Theory of Oxides for Photoelectrochemical Hydrogen Production

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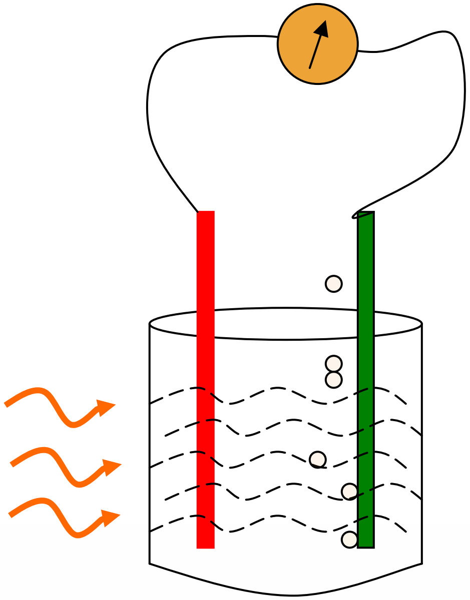


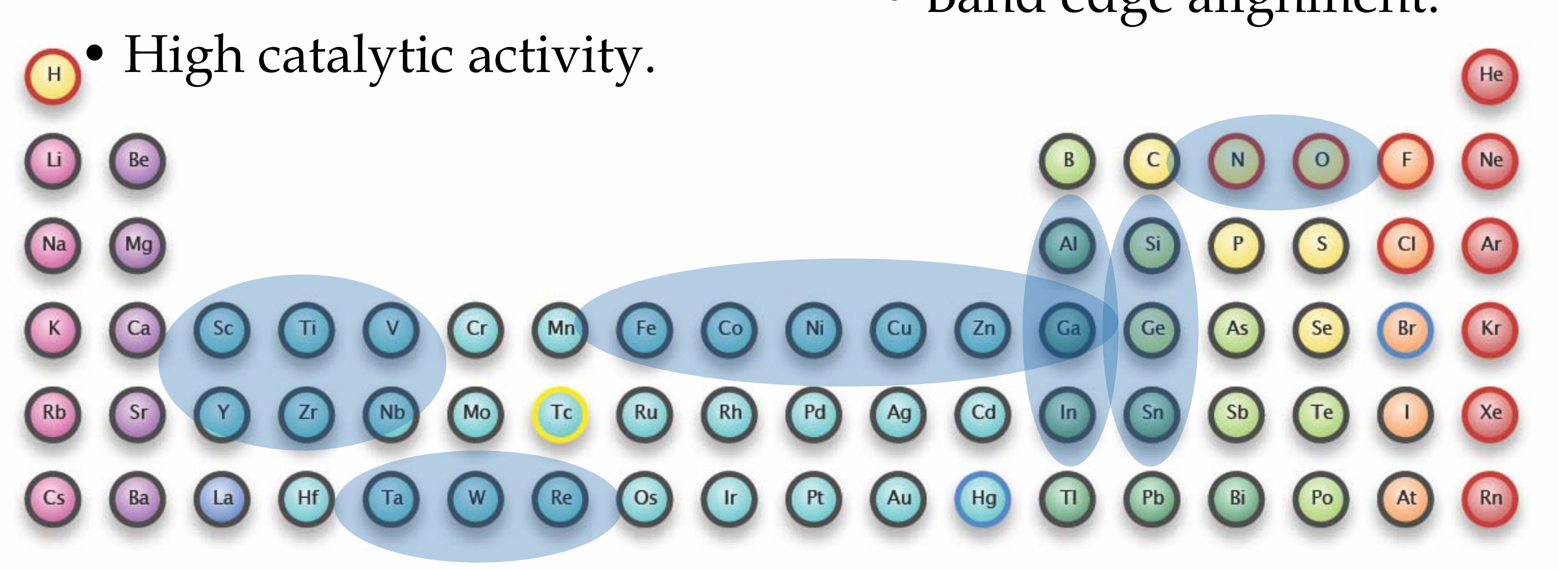
Project ID #
PDP34

R&D feedback loop

Catalyst Criteria

- Structural stability in solution.
- Low cost.
- High catalytic activity.

- Band gap: 1.5 – 2 eV.
- Visible light absorption.
- Band edge alignment.

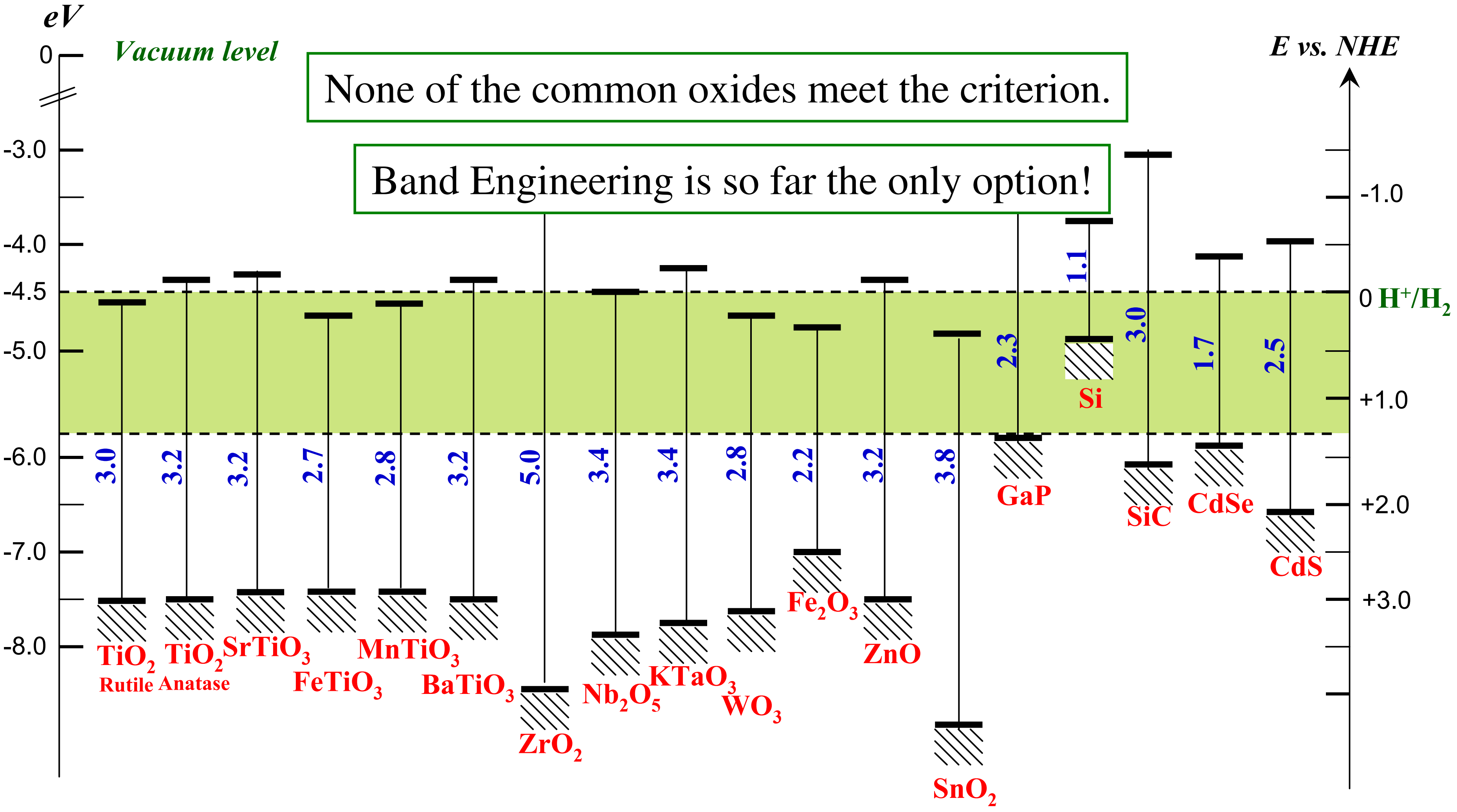


- Binary oxides satisfy a number of criteria, but are limited by their large band gaps which fail to absorb photons in the visible range.
- Our aim is to explore new oxide systems which may overcome these intrinsic limitations through combining multiple cations.

Band Gap Positions in Various Semiconductors

None of the common oxides meet the criterion.

Band Engineering is so far the only option!



@ pH = 0

Q. How many oxides one can try experimentally?

“There are easily **50,000 combinations of ternary oxides** and almost **2 million quaternary oxides**.”

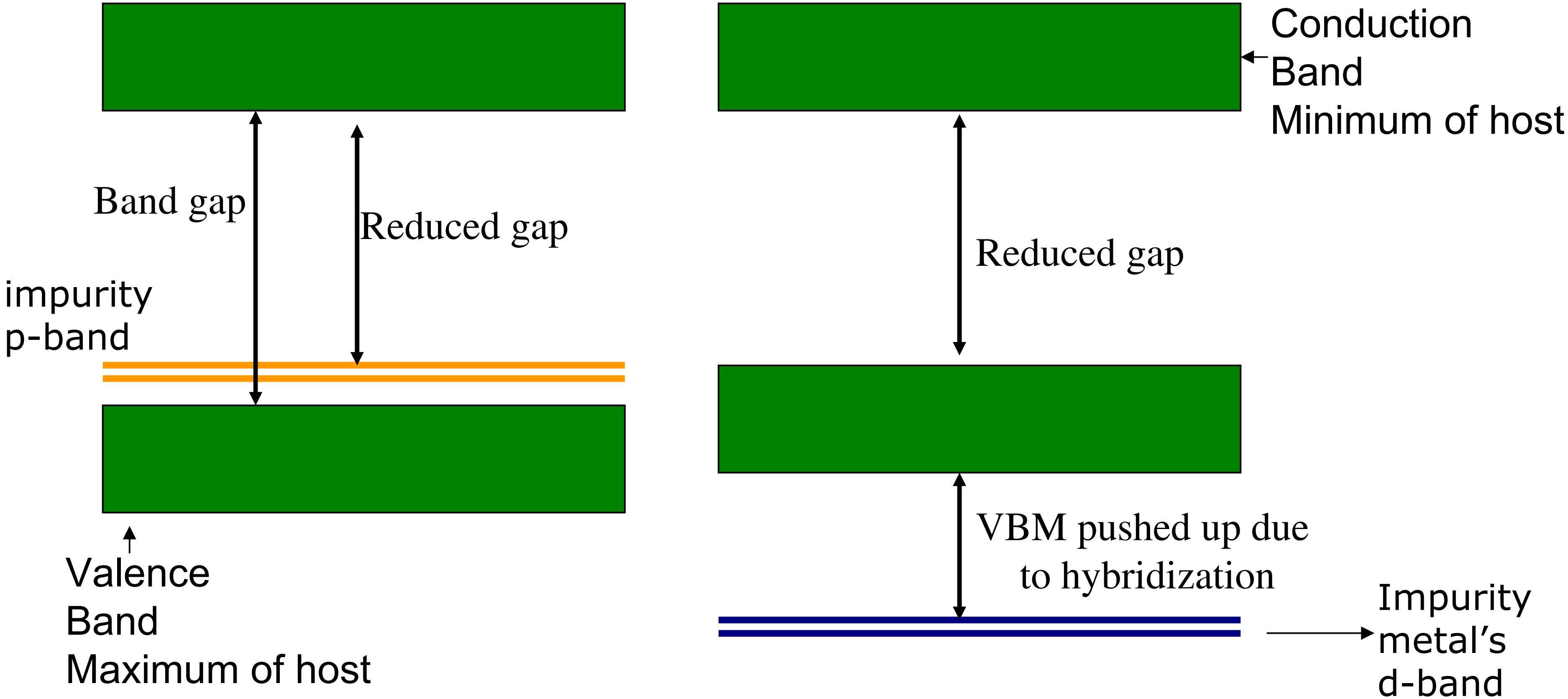
“A collaboration of theory, synthesis and characterization groups is necessary to achieve fundamental PEC goals.”

John Turner
from January PEC work group meeting
UC Santa Barbara

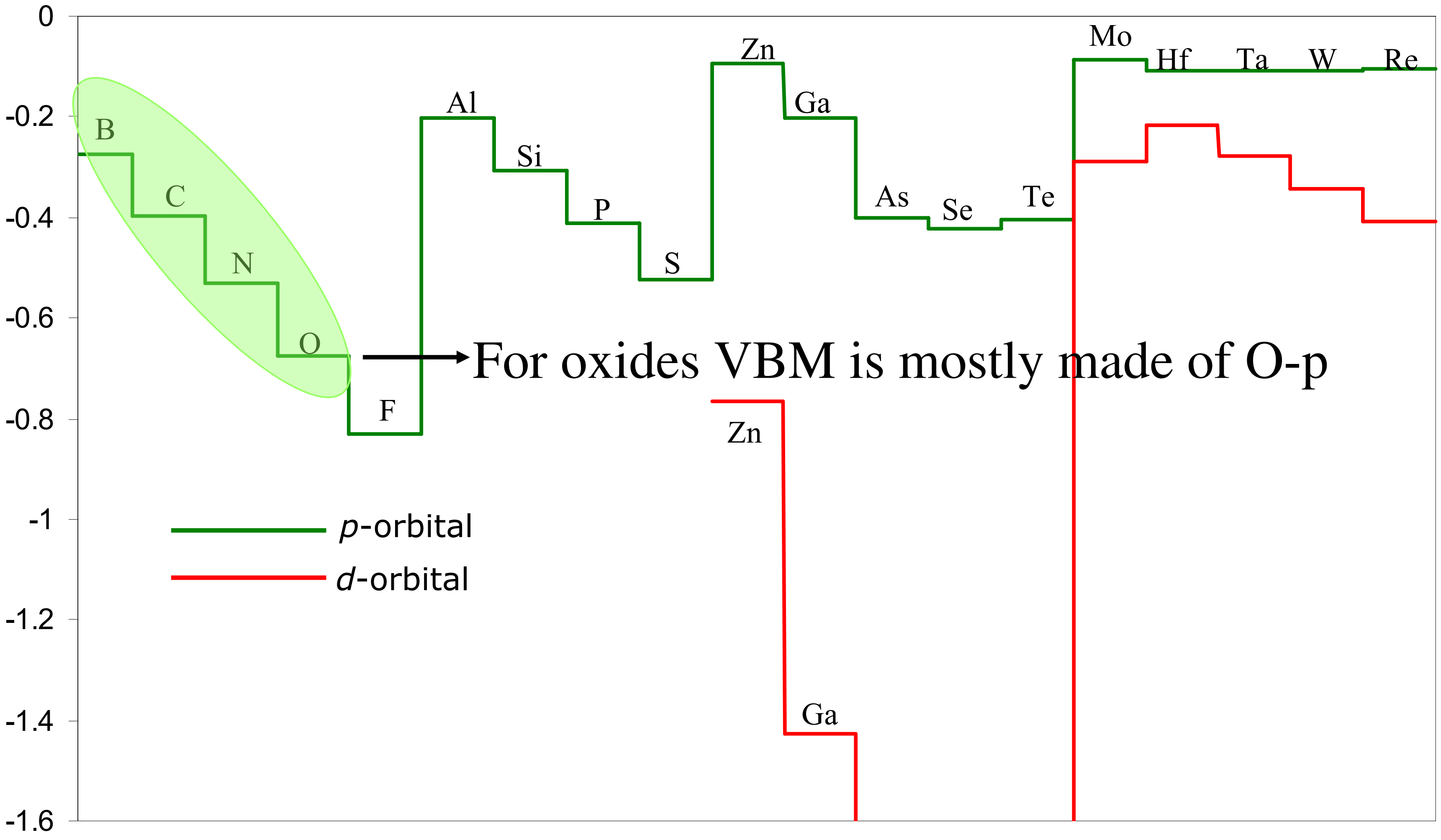
Theory can guide to narrow the range of materials search for PEC.

Q. What do we mean by "*band engineering*"?

-Reduce the band gap.
-Have the right position of the band-edges.



Energy levels of *p*-and *d*-orbital for several atoms



For oxides VBM is mostly made of O-p

Density Functional Theory Calculations (DFT)

DFT is a first-principle quantum mechanical theory

DFT maps a many variables problem to a single variable problem.

It says, if **electronic density** is known, all the **ground state properties** of the system can then be **uniquely** determined.

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\vec{r})\right]\psi_i = \varepsilon_i \psi_i$$

$$\Longrightarrow E_{DFT} = \sum_i^N \varepsilon_i - \frac{1}{2}\int \frac{\rho(r)\rho(r')}{|r-r'|}\,dr\,dr' + E_{xc}[\rho] - \int v_{xc}(r)\rho(r)\,dr$$

In principle, DFT is an exact theory.

Approximations enter the theory when density functionals are constructed. Two most popular approximations are:

1. Local density approximation (LDA), and
2. Generalized gradient approximation (GGA).

Scope of DFT

DFT can give us access to a number of important properties:

- Band structure.
- Optical absorption.
- Defect and doping effects.
- Surface chemistry.
- Structural stability.

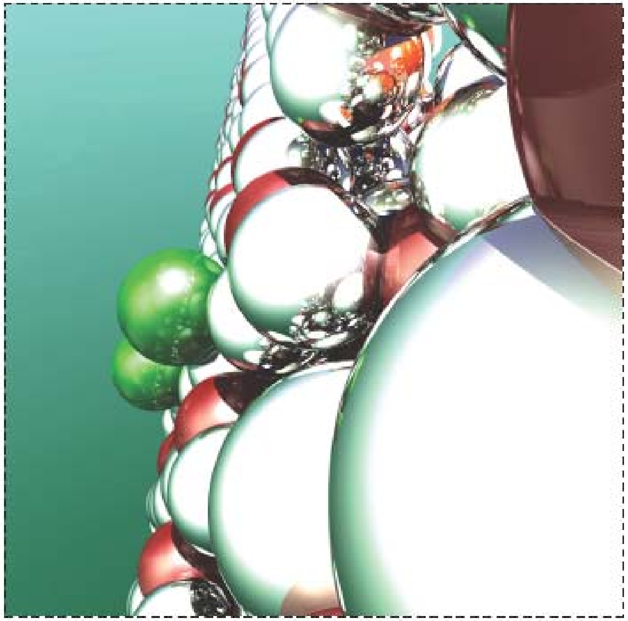


Figure: Impurity absorption on a metal oxide surface

We run state-of-art commercial DFT codes (VASP, WIEN2K) along with our own in-house analysis software.

Calculations are performed on both the NREL and NERSC supercomputers.

Oxide Theory Publications (07/08)

1. **‘Electronic structure of ZnO:GaN compounds: Asymmetric bandgap engineering’**

   M. N. Huda, Y. Yan, S.-H. Wei and M. M. Al-Jassim, Phys. Rev. Lett. In Review (2008).

2. **‘Density-functional theory study of the effects of atomic impurity on the band edges of monoclinic WO_3’**

   M. N. Huda, Y. Yan, Chang-Yoon Moon, S.-H. Wei and M. M. Al-Jassim, Phys. Rev. B, In Press (2008).

3. **‘Electronic, energetic and chemical effects of intrinsic defects and Fe-doping of $CoAl_2O_4$ ’**

   A. Walsh, S.-H. Wei, Y. Yan, M. M. Al-Jassim, J. Phys. Chem. C, In Review (2008).

4. **‘Nature of the bandgap in In_2O_3 revealed by first-principles calculations and X-ray spectroscopy’**

   A. Walsh, J. L. F. DaSilva, S.-H. Wei et al., Phys. Rev. Lett. **100**, 167402 (2008).

5. **‘Doping asymmetry in wide-bandgap semiconductors: Origins and solutions ’**

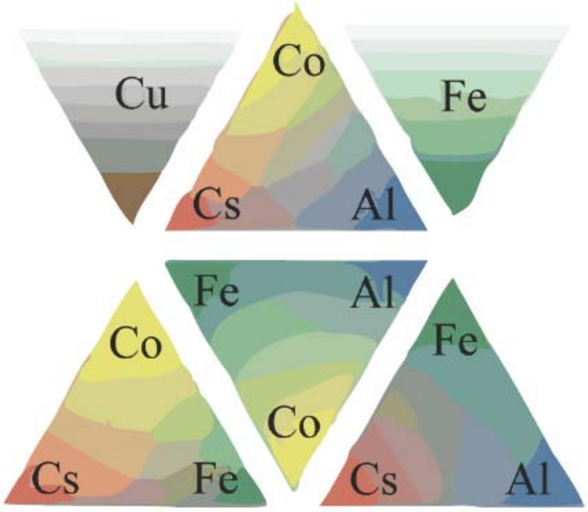
   Y. Yan and S.-H. Wei, Phys. Stat. Sol. B 245, 641 (2008).

6. **‘Structural, magnetic, and electronic properties of the Co-Fe-Al oxide spinel system: DFT calculations’**

   A. Walsh, S.-H. Wei, Y. Yan, M. M. Al-Jassim, J. A. Turner, M. Woodhouse and B.A. Parkinson, Phys. Rev. B 76, 165119 (2007).

Co-Fe-Al Oxide System (I)

- Large scale theoretical screening of new oxide systems is limited by the lack of a single property defining a good PEC material.
- We take our initial lead from high-throughput experimental screening by the Parkinson group at Colorado State University[1].



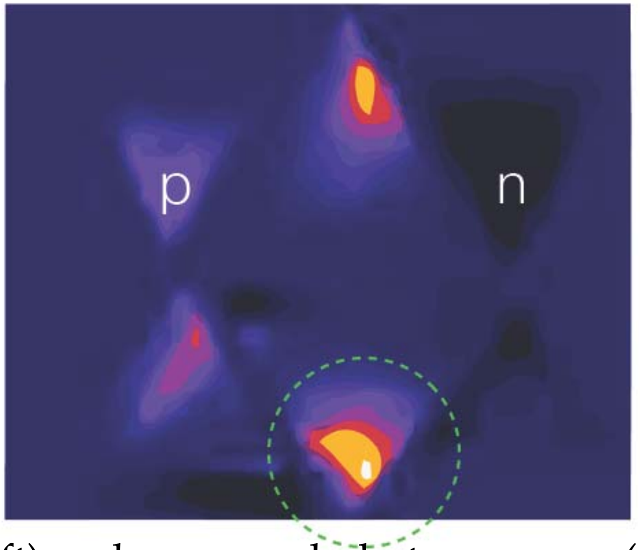


Figure: Schematic inkjet salt printing (left) and measured photoresponse (right), relative to the p-type and n-type standards.

1. M. Woodhouse et al., Chem. Mater. 17, 4318 (2005); Chem. Mater. 20, 2495 (2008).

Co-Fe-Al Oxide System (II)

- Experimental screening found a ternary oxide from the Co-Fe-Al system to exhibit good p-type behavior with a band gap ~1.7 eV.
- XRD showed the spinel structure over a large compositional range.
- Previously reported stable Co-Fe-Al phases:

Co_3O_4

Co_2AlO_4

$CoAl_2O_4$

Fe_3O_4

Fe_2AlO_4

$FeAl_2O_4$

Fe_2CoO_4

$CoFe_2O_4$

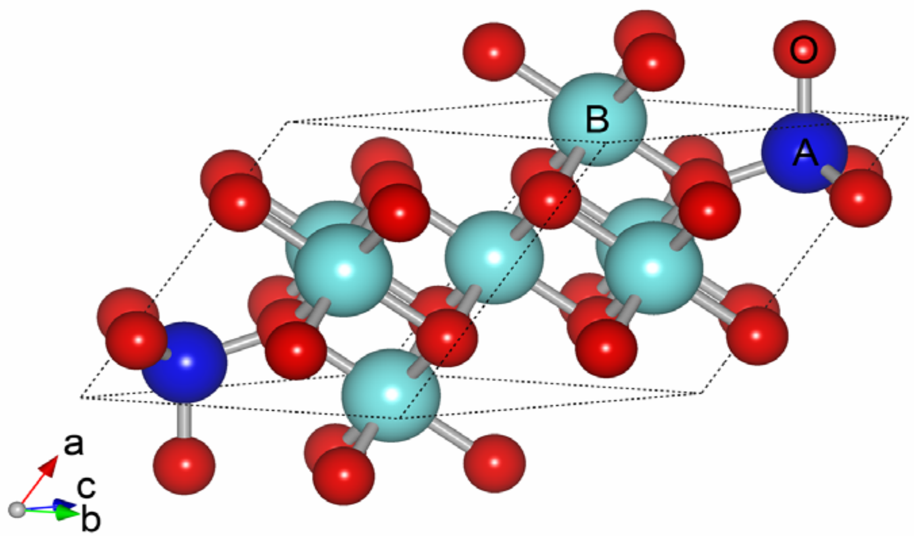
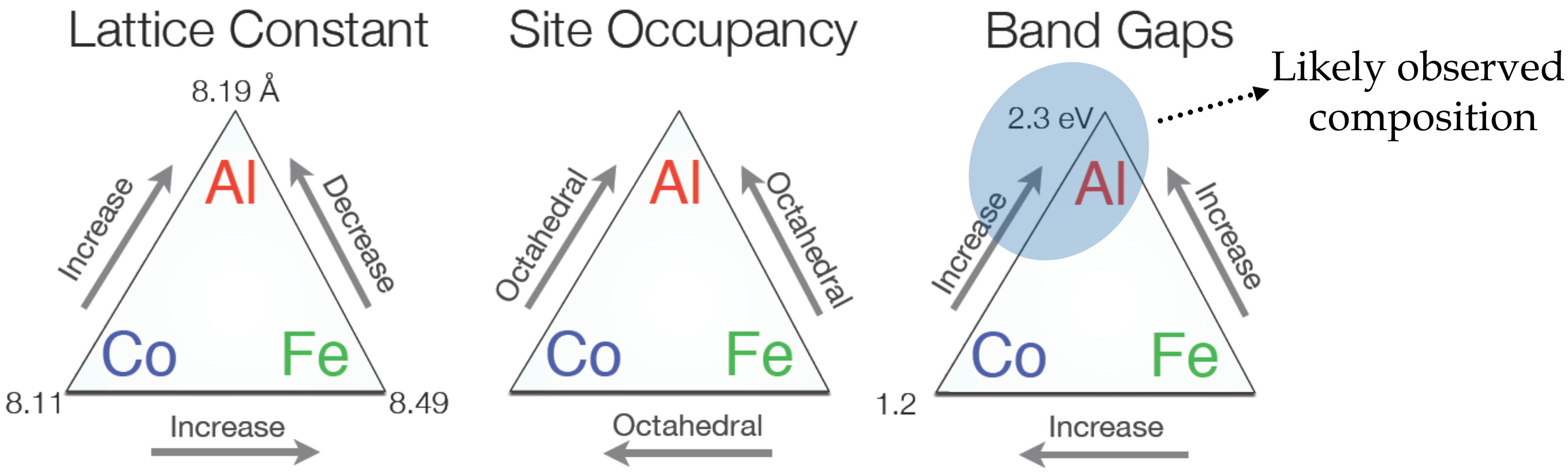


Figure: Spinel crystal structure, with two cations sites, labeled A (tetrahedral) and B (octahedral).

Co-Fe-Al Oxide System (III)

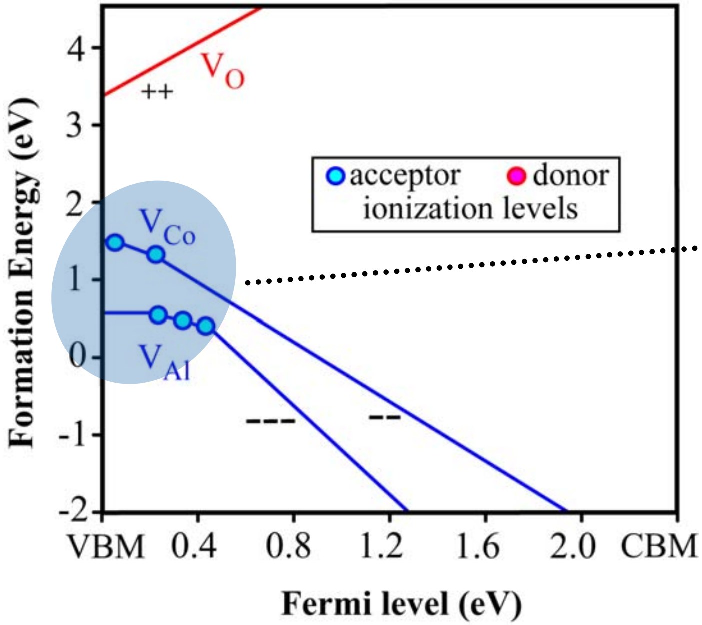
- Our initial theoretical study explored the chemical trends along the Co-Fe-Al binary and ternary spinel phase diagram.



- We found that as Al is substituted into Co_3O_4, it has preferential occupation for the octahedral spinel sites. This results in an increase in the fundamental band gap from ~1 eV up to ~ 2 eV for the $CoAl_2O_4$ end compound.

Co-Fe-Al Oxide System (IV)

- To understand the origin of conductivity in these poorly explored materials, we investigated the formation of intrinsic defects and Fe-doping in the prototype $CoAl_2O_4$.

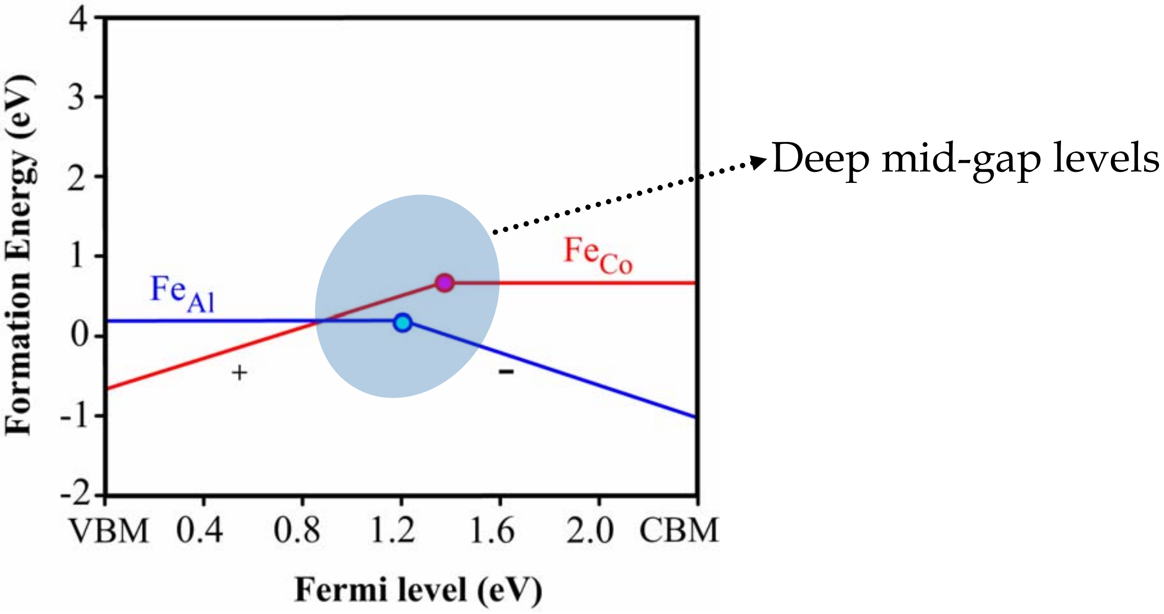


Low formation energy acceptor defects

- Cation vacancies are low in energy, while oxygen vacancies are high.
- This confirms the p-type nature and suggests oxygen rich growth.

Co-Fe-Al Oxide System (V)

- Fe is found to readily substitute on both the Co and Al sites, due to the small steric mismatch and +2/+3 oxidation states of Fe.



- Deep donor/acceptor levels are formed corresponding to Fe(II)↔Fe(III) transition.
- These band can contribute to lower energy photon absorption.

Co-Fe-Al Oxide System (VI)

- The drawback of cobalt spinels is the weak absorption in the visible range arising from the nature of the d-d optical transitions.

- To overcome these limitations we are currently investigating isovalent cation substitution.

- Based on changes in the electronic energy levels on transition from Al to Ga to In, we predict a dramatic increase in visible light absorption.

Experimental verification of these predictions are in progress.

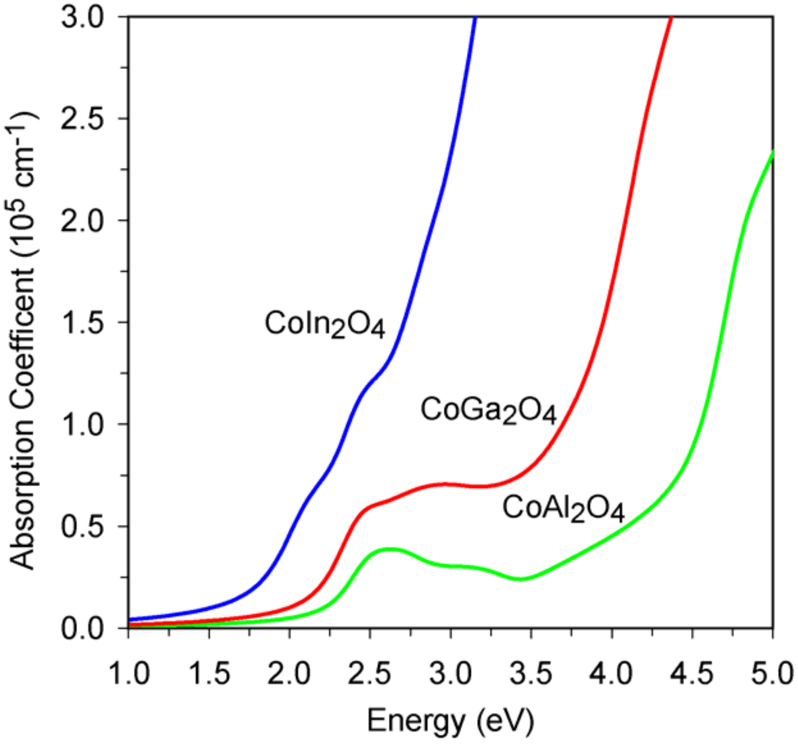
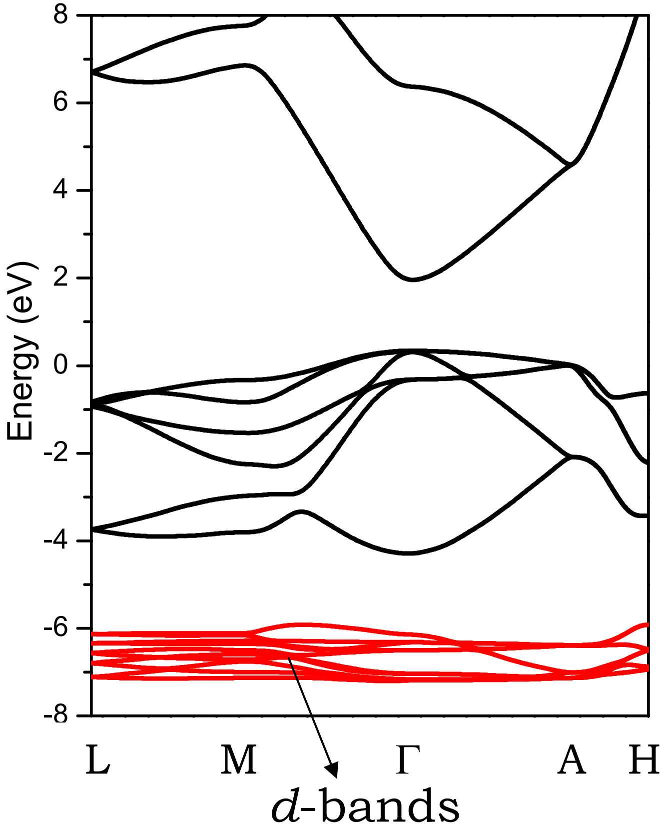
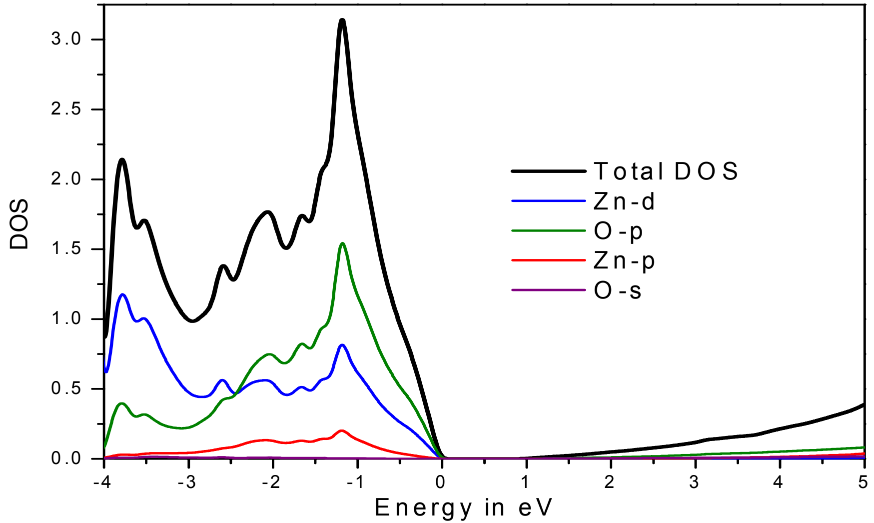


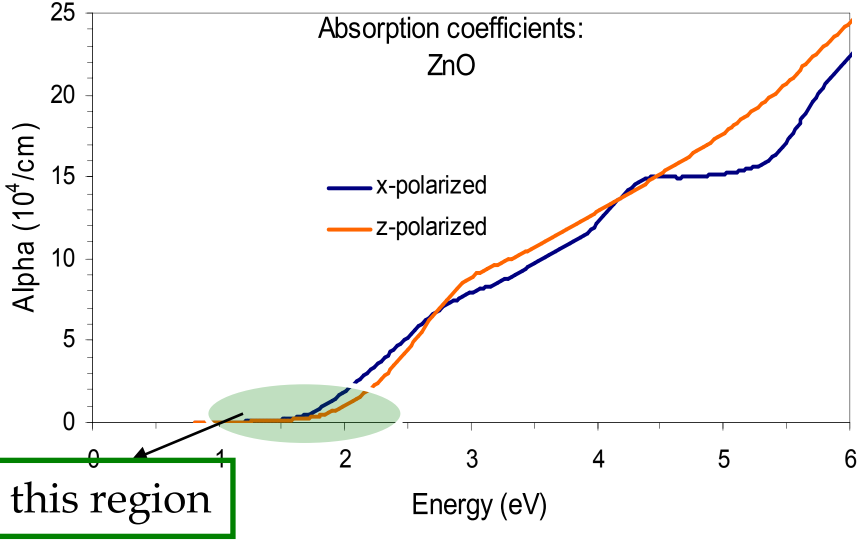
Figure: Calculated absorption spectra.

Band engineering of ZnO for PEC

ZnO Structure

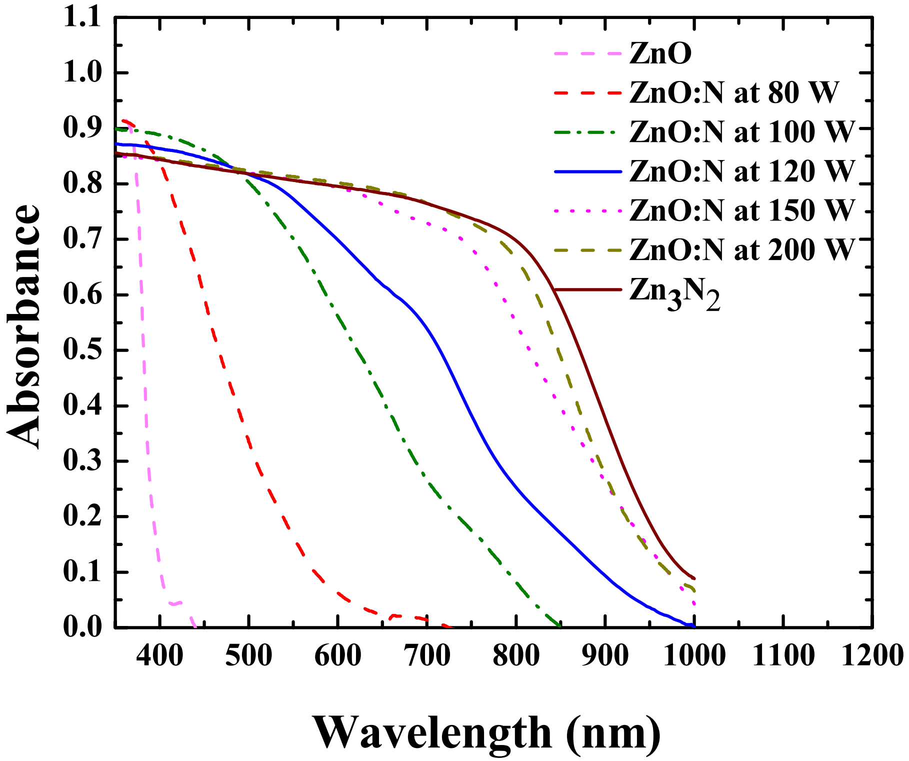






Goal is to improve absorption in this region

ZnO:N



K.-S. Ahn, Y. Yan, and M. Al-Jassim, J. Vac. Sci. Technol. B, L23 (2007)

K.-S. Ahn, et al . J. Electrochemical Society, 154 B956-B959 (2007)

Excellent absorption **Bad photocurrent**

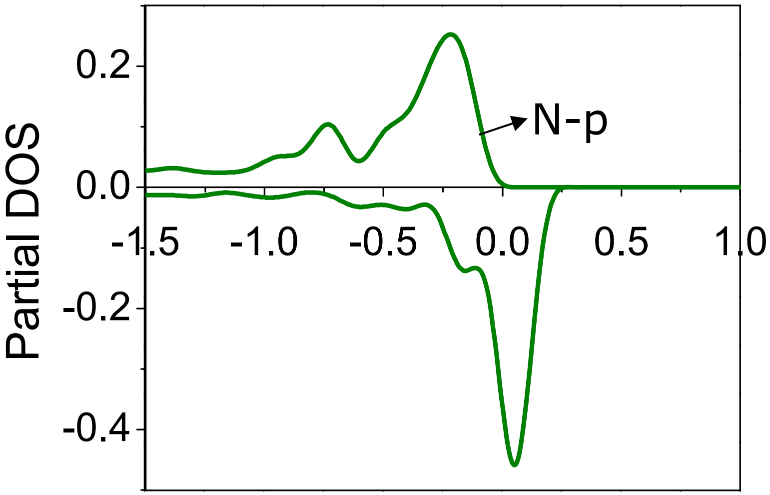
What is the reason:

-N substitution creates a deep level.

This means:

Localized wavefunctions.

Stronger recombination centers.



Isovalent doping/alloying would improve the situation.

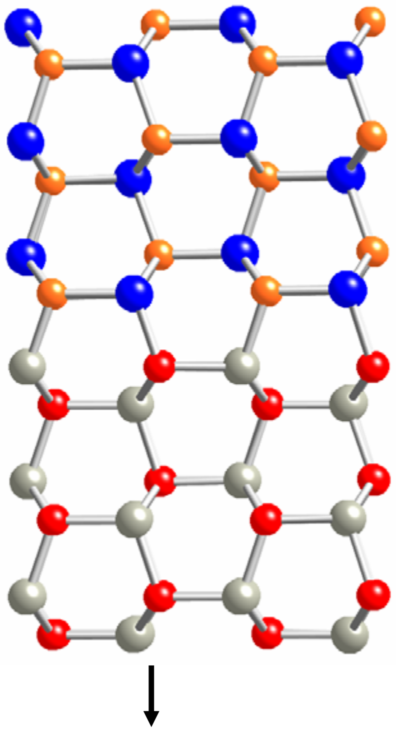
Zn-O and Ga-N are isovalent.

Two ways of making a ZnO-GaN composite system*:

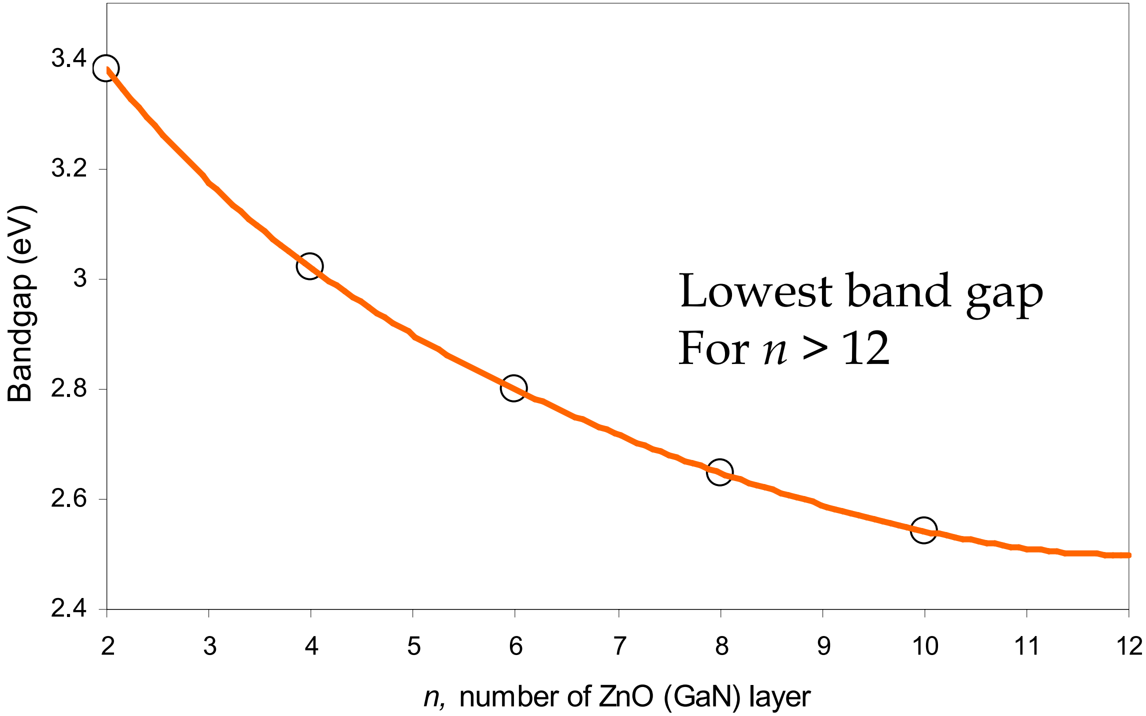
1. **ZnO:GaN super lattice**
2. **Random alloy system**

***Electronic structure of ZnO:GaN compounds: Asymmetric bandgap engineering,**
M. N. Huda, Y. Yan, S.-H. Wei and M. M. Al-Jassim, Phys. Rev. Lett. In Review (2008).

$(ZnO)_n(GaN)_n$ Super-lattice

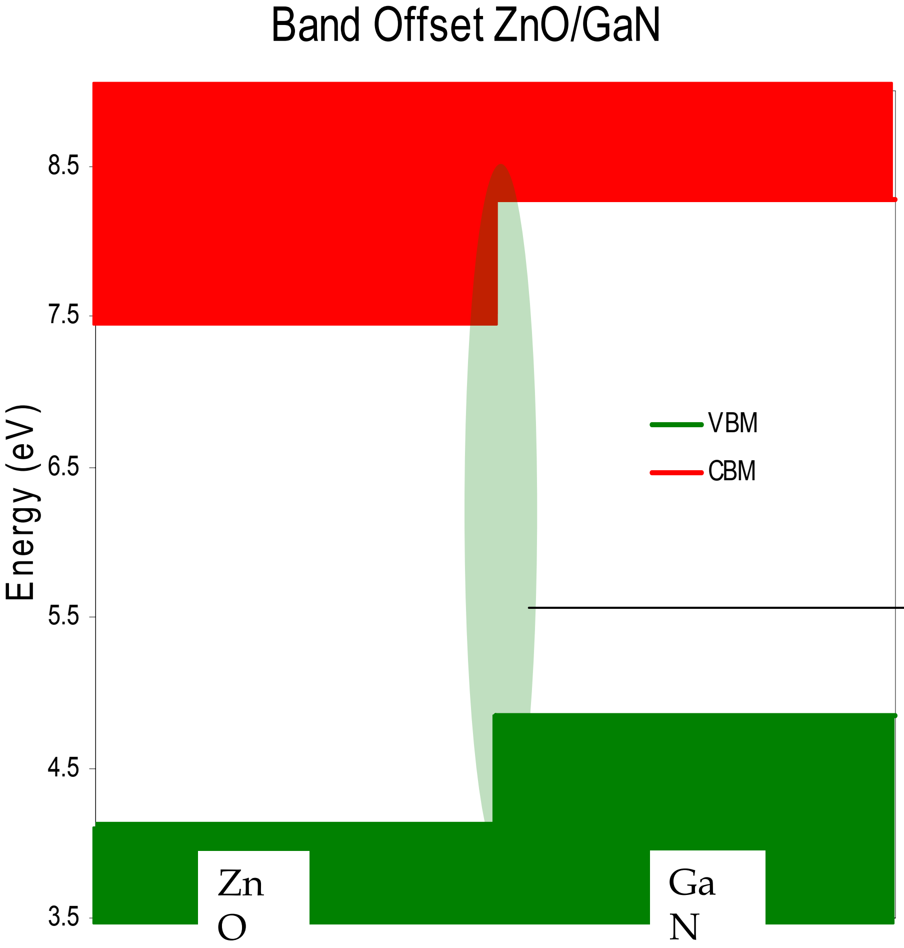


Most stable interface



Lowest band gap
For $n > 12$

<u>At large number of layers, bandgap is smaller.</u>

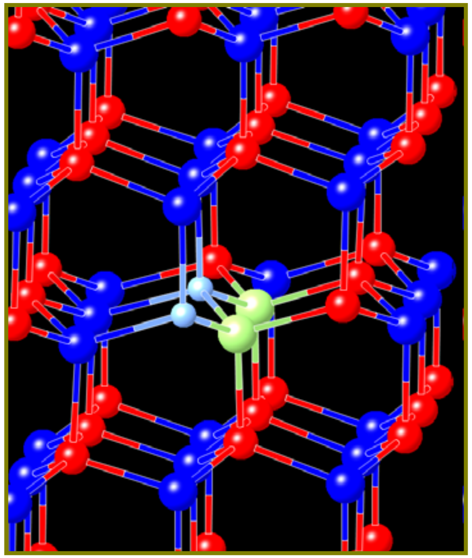


The smallest band gap is only at the interface

VBM (valence band maxima) is localized at GaN
CBM (conduction band minima) is localized at ZnO.

Band offset 0.722 eV Measured value is 0.80 eV*

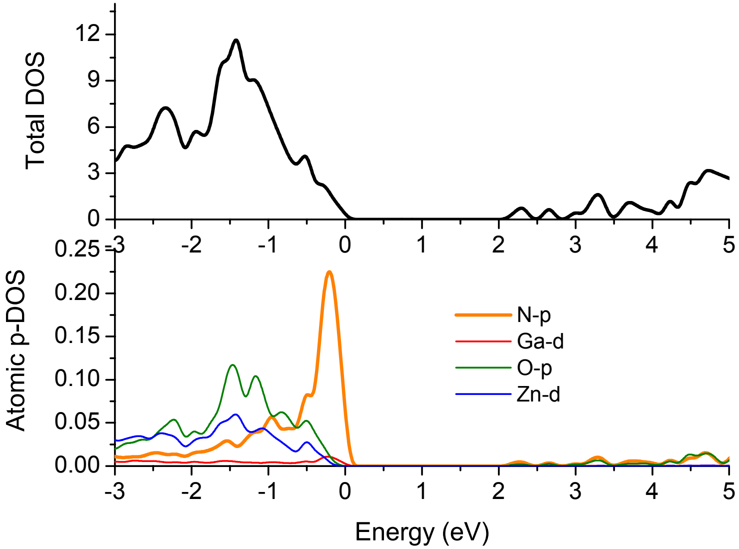
ZnO:GaN random Alloy
Dilute regime



Ga-N in host ZnO (or vice versa) tend to cluster together.

For example, second pair Ga-N doping in already Ga-N doped ZnO is only 0.068 eV.

Band gap decrease further as the cluster size increase.



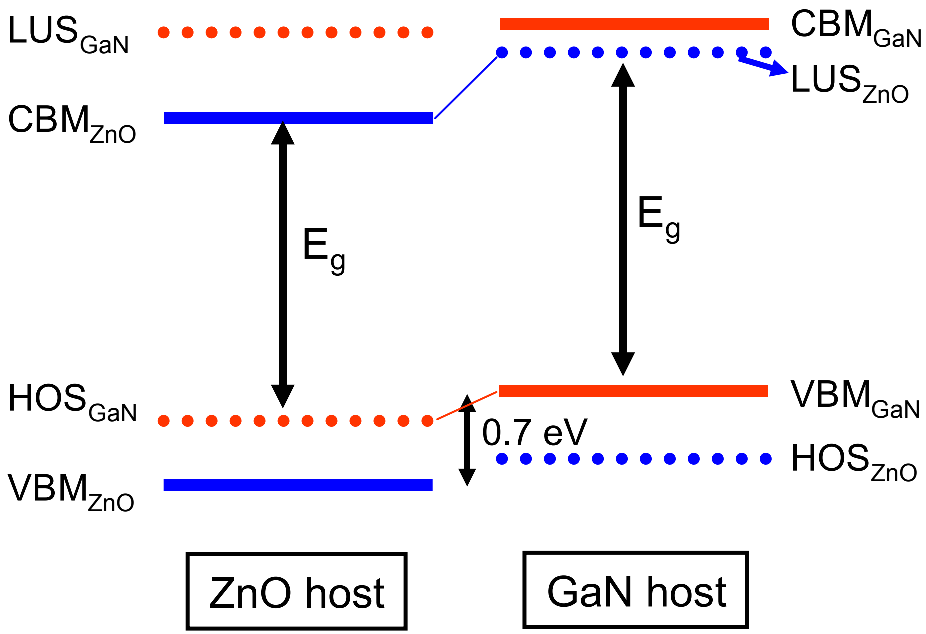
Band gap reduction is asymmetric:

Host	Eg reduction
Ga-N in ZnO	0.410
Zn-O in GaN	0.102

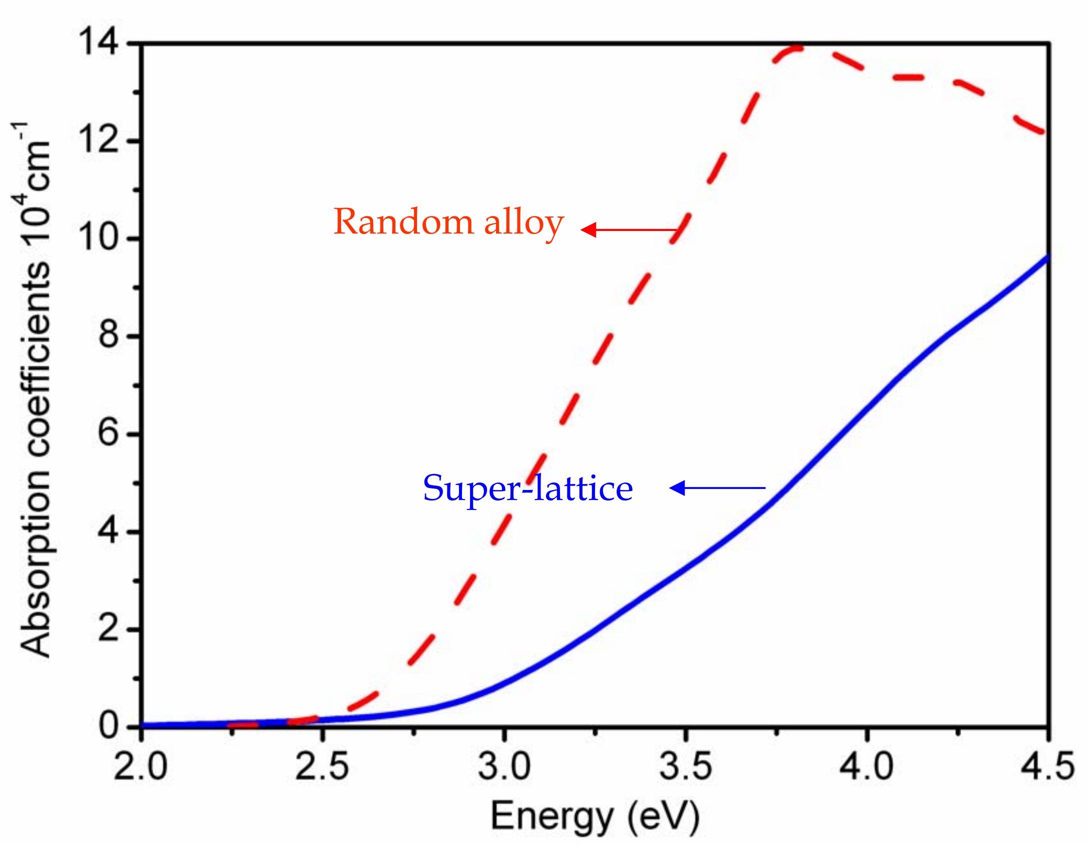
Question: Why?

ZnO and GaN has similar band gap, Band edges and are isovalent.

Can be explained by confinement effects:

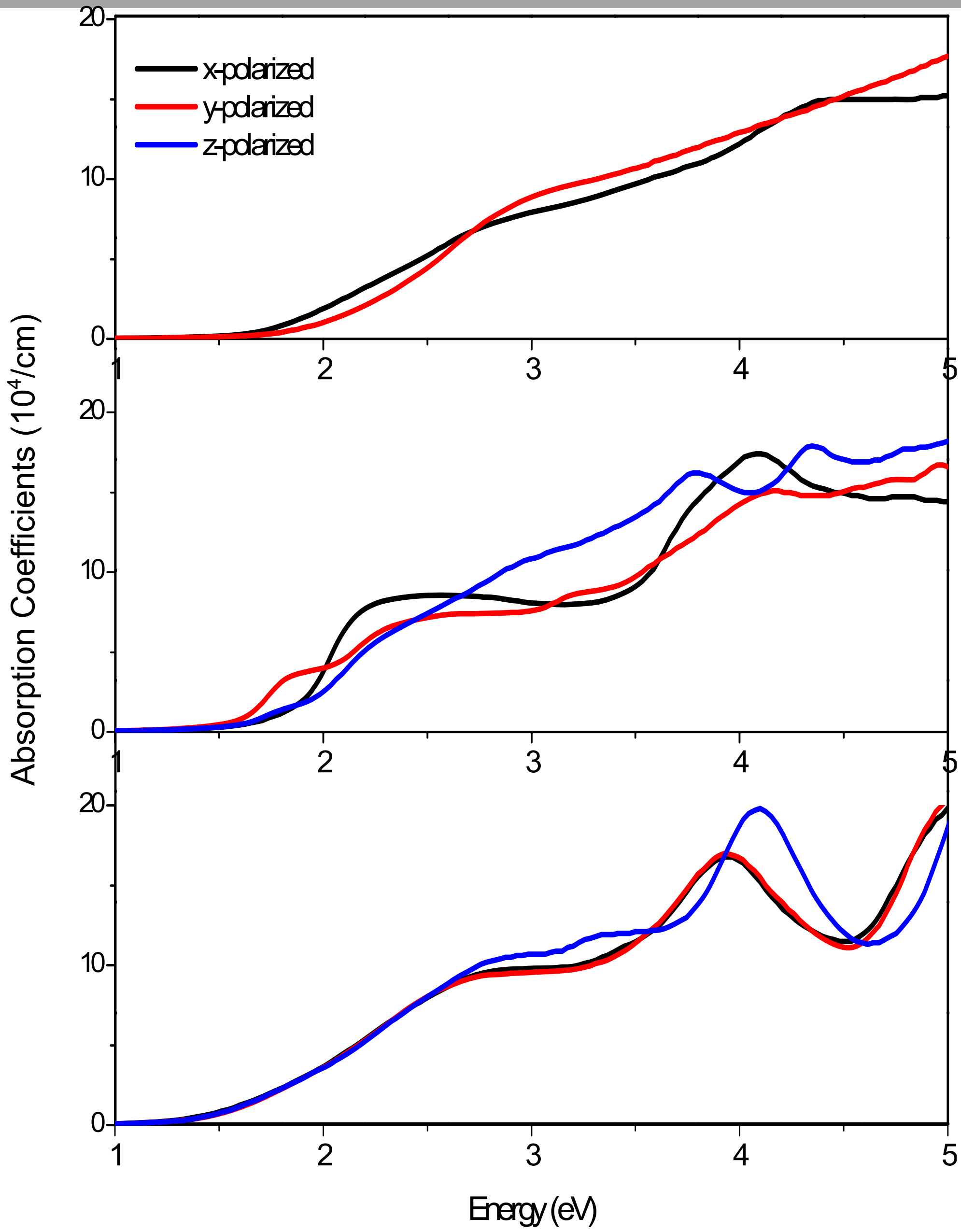


Supper-lattice or Random-alloy?



Calculated total absorption coefficient spectra of superlattice of $(ZnO)_8(GaN)_8$ (solid blue curve) and $(ZnO)_{1-x}(GaN)_x$ random alloys (x=0.0740).

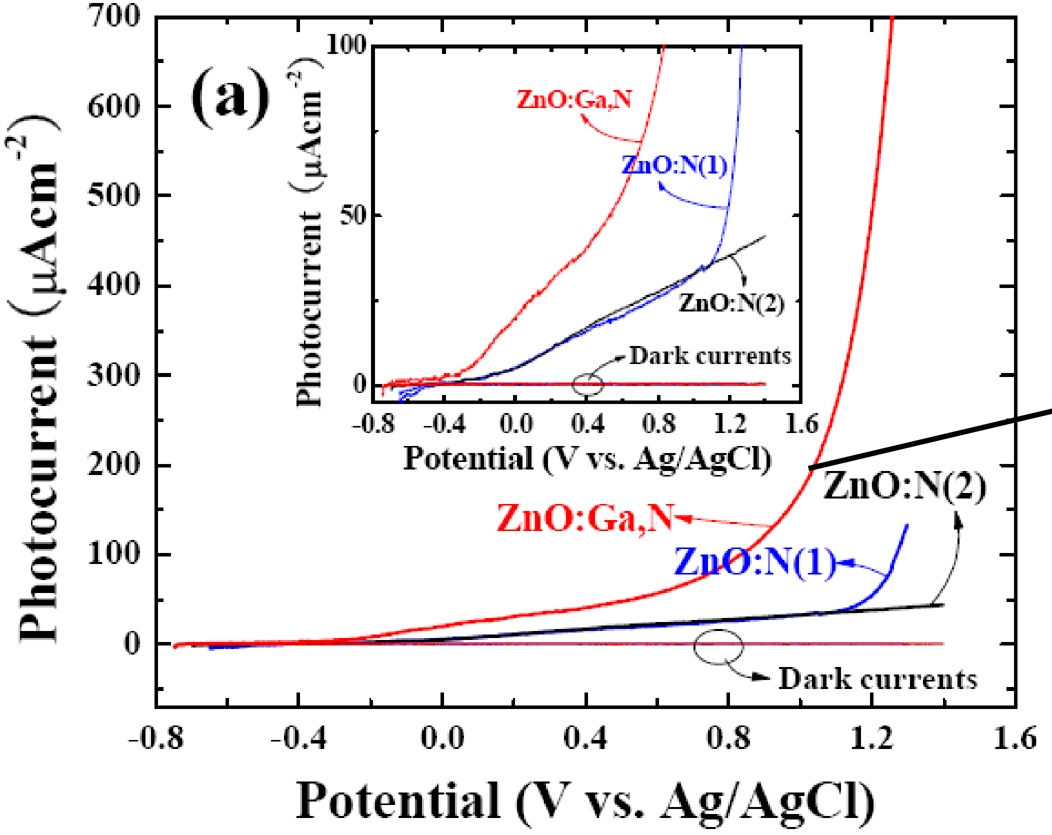
This shows that the <u>random alloy</u> approach is better for optical absorption



Pure ZnO

Ga-N substitution

2Ga-2N substitution



Improved photo-current

*Kwang-Soon Ahn, Yanfa Yan, Sudhakar Shet, Todd Deutsch, John Turner, and Mowafak Al-Jassim *Appl. Phys. Lett.* **91**, 231909 (2007).

Current Theory work

- The focus is now on Cu-based delafossites.
- Explaining the observed PEC results in Fe_2O_3 and to improve its performance.
- Ternary oxides, such as, $CuIn_2O_4$ and $CuGa_2O_4$ and new alloys from them.
- Search for other new oxides.

Conclusions

- Isovalent metal substitution in spinel structure has shown dramatic improvement in absorption.
- Optical absorption and photo-current properties can be improved by charge passivated doping.
- ZnO is a better host than GaN to improve the photo-response in dilute regime.
- **Theory can be used as a predictive tool, as well as to understand the physics, to design new materials.**