

Design of Shallow p-type dopants in ZnO

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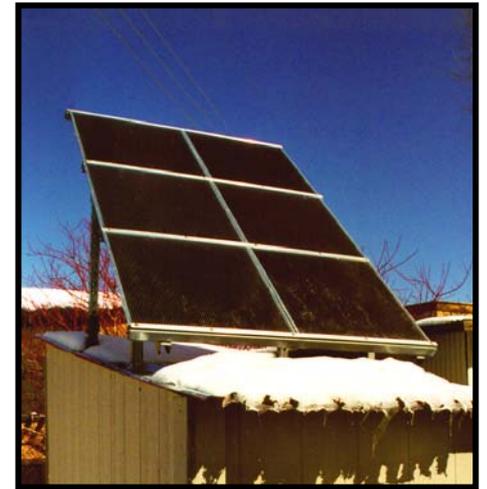
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Introduction

- ZnO is a promising material for short wave-length 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

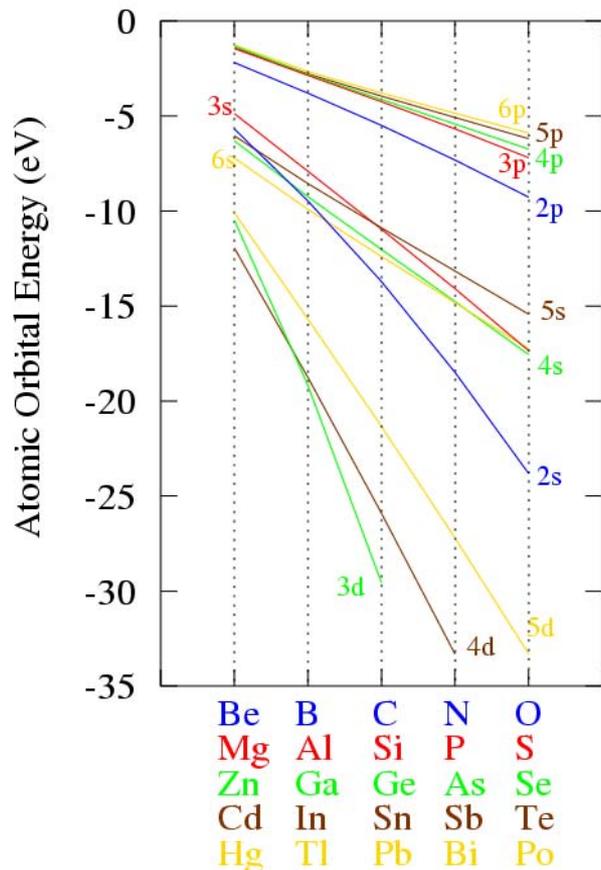
Using first-principles band structure methods we will address:

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



Chemical Trends of Atomic Energy Levels

Chemical trends of atomic energy levels



PERIODIC TABLE
Atomic Properties of the Elements

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Frequently used fundamental physical constants
For the most accurate values of these and other constants, visit physics.nist.gov/constants
1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ¹³³Cs
speed of light in vacuum c 299 792 458 m s⁻¹ (exact)
Planck constant h 6.626 070 15 × 10⁻³⁴ J s (exact) ($h = h/2\pi$)
elementary charge e 1.602 2 × 10⁻¹⁹ C
electron mass m_e 9.109 382 91 × 10⁻³¹ kg
proton mass m_p 1.672 6 × 10⁻²⁷ kg
fine-structure constant α 1/137.036
Rydberg constant R_∞ 10 973 732 m⁻¹
 R_H 3 299 647 × 10¹⁰ Hz
 $R_\infty hc$ 13.6057 eV
 k 1.3807 × 10⁻²³ J K⁻¹

Legend:
Solids (blue)
Liquids (green)
Gases (red)
Artificially Prepared (yellow)

Group	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	H Hydrogen 1.00794																	He Helium 4.002602
2	Li Lithium 6.941	Be Beryllium 9.012182											B Boron 10.811	C Carbon 12.0107	N Nitrogen 14.0064	O Oxygen 15.9994	F Fluorine 18.9984032	Ne Neon 20.1797
3	Na Sodium 22.989770	Mg Magnesium 24.3050											Al Aluminum 26.981538	Si Silicon 28.0855	P Phosphorus 30.973761	S Sulfur 32.065	Cl Chlorine 35.453	Ar Argon 39.948
4	K Potassium 39.0983	Ca Calcium 40.078	Sc Scandium 44.955910	Ti Titanium 47.887	V Vanadium 50.9415	Cr Chromium 51.9961	Mn Manganese 54.938045	Fe Iron 55.845	Co Cobalt 58.933200	Ni Nickel 58.6934	Cu Copper 63.546	Zn Zinc 65.409	Ga Gallium 69.723	Ge Germanium 72.64	As Arsenic 74.92160	Se Selenium 78.96	Br Bromine 79.904	Kr Krypton 83.798
5	Rb Rubidium 85.4678	Sr Strontium 87.62	Y Yttrium 88.90585	Zr Zirconium 91.224	Nb Niobium 92.90638	Mo Molybdenum 95.94	Tc Technetium (98)	Ru Ruthenium 101.07	Rh Rhodium 102.90550	Pd Palladium 106.42	Ag Silver 107.8682	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.760	Te Tellurium 127.60	I Iodine 126.90447	Xe Xenon 131.293
6	Cs Cesium 132.90545	Ba Barium 137.327		Hf Hafnium 178.49	Ta Tantalum 180.9479	W Tungsten 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.222	Pt Platinum 195.078	Au Gold 196.96655	Hg Mercury 200.59	Tl Thallium 204.3843	Pb Lead 208.98038	Bi Bismuth 208.98038	Po Polonium (209)	At Astatine (210)	Rn Radon (222)
7	Fr Francium (223)	Ra Radium (226)		Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (266)	Bh Bohrium (264)	Hs Hassium (277)	Mt Meitnerium (268)	Uun Ununennium (281)	Uuu Ununennium (272)	Uub Ununennium (285)	Uuq Ununennium (288)	Uuh Ununennium (292)				
				La Lanthanum 138.9055	Ce Cerium 140.116	Pr Praseodymium 140.90766	Nd Neodymium 144.24	Pm Promethium (145)	Sm Samarium 150.36	Eu Europium 151.964	Gd Gadolinium 157.25	Tb Terbium 158.92534	Dy Dysprosium 162.50	Ho Holmium 164.93032	Er Erbium 167.259	Tm Thulium 168.93402	Yb Ytterbium 173.04	Lu Lutetium 174.967
				Ac Actinium (227)	Th Thorium 232.0381	Pa Protactinium 231.03688	U Uranium 238.02891	Np Neptunium 237	Pu Plutonium (244)	Am Americium (243)	Cm Curium (247)	Bk Berkelium (247)	Cf Californium (251)	Es Einsteinium (252)	Fm Fermium (257)	Md Mendelevium (258)	No Nobelium (259)	Lr Lawrencium (262)

Atomic potential becomes more negative when the atomic number increases from left to right in the Periodic Table

Method of Calculation

Method of calculation



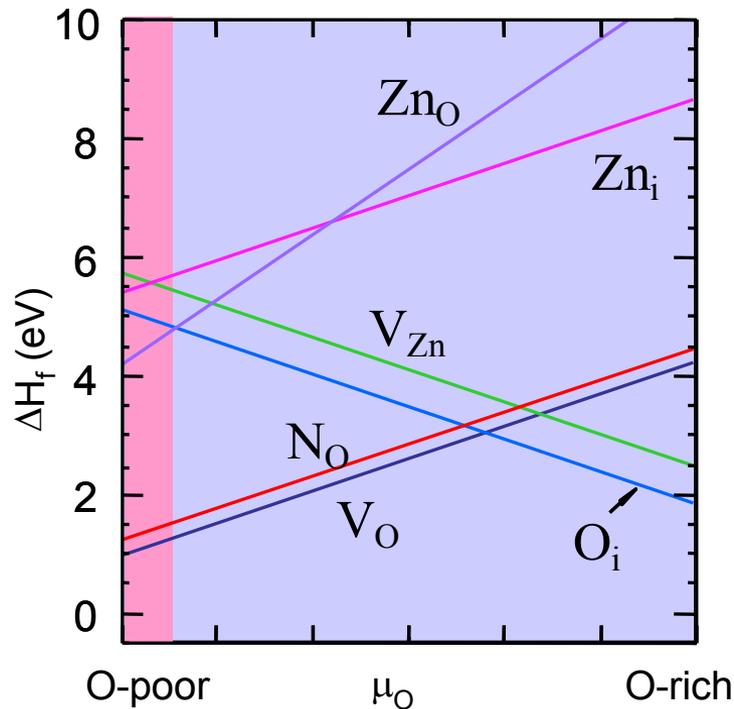
- Band structure and total energy are calculated using the first-principles band structure method (FLAPW, PP) with local density approximation (LDA)
- Defects are described using the supercell approach. A uniform background charge is added for charged defect calculation
- All the internal structural 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

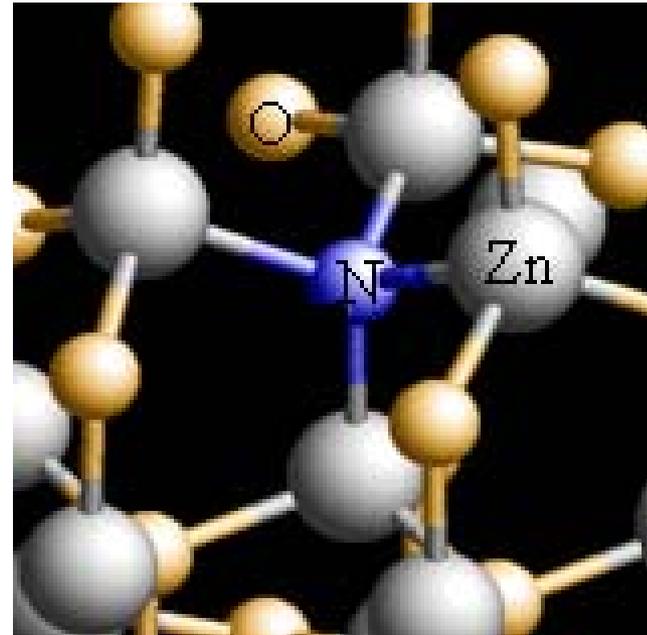
Main reasons of failure-to-dope

- 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



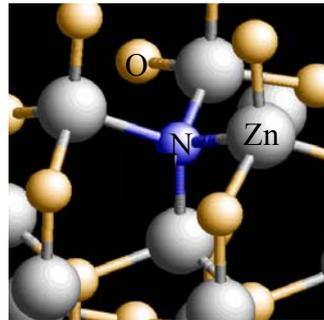
Calculate minimum defect formation energy of neutral N_O

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

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

Acceptor energy levels in ZnO

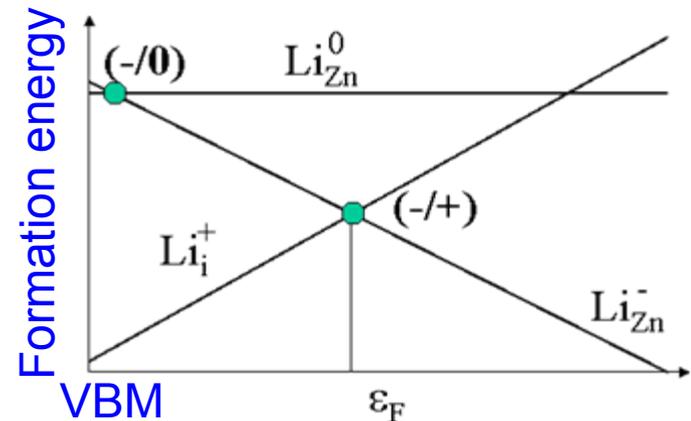
CBM



(0/-)

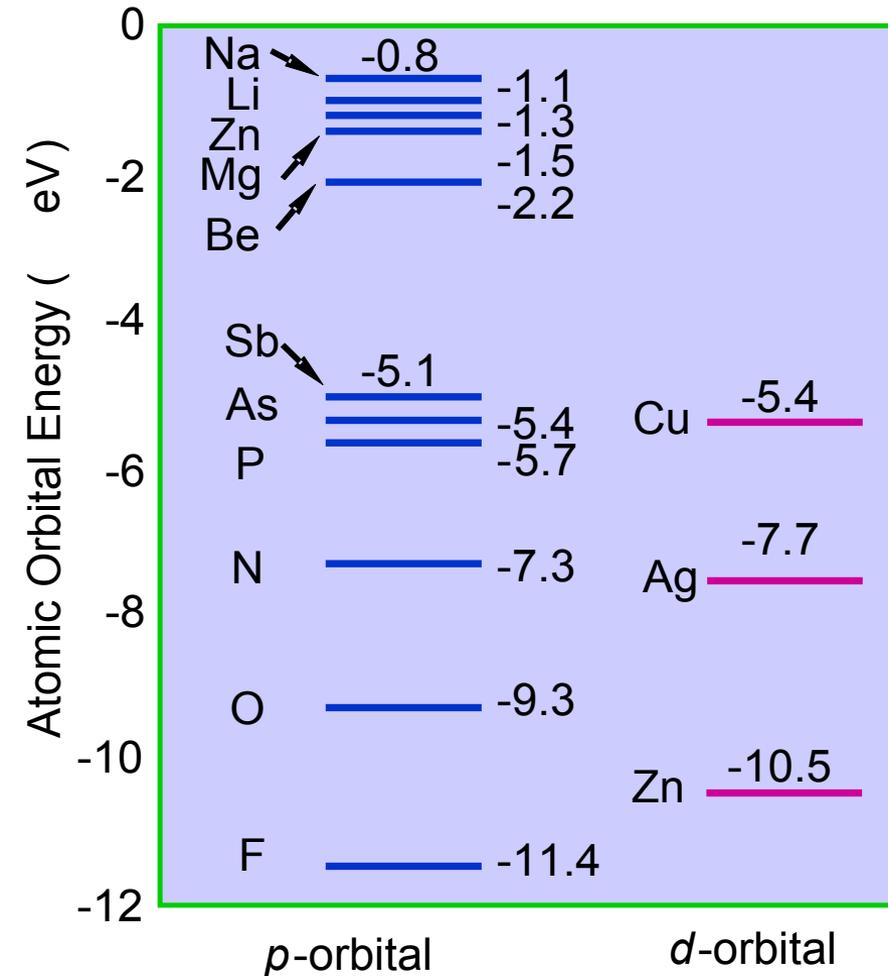
Sb _O	1.10	Cu _{Zn}	0.74	
As _O	0.90	Ag _{Zn}	0.40	
P _O	0.70	Na _{Zn}	0.17	
		Li _{Zn}	0.09	
N _O	0.35	V _{Zn}	0.34 (0/2-)	
			0.18 (0/-)	

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 codoping techniques
- 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

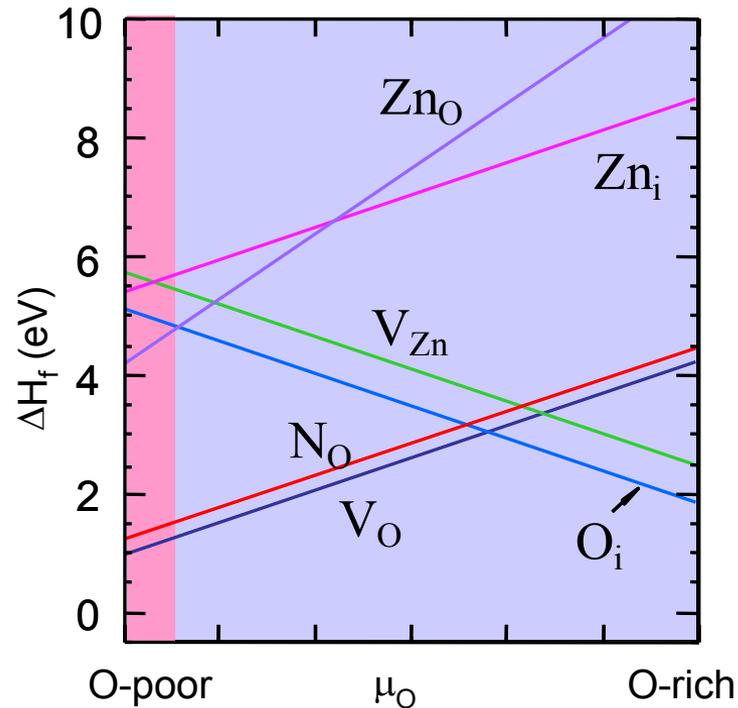
- What controls the dopant solubility is the dopant chemical potential, μ_A . Therefore, the key to enhance the solubility of the dopant is to raise the chemical potential and avoid the formation of the precipitates of the dopants

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

- 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



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

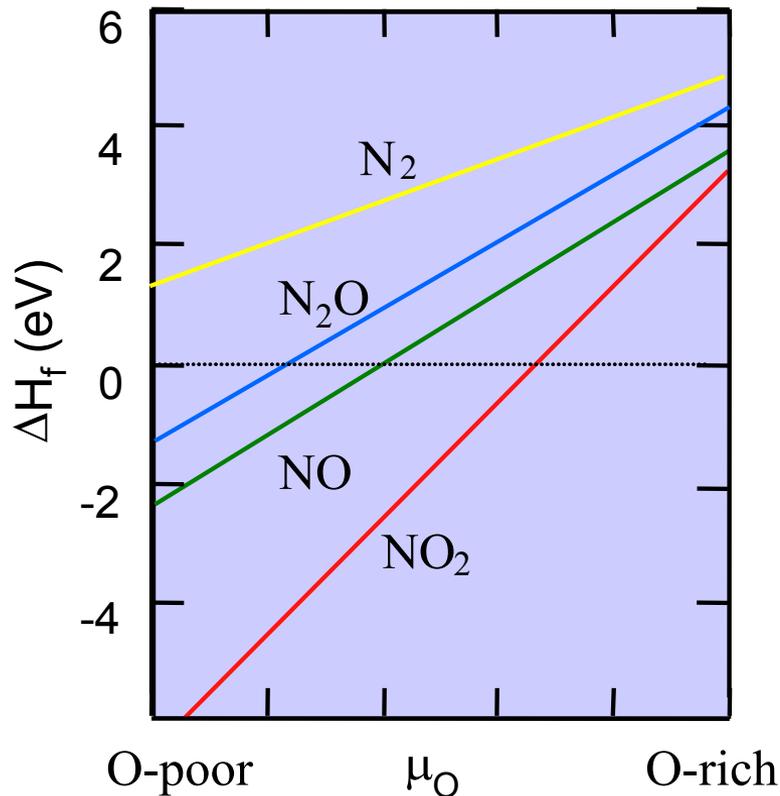
$$\Delta H_f = E(\text{ZnO:V}_{Zn}) - E(\text{ZnO}) + \mu_{Zn}$$

Enhanced solubility by molecular doping: ZnO:N

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

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

$$\mu_{\text{N}}(\text{N}_2) < \mu_{\text{N}}(\text{N}_2\text{O}) < \mu_{\text{N}}(\text{NO}) < \mu_{\text{N}}(\text{NO}_2)$$

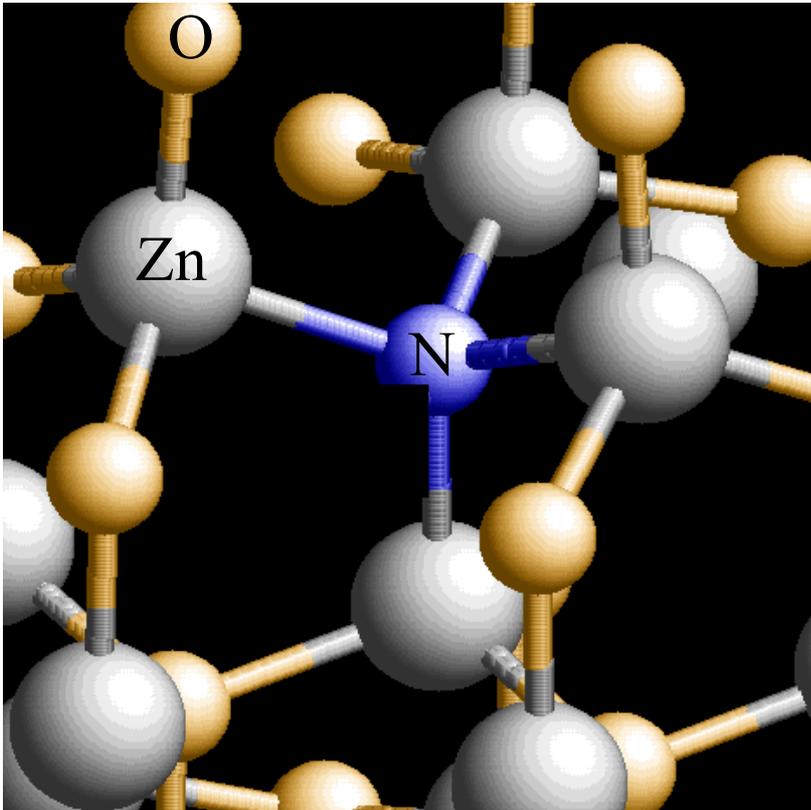


N chemical potential depends on the doping sources (N_2 , N_2O , NO , NO_2)

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 $(\text{N}_2)_\text{O}$, which is a compensation donor in ZnO

Single N atom in ZnO



Transition energy level of N_O

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

Calculate minimum defect formation energy N_O

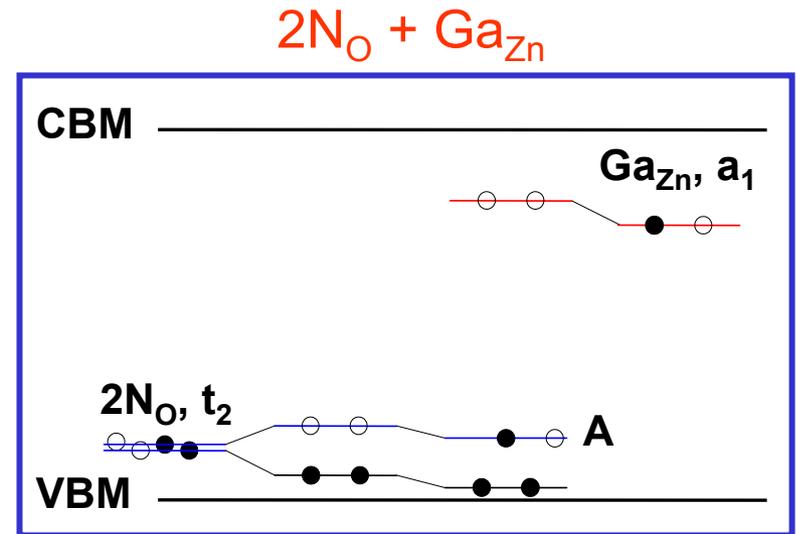
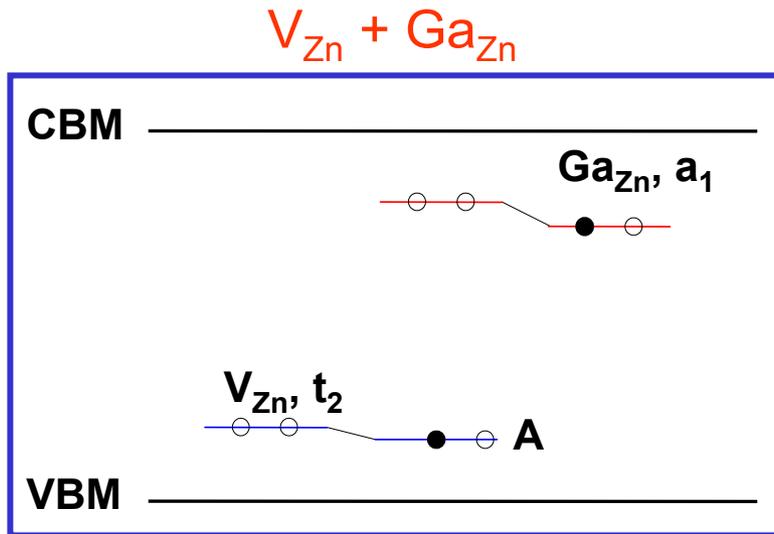
$$H_f(N_O)_{\min} = 1.2 \text{ eV} \quad (N_2)$$

$$H_f(N_O)_{\min} = 0.4 \text{ eV} \quad (\text{NO}, \text{Zn}_3\text{N}_2)$$

Design shallow defect levels in ZnO using band structure calculation method

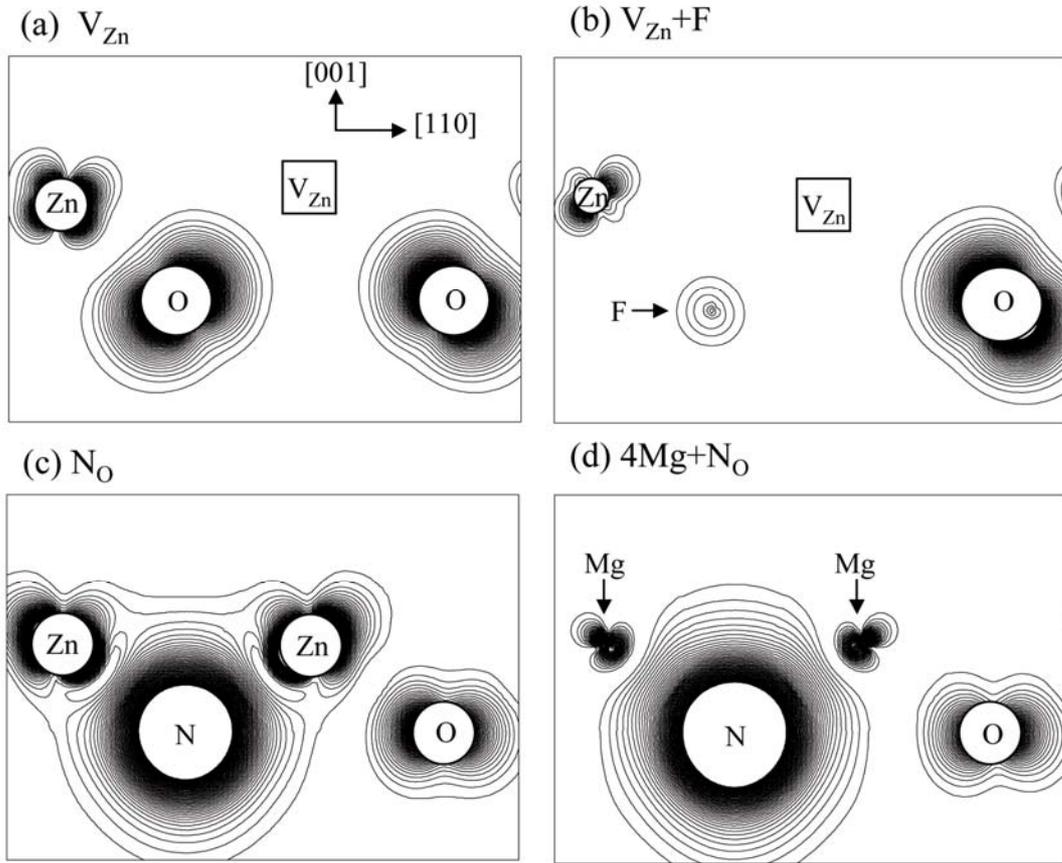
Effects of conventional co-doping

- Can co-doping lower the defect transition energy levels?

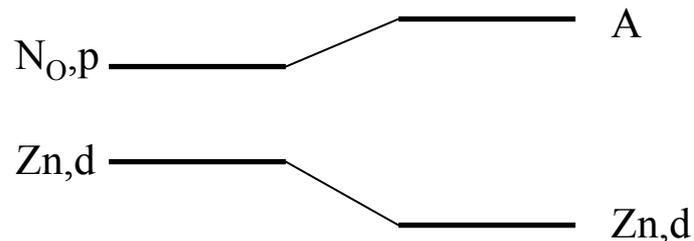


- The level repulsion effect is rather small because the donor state and the acceptor states have different symmetry
- The defect transition energy level may be lowered only if the defect complex consists a single donor and a single acceptor

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

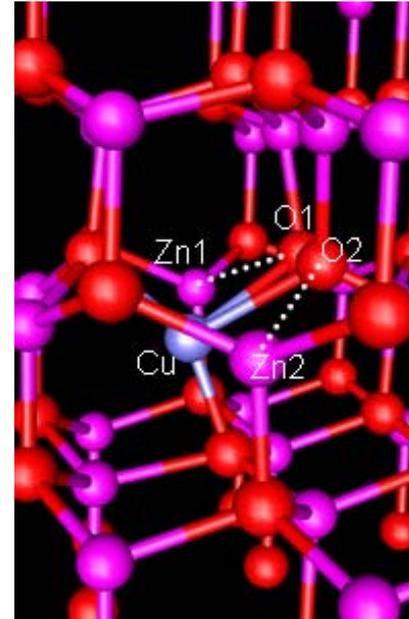
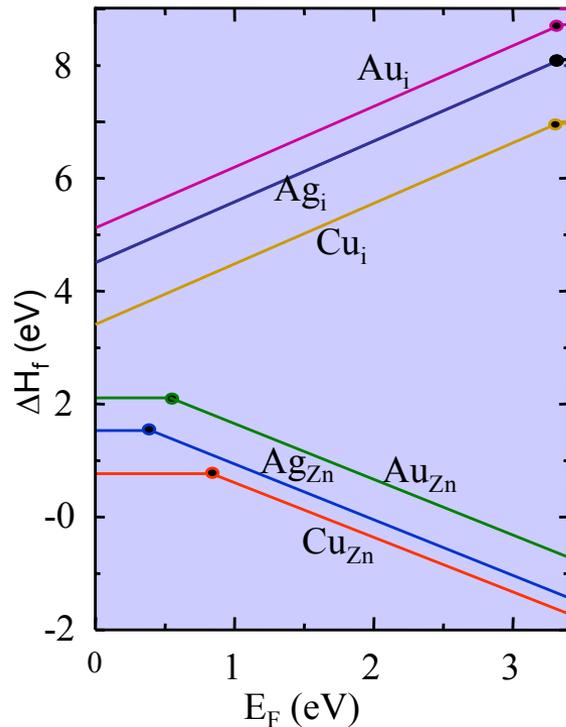


Design shallow p-type dopants in ZnO

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	—

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

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

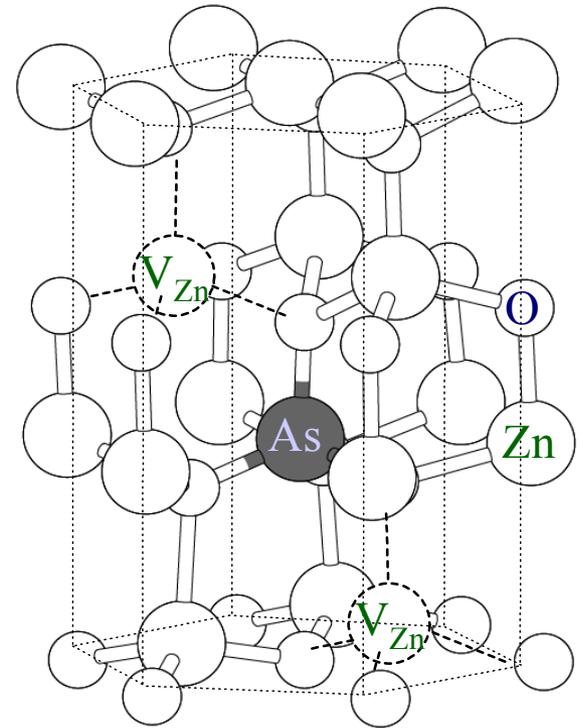
Sb_O	<u>1.10</u>	
As_O	<u>0.90</u>	
P_O	<u>0.70</u>	(0/-)
N_O	<u>0.40</u>	

VBM

Large size mismatched p-type doping in ZnO:As

The new model:

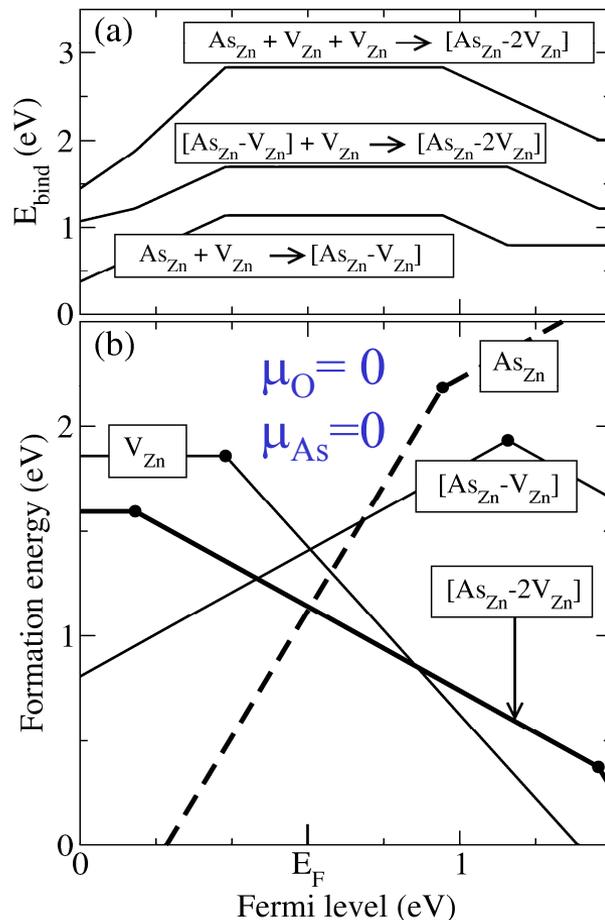
- Atomic size of As and Zn are similar
- As_{Zn} has relatively lower formation energy but it is a (triple) donor
- V_{Zn} is a native (double) acceptor with low formation energy
- One As_{Zn} and two V_{Zn} bind strongly and form a new acceptor complex ($\text{As}_{\text{Zn}}-2\text{V}_{\text{Zn}}$)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

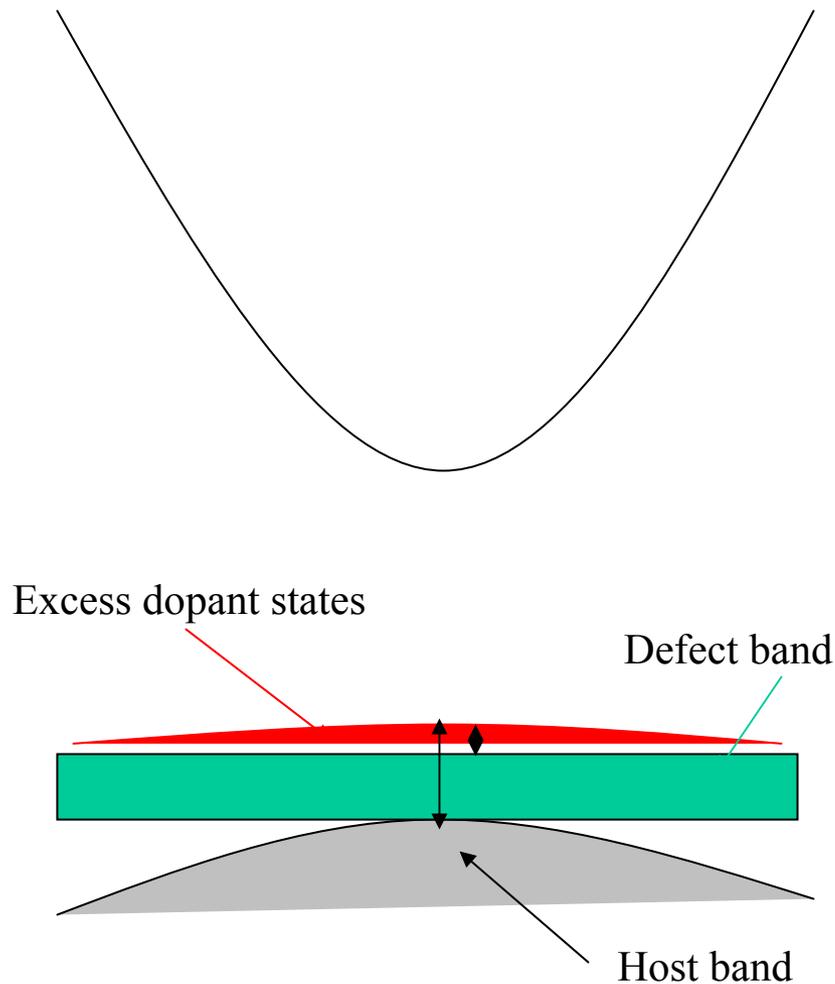


➤ Strong Coulomb interaction and strain compensation lowers the formation energy of the $\text{As}_{\text{Zn}}-2\text{V}_{\text{Zn}}$ defect complex

➤ Coupling between the As_{Zn} donor states and the V_{Zn} acceptor states lowers the ionization energy of the complex relative to V_{Zn}

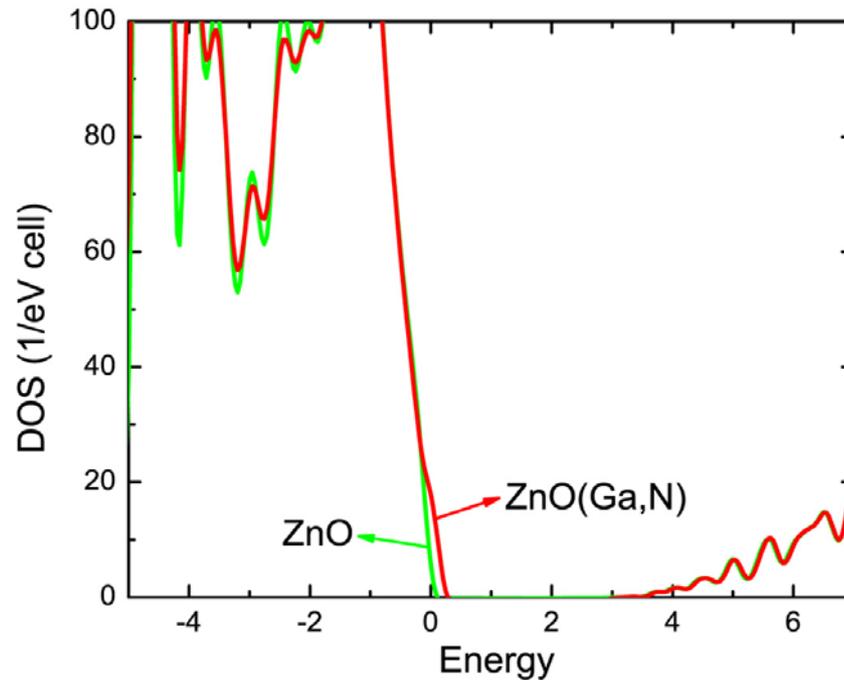
Modify the host band structure to
reduce ionization energy and
compensation

Universal approach to overcome the doping asymmetry in wide-band-gap semiconductors



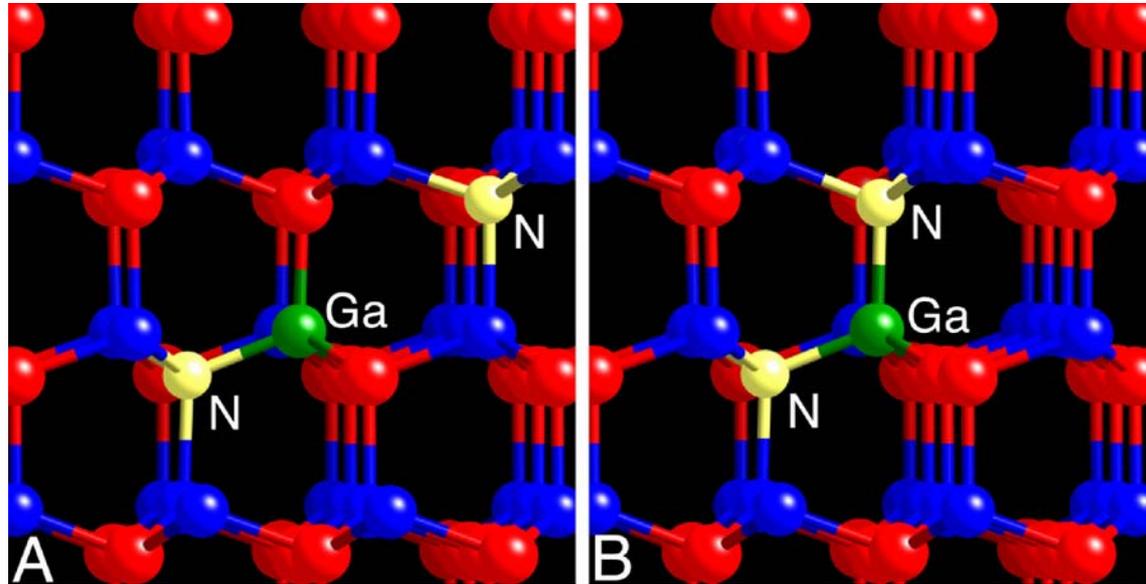
- First, through effective doping of mutually **passivated defect pairs**, we introduce a fully compensated defect band near the VBM or CBM of the host
- Second, after the fully compensated insulating phase is formed, use **excess dopants** to dope the passivated system by ionizing the defect band

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

Thank You for Your Attention!