II.E.6 Theory of Oxides for Photo-Electrochemical Hydrogen Production

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Objectives

- Theoretical prediction and design of metal oxides systems suitable for photo-electrochemical (PEC) hydrogen production, which can be tested in the laboratory.
- Theoretically tune the band gap of metal oxides by impurity incorporation/alloying to achieve the correct bandgap range.
- Study the optical absorption properties of the band-engineered materials to determine methods for improvement.
- To improve the conduction-properties of these metal oxides.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (MYPP):

(Y) Materials Efficiency
(Z) Materials Durability

Technical Targets

This project is conducting theoretical studies to predict and design metal-oxides-based photo-electrodes for PEC hydrogen production. Insights gained from these studies will provide guidance to synthesize the materials in the laboratory. To meet the following DOE

2013 technical targets from the MYPP PEC hydrogen production goals:

- Band gap of 2.3 eV
- 10% conversion efficiency
- 1,000-hr lifetime

Accomplishments

- Two metal oxide systems have been identified and were studied thoroughly to design a suitable photo-electrode by bandgap-engineering through the introduction of impurities.
- For the Co-Fe-Al oxides it has been found that they prefer spinel structure and are usually p-type. Our theoretical study explained these features and suggested ways to improve the system's optical absorption properties.
- For the ZnO system, the experimental finding of poor photocurrent for nitrogen-doped ZnO has been explained theoretically, and it was predicted that isovalent random-allying would increase the photo-current.

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Introduction

Production of hydrogen through splitting water under solar irradiation by the PEC process is one of the most promising methods. There has been significant progress in this field using ultraviolet solar energy. However, for optimal use of solar energy, the optically visible range of the spectra must be used. To absorb maximum solar energy, the desired photo-electrode must be a semiconductor of band gap around 2.0 eV, and the positions of its band edges must be matched with the water-splitting potentials. Also, in general, the photo-electrodes must be stable in aqueous solutions. So to achieve suitable photo-electrode materials, the electronic properties of the materials and their response to defect formation must be understood. It is known that the most stable semiconductors in aqueous solutions are oxides [1]. There are easily 50,000 combinations of ternary oxides and almost 2 million quaternary oxides [2]. A collaboration of theory, synthesis, and characterization groups is necessary to achieve fundamental PEC goals.

Unfortunately, at present, most semiconductors cannot meet all the criteria for PEC hydrogen production either due to very large band gap or due to improper placements of the band edges. Therefore, band-engineering is necessary to design the

semiconductors suitable for PEC. The most common method used for this is the incorporation of impurities, such as C and N. However, although impurities can reduce the band gap, their incorporation would lead to poor photo-response because the partially occupied impurity band can act as a killer for photo-generated carriers. It has been argued that passive donor-acceptor co-doping/alloying may suppress the recombination and yet maintain a reduced band gap. On the other hand, poor absorption, hence poor photo-current, may also occur due to very low transition probabilities between the band-edges of the materials. This can be remedied by alloying with suitable isovalent impurities to change the band-edge characteristics of the host semiconductors. These types of compound alloying pose several critical problems, such as choosing the appropriate host and alloying materials, the alloying approach, and the alloying concentration. A thorough theoretical understanding of the donor-acceptor alloying physics is necessary to pre-screen the potential alloying materials for a given purpose. This would avoid the expensive and time consuming trial-and-error method in experimental setup, and guide the experiment to achieve the goal quicker.

Approach

Density functional theory (DFT) [3] has been used to study the electronic properties of the photo-electrodes. DFT is an efficient method that replaces a many-variable (electrons) problem with a single variable (electron density) problem. In principle, DFT is an exact theory. However, several approximations enter in "density functional" when solving the Schrödinger-like Kohn-Sham equations [4]. Two of the most widely used approximations are, (i) local density approximation, and (ii) generalized density approximation (GGA). In our calculations we use GGA. An extension of DFT, namely DFT+U, has also been used as needed, where U is an additional Coulomb interaction added to the desired orbital of materials. For most of our calculations we used the projected augmented wave (PAW) method, as implemented within the Vienna *ab initio* simulation package (VASP 4.6.21) [5]. Because of its construction, the PAW method is believed to agree better with the all-electron results. One reason is that PAW potentials reconstruct the exact valence wave-function with all nodes in the core. The optical properties were calculated by the optic code as implemented in WIEN2k [6].

Results

Co-Fe-Al Oxides

Recently, Woodhouse *et al.* [7] have reported very interesting behavior for the Co-Fe-Al oxide spinel system. With reported optical band gaps of between 1.1 eV and 1.65 eV for Co_3O_4 and 0.14 eV for low-temperature Fe_3O_4, these two binary oxides have limited application in the PEC splitting of water. On introducing Al, the Co-Fe-Al oxide spinel system can exhibit optical band gaps of between 1.6 and 2.0 eV and generate a strong *p*-type photocurrent, which is ideal for PEC applications. In addition, other interesting behavior is found. For example, when the experiment is repeated without the Fe precursor, the photocurrent in the sample is reduced threefold, indicating that Fe does have an important role to play. X-ray diffraction revealed that the lattice constants of the synthesized materials are very similar within a large compositional range, which is very close to that of Co_3O_4. Unfortunately, although it is thought that the active material is Co and Al rich, further insight is restricted by the limited amount of information available about the properties of these spinels.

With a view to providing a better basic understanding of these Co, Al, and Fe containing oxides, we have calculated the electronic structure of nine stoichiometric spinels in both the normal and inverse structures, including the hypothetical Al_3O_4 compound. Calculations are performed using gradient corrected density functional theory (GGA-DFT) with the Co and Fe 3d states treated with on-site correction for Coulomb interactions (DFT+U). The results can be summarized as follows: (i) The trends in the calculated lattice constants agree well with available X-ray diffraction data. The lattice constants increase along $Co_{3-n}Al_nO_4$ (n=0–3) and $Co_{3-n}Fe_nO_4$ (n =0–3), but decrease along $Fe_{3-n}Al_nO_4$ (n=0–3); (ii) Preference for the octahedral sites are found in the order Fe<Co<Al; (iii) The electronic band gaps of Co_3O_4 and Fe_3O_4 are shown to remain largely unchanged as Al is substituted into the lattice forming M_2AlO_4 (M=Fe,Co), but increase greater than 1 eV for MAl_2O_4 as the M octahedral sites are fully replaced; (iv) From the Co-Fe-Al spinel oxides studied, $CoAl_2O_4$ has been preliminarily identified as having the properties most suitable for PEC catalysis.

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. While the Co and Fe 3d states have been shown to be active in determining the electronic and magnetic properties of these spinels, Al makes little contribution to the valence density of states. As such, when a ternary oxide is formed with majority Co and minority Al composition (Co_2AlO_4), Al occupies only half of the available octahedral sites, but it is the remaining octahedral and tetrahedral Co sites that determine the properties. Hence, the electronic band gap is largely unchanged from Co_3O_4 to Co_2AlO_4. Increasing the Al composition of the ternary oxide to $CoAl_2O_4$ results in a loss of the octahedral Co sites, and as such, the band gap

is increased as the octahedral Co $3d$ contribution to the conduction band minimum (CBM) is no longer present.

To understand the conductivity of these materials, we investigated the formation energies of intrinsic defects and Fe-doping in prototype $CoAl_2O_4$. It was found that acceptor defects like Co-vacancies or Al-vacancies have much lower formation energies compared to the donor-like defect O-vacancies. This confirms the p-type nature of these materials, and suggests oxygen-rich growth conditions to optimize their performance. On the other hand, Fe substitution in either Co- or Al-site create mid-gap levels. However, one of the major drawbacks for these materials is that at the visible range, the absorption is poor mainly due to d-d transition. To improve these limitations we have considered isovalent cation substitution for Al. Based on changes in the electronic energy levels on transition from Al to Ga to In, we have predicted dramatic increase in visible light absorption (Figure 1).

ZnO-Based System

ZnO is a wide band gap semiconductor with a band gap of 3.4 eV. Moreover, its CBM lies too low for the hydrogen breaking potential for water splitting. Therefore, two goals need to meet here, (i) band gap reduction, and (ii) push up the CBM at higher energy. Both of these goals can be handled by band-engineering. There are two ways of performing the band-engineering for oxide: first, to choose impurity atoms with p-orbital higher in energy than the oxygen p-orbital (such as N, C, etc). As the valence band maximum (VBM) of ZnO is mainly composed of O-p, this would place the impurity band above the host's VBM, and would facilitate

absorption from the "impurity band" to the CBM with effectively smaller band gap. The second approach is to substitute the cation, Zn, by a metal atom with shallower d-orbital (such as Cu, Ag, etc.). This impurity d-orbital would sit inside the valence band and push the VBM higher, hence reducing the band gap. In this report we would comment on the first approach.

It has been found experimentally that N substitution in ZnO reduces the band gap and increases the optical absorption as the N concentration increases [8], but the photocurrent increase was insignificant. A single N substitution in ZnO produces a defect level above the VBM of pure ZnO. This defect level is deep and does not contribute to the conduction properties. In our calculation we found, the top of the N-"doped" ZnO valence band (which is unoccupied) is 0.35 eV higher in energy than the undoped ZnO. In addition to creating this deep level, as an N atom has one less electron than an O atom, N substitution also creates charge imbalance. It creates a carrier recombination center that degrades the carrier concentration of the host, hence poor photo-current. To compensate the charge defect by the impurity band, isovalent impurities incorporation would be necessary. As Ga-N is isovalent to Zn-O, Ga codoping with N would be a remedy to avoid this problem. Also the bulk GaN lattice constant and band gap is similar to ZnO, so the local lattice mismatch would be minimum. ZnO and GaN have a type-II band alignment. Here, we consider two representative cases for the compound alloy system: (i) $(ZnO)_n(GaN)_n$ superlattices and (ii) a random $(ZnO)_{1-x}(GaN)_x$ alloy system, i.e., random distribution of one compound into another that serves as the host. Case (i) can be obtained by epitaxial growth, whereas case (ii) is likely to be found in sintered mixed compound powders [9].
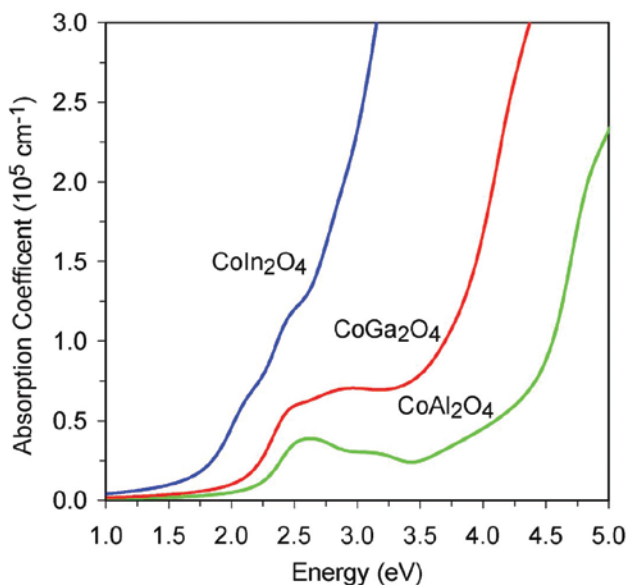
We first discuss the electronic properties of the superlattice that also allow us to calculate the band offsets between ZnO and GaN. Both ZnO and GaN have strong polarities along their c-axis. Their polar surfaces, $\pm(0001)$, are usually unstable and can lead to large carrier separation. Thus, in our study, the ZnO:GaN superstructures are constructed on the non-polar surfaces, e.g., $(1\bar{1}00)$. We have considered a series of possible interfacial structures on the $(1\bar{1}00)$ surface. The one with the lowest energy among these structures has the minimum number of "wrong bonds" (i.e., Ga-O and Zn-N bonds) at the interface. We have considered superlattices with different thicknesses of the $(ZnO)_n(GaN)_n$ layer. Figure 2 shows the GGA+U corrected bandgap variations with respect to the layer thickness, n. The band gap opening with thinner layers is a direct consequence of the quantum confinement. This shows that the band gap – and hence, the absorption properties – can be tuned by the superlattice thickness, n. For $(ZnO)_n(GaN)_n$ superlattices, the top of the valence band is mainly composed by the N-p orbitals located at the GaN side with large weight near the interface. On the
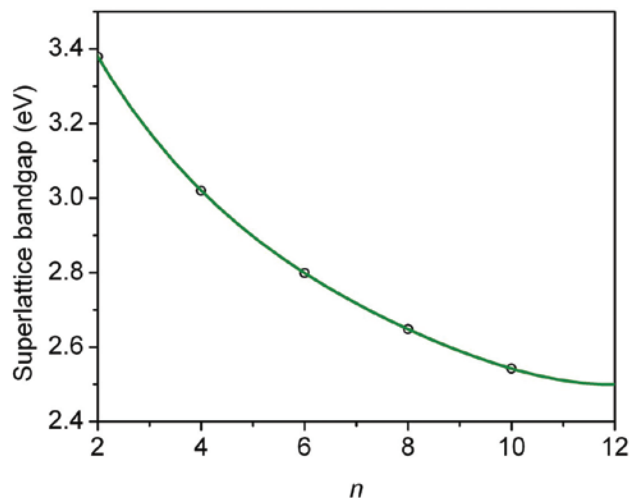

FIGURE 1. Calculated Absorption Spectra for CoM_2O$_4$ (M = Al, Ga, In) Spinel Systems

FIGURE 2. Calculated GGA+U Corrected Bandgaps as a Function of the Layer Thickness n of Superlattice $(ZnO)_n(GaN)_n$

FIGURE 3. Calculated Total Absorption Coefficient Spectra of Superlattice of $(ZnO)_8(GaN)_8$ and $(ZnO)_{1-x}(GaN)_x$ Random Alloys ($x=0.0740$)

other hand, the bottom of the conduction band is mainly composed by the O-2s and cation -4s orbitals, and mainly localized on the ZnO side. These results indicate that only the regions around the interface, where the bonding between Ga-O and Zn-N occurs, would absorb photons with energies corresponding to the reduced band gap.

We have also calculated the band offsets between ZnO and GaN. Our calculated GGA+U VBM offset between ZnO and GaN is 0.7 eV, with higher GaN VBM. As GaN and ZnO have similar bandgaps, the band offset between their CBM is almost the same. It should be noted that the experimentally measured band offset depends on the interfacial structure and chemical compositions. It has been shown that, depending on the cation- or anion-rich interface, the band offset can vary from 0.5 to 1.0 eV. Therefore, our calculated band offsets are in the range of experimentally reported values [10].

We now discuss the electronic structures of $(ZnO)_{1-x}(GaN)_x$ random alloy systems. We have considered both randomly distributed Ga-N pairs in a ZnO host and randomly distributed Zn-O pairs in a GaN host. The introduction of Ga-N in ZnO does not alter the basic band structure of ZnO, except at the VBM. Because N is less electronegative than O, the top of the VBM now consists mainly of N-p orbitals and is raised about 0.43 eV compared to the VBM of the host ZnO, whereas the shift of the CBM is only 0.02 eV upward, giving a net band gap reduction of 0.41 eV. The calculated GGA+U corrected band gap is 2.93 eV. Increasing the N concentration leads to broadening of the N-p bands and further reduction of the band gap.

For Zn-O pairs distributed in a GaN host, a different picture emerged. The substitution of Ga-N with ZnO causes only a small change to the basic band gap of GaN. As O is more electronegative than N, one would
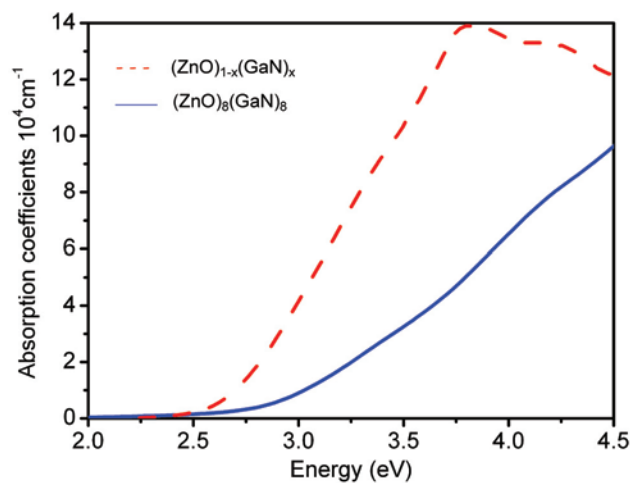
not expect that substitution of N by an O will raise the VBM of GaN. However, we found that at $y=1-x=0.0185$, the VBM is raised by 0.04 eV. This is because the Zn-d bands are shallower than the Ga-d bands. The coupling between N-p and Zn-d causes the up shift of VBM. The total band gap reduction is found to be only 0.10 eV, which is much smaller than that of a Ga-N pair in a ZnO host, 0.41 eV. Our results thus suggest that clearly the band gap reduction for the ZnO:GaN system is asymmetric, i.e., band gap reduction is much more effective for Ga-N in a ZnO host than for Zn-O in a GaN host. Thus, it is important to choose the right host material to achieve effective bandgap reduction.

Finally, we compare the superlattice and the random-alloy systems as discussed above. Our calculations reveal that both systems can result in reduced band gaps. To achieve a band gap, for example, of around 2.6 eV using the superlattice system, we need an 8-layer superlattice. To achieve the same bandgap using the random-alloy system, we need an alloy with a Ga-N concentration of 7.4%. Figure 3 shows the calculated total absorption coefficients for the superlattice system for $(ZnO)_8(GaN)_8$ and the random-alloy system $(ZnO)_{1-x}(GaN)_x$ with $x=0.0740$. Both systems have a similar band gap of 2.6 eV. However, the random-alloy system exhibits much larger absorption coefficients than the superlattice system in the longer-wavelength regions. The main reason for this difference is that in the superlattice system, the VBM is localized at the GaN side and the CBM is localized at the ZnO side. The overlap of the CBM and VBM wave functions occurs only in the interface regions; therefore, the transition matrix elements and the absorption of light in the long-wavelength regions are small. On the other hand, in the random-alloy system, all the incorporated Ga-N pairs would participate in the absorption. Thus, in

general, the random-alloy system is more efficient than the superlattice systems in light absorption in the longer-wavelength regions. Experimental results also showed improved photo-current for the isovalent random-alloy ZnO:GaN system [11].

Conclusions and Future Directions

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.
- Photo-response of ZnO can be improved by isovalent random-alloying in dilute regime by GaN. Also, it has been predicted that ZnO is a better host than GaN for PEC purposes.
- Theory can be used as a predictive tool to design new materials, as well as to understand the physics.

Future Directions

- Focusing on Cu-based delafossites.
- Explaining the observed PEC results in Fe_2O_3 and improving its performance.
- Researching ternary oxides, such as, $CuIn_2O_4$ and $CuGa_2O_4$ and similar alloys.
- Searching for new oxide systems.

FY 2008 Publications/Presentations

Publications

1. Huda, M.N.; Yan, Y.; Wei, S.H.; Al-Jassim, M.M. "Electronic structure of ZnO:GaN compounds: Asymmetric bandgap engineering" *Physical Review Letter*, in Review. 2008.

2. Huda, M.N.; Yan, Y.; Chang-Yoon, M, Wei, S.H.; Al-Jassim, M.M. "Density-functional theory study of the effects of atomic impurity on the band edges of monoclinic WO_3." *Physical Review B*. Vol. 77, 2008; p. 195102.

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Presentations

1. "Electronic structure of ZnO:GaN compounds: Asymmetric band gap engineering." Presented at a Workshop on Recent Development in Electronic structure Methods, University of Illinois at Urbana-Champaign, Illinois. June 2008.

2. "Exploiting the coexisting simplicity and complexity of metal oxides for renewable energy applications." Presented at Chemistry Department Seminar. University College London. June 2008.

3. "First-principles examination of the Co-Fe-Al oxide spinel system for water splitting." Presented at the American Chemical Society Meeting. New Orleans, Louisiana. April 2008.

4. "Materials Discovery by Design: Application of Electronic Structure Theory to Materials in Renewable Energy." Presented at the Materials Science Department seminar. University of Texas. Dallas, Texas. April 2008.

5. "Materials Discovery by Design: Application of Electronic Structure Theory to Materials in Renewable Energy." Presented at a Physics Department seminar. University of Texas. Arlington, Texas. April 2008.

6. "Density-functional theory study of the effects of atomic doping on the band edges of monoclinic WO_3." Presented at the American Physical Society Meeting. New Orleans, Louisiana. March 2008.

7. "A density functional study of the band gap tuning by atomic doping in ZnO." Presented at the Materials Research Society meeting. Boston, Massachusetts. November 2007.

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