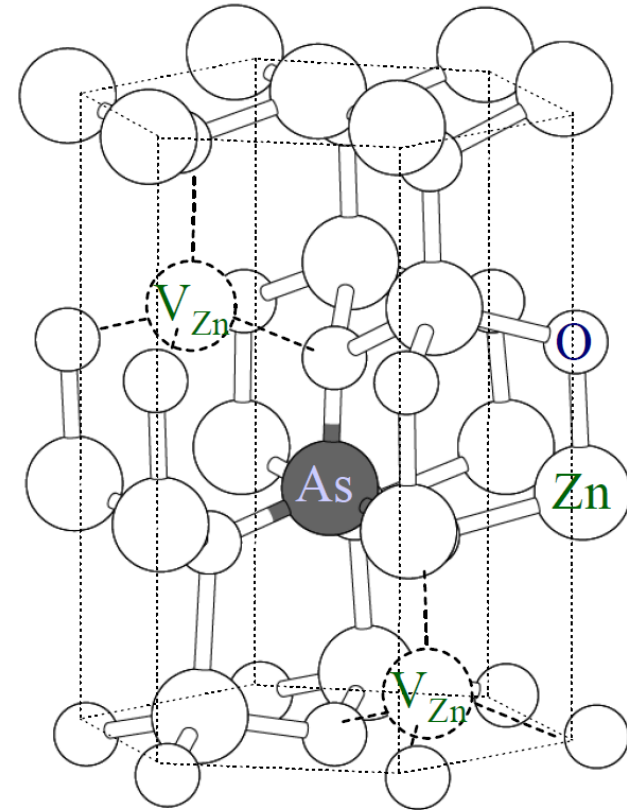
Conclusion: these dopants should substitute Zn, instead of O, and behave as donors, which is indeed what we found.

*Wahl et al. PRL **95**, 215503 (2005) confirmed As_{Zn} by channeling experiment*

Large Size Mismatched p -type Doping in ZnO:As

The new model:

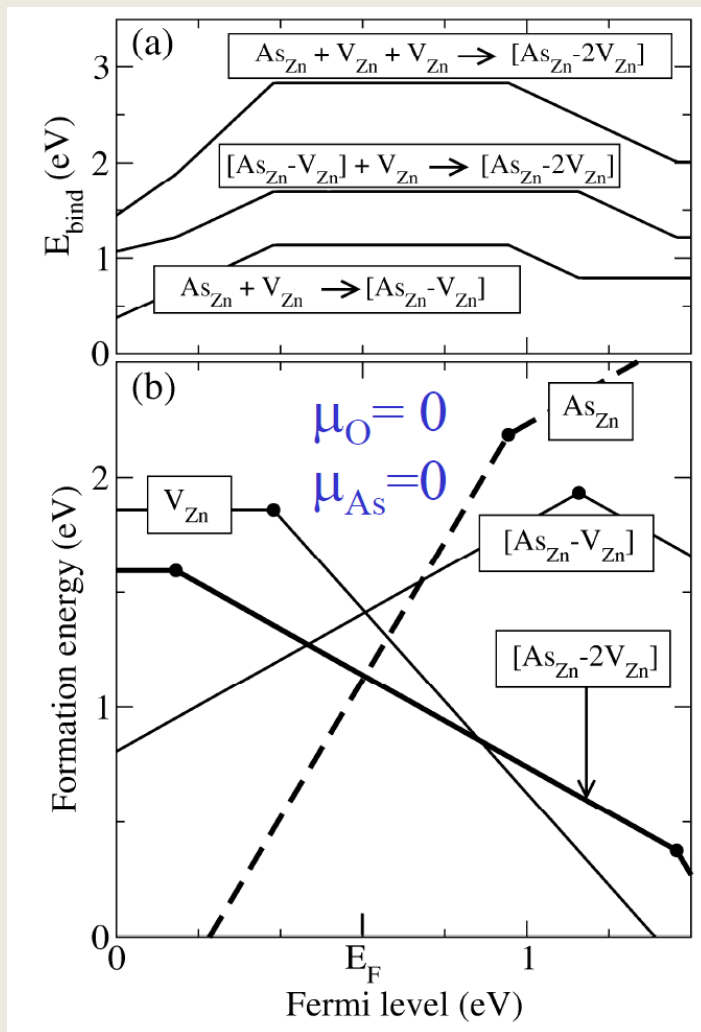
- Atomic size of As and Zn are similar
- As_{Zn} has relatively lower formation energy but it is a (triple) donor
- V_{Zn} is a native (double) acceptor with low formation energy
- One As_{Zn} and two V_{Zn} bind strongly and form a new acceptor complex ($As_{Zn}-2V_{Zn}$)
- The complex has low formation energy and low ionization energy (~ 150 meV)



$[As_{Zn}-2V_{Zn}$ complex]

Large Size Mismatched p -type Doping in ZnO:As

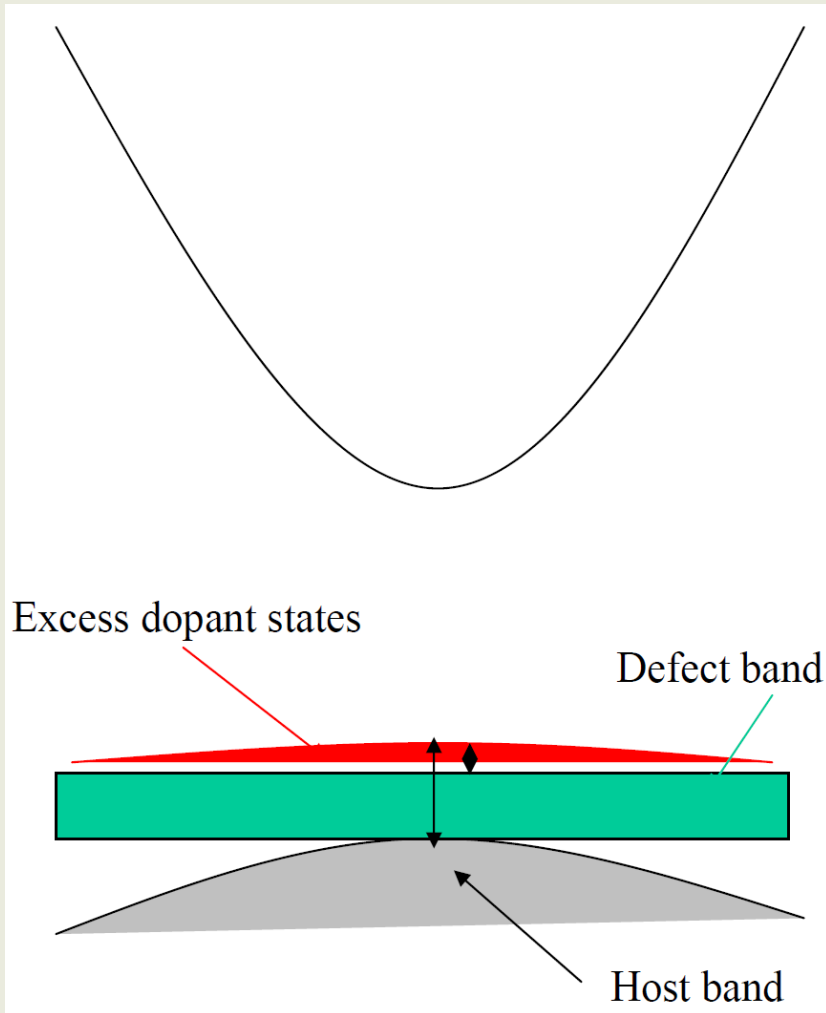
Calculated binding energy and defect formation energy for various As-related defect complexes in ZnO



- Strong Coulomb interaction and strain compensation lowers the formation energy of the $\text{As}_{\text{Zn}} - 2\text{V}_{\text{Zn}}$ defect complex
- Coupling between the As_{Zn} donor states and the V_{Zn} acceptor states lowers the ionization energy of the complex relative to V_{Zn}

**Modify the Host Band Structure to
Reduce Ionization Energy and
Compensation**

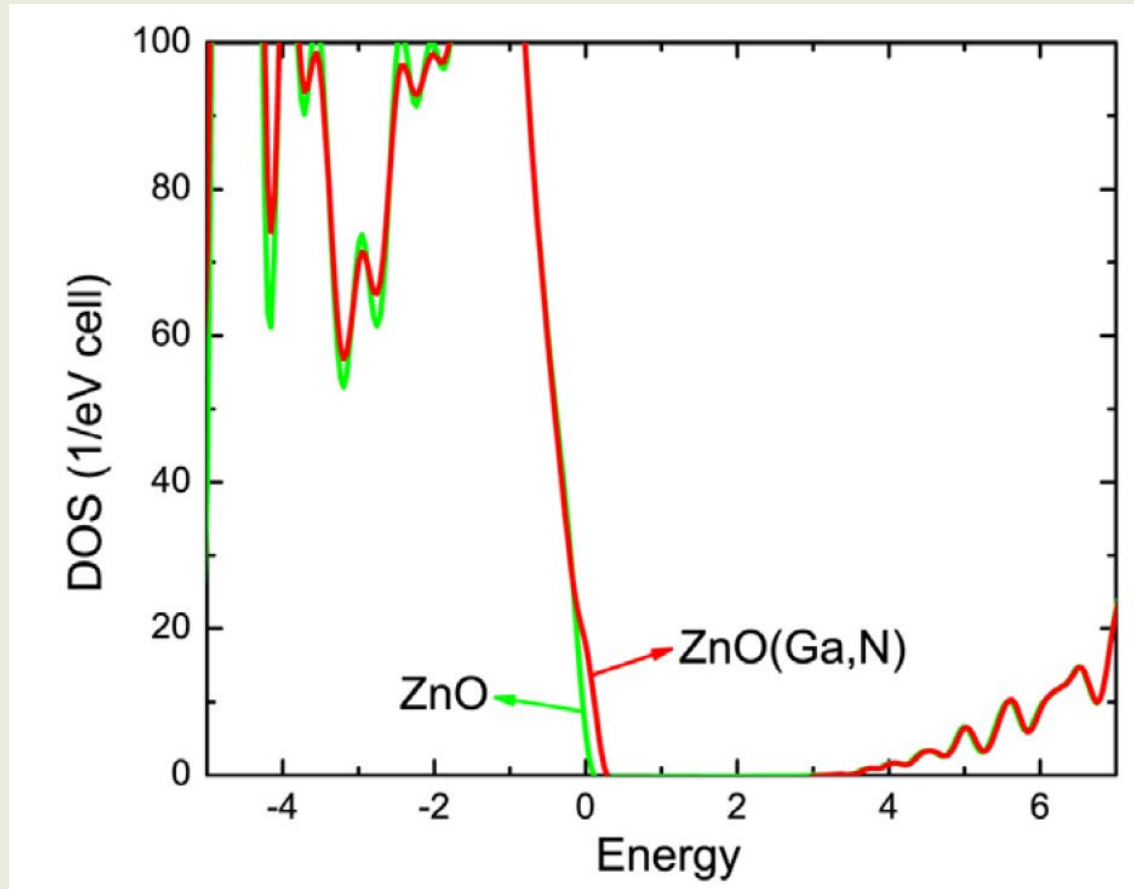
Universal Approach to Overcome the Doping Asymmetry in Wide-band-gap Semiconductors



- First, through effective doping of mutually passivated defect pairs, we can introduce a fully compensated defect band near the VBM or CBM of the host
- Second, after the fully compensated insulating phase is formed, use excess dopants to dope the passivated system by ionizing the defect band

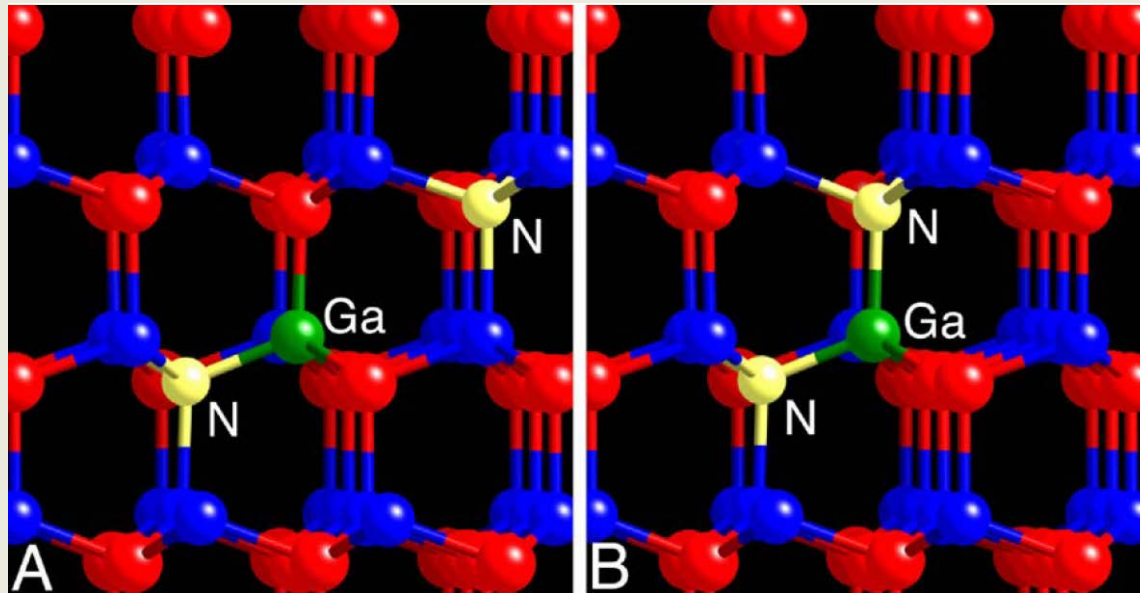
Modify the Valence Band Edge of ZnO by Passivate Doping of Ga with N

- N combined with Ga creates a passivated defect band above the host ZnO VBM.



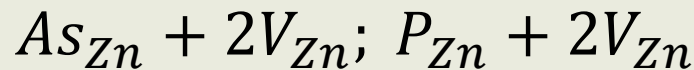
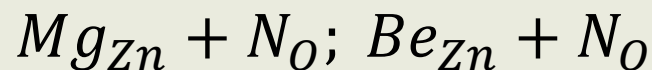
Create shallow acceptor level by doping the passivated ZnO:(Ga+N) system using excess N

- The calculated defect level of N is about 0.1 –0.2 eV above the defect band

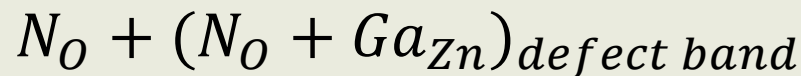


Possible Dopants or Dopant Complexes for *p*-type Doping in ZnO

- Based on defect wavefunction analysis, various microscopic models have been proposed to reduce the ionization energy of acceptor level in ZnO



- Doping of defect band is an effective and universal approach to doped wide band gap materials such as ZnO



Summary

We have analyzed the origin of *p*-type doping difficulty in ZnO. Several strategies have been proposed to overcome the doping difficulty

- Increase defect solubility by “defeating” bulk defect thermodynamics using
 - optimized host elements chemical potential
 - surface enhanced defect solubility
 - molecular doping
 - large size-mismatched antisite doping

- Reduce defect ionization level by
 - combining donor with acceptor to modify defect wavefunctions
 - reducing *p-d* coupling between defect level and host states

- Design new dopable materials by adjusting the band edges states using passivated doping and subsequent doping using the same dopants