

II.E.2 Photoelectrochemical Water Splitting

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Objectives

- Identify, synthesize, and characterize new semiconductor materials that have the possibility of meeting the criteria for a viable photoelectrochemical (PEC) hydrogen-producing device.
- Design and synthesize multi-junction devices for high efficiency water splitting.

Technical Barriers

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

- (Y) Materials Durability
- (Z) Materials Efficiency
- (AB) Bulk Material Synthesis
- (AC) Device Configuration Designs

Technical Targets

The 2013 technical targets from the MYPP PEC hydrogen production goals are as follows:

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

Accomplishments

- Characterized several InGaN compositions grown by molecular beam epitaxy that appear to have strong potential for unbiased water splitting.
- Characterized thin-film SiN grown by hot wire chemical vapor deposition that, under certain conditions, appear to be capable of water splitting.
- Grew CuGaSe₂ material via electrodeposition for semiconductor material synthesis without the use of high vacuum techniques.
- Synthesized and characterized nanostructured ZnO doped with N, Cu, and Ga generated from the theory-synthesis-characterization cycle; observed enhanced photocurrents by band gap reduction, but films were unstable in contact with electrolyte.
- Calculated band structures and absorption characteristics of CoAl oxides and ZnO:GaN solid solutions.
- Synthesized nanocoral ZnO structures with large surface areas that demonstrated enhanced photocurrents compared to compact ZnO films.



Introduction

Photoelectrochemistry combines a light-harvesting system and a water-splitting system into a single monolithic device. A semiconductor immersed in aqueous solution comprises the light-harvesting system. The catalyzed surface of the semiconductor is one part of the water-splitting system, and the other is another electrode in a separate compartment. The key is to find a semiconductor system that can efficiently and sustainably collect solar energy and direct it toward the water splitting reaction.

At present, metal oxides (in particular TiO₂, WO₃, Fe₂O₃) are considered to be primary candidates; however, none of them fulfill the requirements for a successful PEC material. Finding novel materials and approaches that promise to fulfill all the MYPP requirements in one material class would be a significant advance. While stability is important for viable PEC conversion devices, it cannot be the determining factor in choosing PEC material sets. The focus of research in the PEC community on (mainly) oxides for the last 30 years has produced no successes; efficiencies remain abysmally low. A new approach and methodology is warranted to explore new materials with the capability of reaching the efficiencies needed for commercial devices. One can then discuss approaches that can lead to the necessary lifetimes.

Approach

Our approach is two-pronged: (i) study the current material sets used in commercial solar cells, and (ii) perform semiconductor materials discovery and development for new materials that could have application to PEC water splitting. The former represent a relatively little-studied area for PEC research and, since these materials already meet the efficiency requirement, we consider this to be an important area. For the second approach, we employ a multifaceted approach to materials discovery that includes theoretical calculations to identify potentially promising candidates, synthesis of novel semiconductors, and characterization of their physical and PEC properties. We then feedback the results for the next iteration of calculations.

Results

Nitride Materials

Several InGa_{0.25}N samples grown by molecular beam epitaxy by the National Center for Photovoltaics at NREL were characterized. These mixed group III-nitride samples of composition (In_{0.25}Ga_{0.75}N and In_{0.50}Ga_{0.50}N) were grown on n-SiC substrates. The samples were very thin, around 500 nm.

Photocurrent spectroscopic analysis of In_{0.25}Ga_{0.75}N indicated the presence of both an indirect and direct transition, where the indirect E_g was found to be 2.13 eV and the direct transition equal to 2.39 eV. Likewise for In_{0.50}Ga_{0.50}N, both types of transitions were observed. The measured energies varied across electrodes fabricated from a wafer of a single sample run. The indirect E_g and direct transition averages were 1.55 ± 0.07 eV and 1.94 ± 0.04 eV, respectively. Theoretical calculations on electronic band structure predict a direct transition band gap, but our analysis points to an indirect electronic transition band gap possibly due to an impurity level in these samples.

The flatband potential (V_{fb}) values were determined by Mott-Schottky (M-S) analysis, illuminated open circuit potential (OCP) measurements and photocurrent onset. Perhaps due to the instability of the In_{0.25}Ga_{0.75}N and In_{0.50}Ga_{0.50}N samples, measured V_{fb} values showed no agreement either between techniques or across electrodes made from the same wafer. M-S derived V_{fb} indicate the band edges straddle the water redox potentials across the pH spectrum, but illuminated OCP indicate the conduction band is too low to drive the hydrogen evolution (reduction) reaction. Both alloys were also found to degrade in 3 M H₂SO₄ and 1 M KOH. The position of the flatband potentials for both In_{0.25}Ga_{0.75}N and In_{0.50}Ga_{0.50}N could not unequivocally be located, thus two-electrode measurements were attempted to determine water splitting capabilities.

Small anodic currents were observed at short circuit conditions during the two-electrode current density-voltage (J-V) tests in sparged solution. In 3 M H₂SO₄, In_{0.25}Ga_{0.75}N was found to pass approximately 12 $\mu\text{A}/\text{cm}^2$ of anodic current at zero applied potential and similarly in 1 M KOH, $\sim 16 \mu\text{A}/\text{cm}^2$ (Figure 2). For In_{0.50}Ga_{0.50}N, the current density was lower, 0.6 $\mu\text{A}/\text{cm}^2$ in 3 M H₂SO₄ and 0.3 $\mu\text{A}/\text{cm}^2$ in 1 M KOH. After the In_{0.50}Ga_{0.50}N surface was treated with a platinum catalyst, the anodic current density at zero applied potential in 3 M H₂SO₄ was observed to increase to 2.3 $\mu\text{A}/\text{cm}^2$ (Figure 1). This result could indicate that the anodic short circuit current is water splitting and not photocorrosion since platinum surface treatments increase the former and decrease the latter. However, the observed short circuit current densities were found to be disappointingly lower than that predicted from the materials' band gaps but perhaps not unexpected with these new materials.

The most promising result was the reduction of the E_g , as the 3.4 eV band gap of GaN of was lowered to 2.13 eV for In_{0.25}Ga_{0.75}N and 1.55 ± 0.07 eV for In_{0.50}Ga_{0.50}N; however, where GaN exhibits a direct band gap, both InGa_{0.25}N materials show indirect band gaps again perhaps due to some impurity.

We also characterized three InGa_{0.25}N sample compositions (In_{0.2}Ga_{0.8}N, In_{0.3}Ga_{0.7}N, In_{0.35}Ga_{0.65}N) obtained from Los Alamos National Laboratory (LANL). The results were very similar to those obtained from the NREL samples (indirect gap, ambiguous V_{fb} , appearance of low efficiency water splitting), but the initial results warrant further investigation of these materials.

Thin-Film SiN System

PEC characterization was conducted on hot wire, chemical vapor deposited SiN on stainless steel

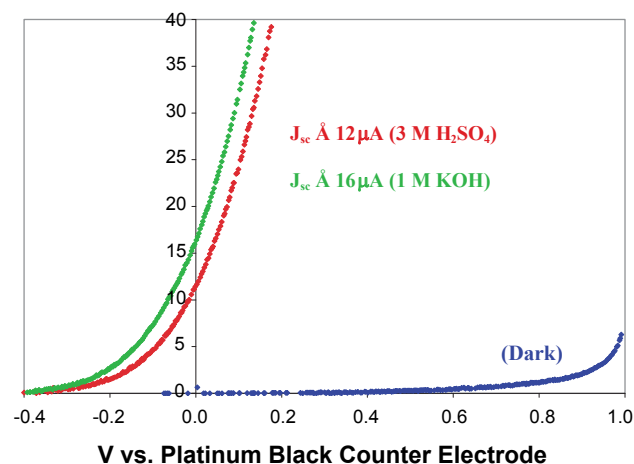


FIGURE 1. In_{0.25}Ga_{0.75}N current density at zero applied potential (y-intercept) in 3 M H₂SO₄ and 1 M KOH; data were collected under AM 1.5 illumination with a tungsten bulb.

substrates. We did this to determine the band gap and band edge alignment. Corrosion analyses were also conducted in a basic environment.

All of the SiN samples exhibited indirect transitions, and n-type behavior as the open-circuit potential shifted negative upon illumination. There also appears to be a substantially linear trend as nitrogen content increases (Figure 2). If nitrogen content is increased 1%, band gap increases about 0.02 eV. It appears that the higher nitrogen content samples (14-16%) exhibited indirect transition band gaps in the ideal range for water splitting (>1.7 eV). Because the material has an indirect band gap the photon penetration depth is most likely deeper than the material thickness and more material is needed to absorb all above-gap light.

Pinholes present in the as deposited films left the stainless steel substrate exposed to the electrolyte and precluded flatband potential determination in these SiN samples.

PEC characterization was done for SiN samples grown by hot wire chemical vapor deposition on fluorine doped tin oxide (FTO) coated glass substrates. The less reactive FTO substrates allow for band edge alignment analyses to be completed even if pinholes remain. The deposition time was extended to yield thicker samples. Preliminary results from illuminated OCP are fairly promising. Although most of the flatband potentials found from this technique fall below the hydrogen redox potential, they are not far off and in a few cases they exceed the potential. The data indicate that under some conditions these materials should be capable of photoelectrolysis. The water-splitting capability will be reported in the next annual report.

Thin-Film Materials: CIS-Based System

Electrodeposition of CuInSe_2 and Cu(In,Ga)Se_2 thin films for photovoltaics has been reported, however the gallium content in these materials is low. Gallium

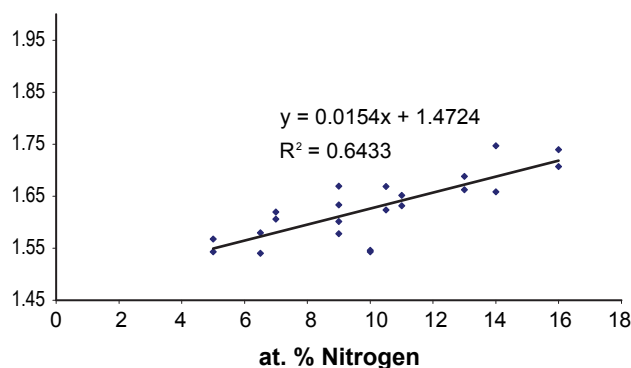


FIGURE 2. Indirect Transition Band Gaps of SiN at Various Nitrogen Concentrations

incorporation has previously been shown to be difficult to obtain via electrodeposition due to its exceedingly negative reduction potential in aqueous solution. Thus, CuGaSe_2 has not been electrodeposited, due to the difficulty in obtaining adequate amounts of gallium in the film.

We accomplished the electrodeposition of high-quality (well-ordered large crystallites) of Cu_3Se_2 on the transparent conducting oxide FTO. Although there is no detectable Ga present in this film, the uniformity and size of the crystal grains (0.5-1.0 microns) is ideal and represents the first highly ordered electrodeposited films made on the FTO substrate. By treating Cu_3Se_2 with evaporated Ga, we have recently been able to achieve high-quality CuGaSe_2 thin-films. The two-step synthesis is not ideal, but it represents progress because of the quality of the precursor (Cu_3Se_2) prepared by the inexpensive and scalable electrodeposition route. FTO is an important substrate since it is a transparent conducting oxide that allows mating of multiple layers in a tandem cell structure as envisioned for this CGS material.

Scanning electron microscopy (SEM) of the electrodeposited films on FTO reveal large Cu_3Se_2 crystallites that span the whole width of the film (Figure 3). This is an ideal configuration since there are no grain boundaries between the two locations of charge collection, the electrolyte on the surface, and FTO back contact. Thin-film materials that have this microstructure typically have high quantum efficiencies. The X-ray diffraction peaks for the electrodeposition are encouraging and indicates a quality Cu_3Se_2 film, approaching the quality of the FTO, which was deposited using chemical vapor deposition.

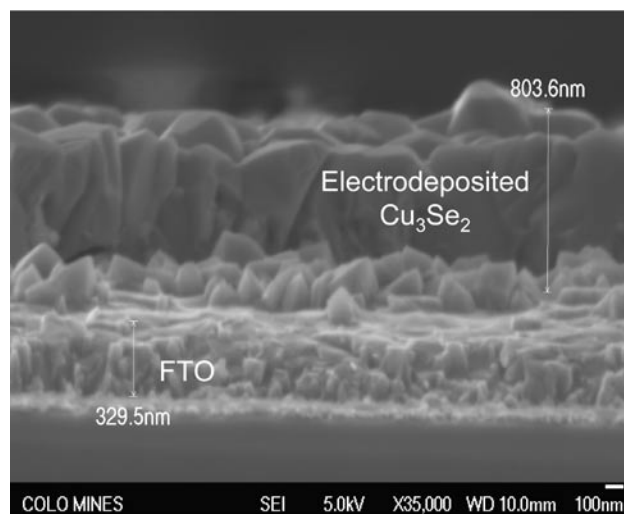


FIGURE 3. SEM Image of Electrodeposited Cu_3Se_2

Synthesis and Characterization of Oxide Semiconductors

ZnO:(Ga, N) thin films were synthesized by dispersing Ga₂O₃ powders in Zn targets and using reactive radio frequency (RF) magnetron sputtering, with post-annealing. The RF powers were used to control the compositions of the films. We found that the sputter yield of GaN is much greater than that of ZnO. ZnO:(Ga, N) thin films with reduced band gap and increased crystallinity were successfully synthesized. The optical and PEC properties of ZnO:(Ga,N) films demonstrated enhanced conversion of visible light into photocurrent as compared to either ZnO and GaN alone, but the material lacked stability during the PEC characterization techniques.

ZnO nanocoral structures were synthesized by a two-step process: the deposition of Zn metal thin films followed by thermal oxidation at 500°C in a quartz tube furnace with flowing O₂. Zn metal thin films were deposited at room temperature on transparent conducting oxide (F-doped SnO₂)-coated glass using RF magnetron sputtering and a pure Zn metal target. The RF power was observed to have a great influence over the grain size and orientation of the synthesized Zn metal films and ultimately the microstructure of the thermally oxidized ZnO films. A set of Zn films was synthesized under the same growth conditions except with a variation in RF powers of 35, 50, 100, 150, and 200 W. After thermal oxidization, only those samples deposited with RF powers of 50 and 100 W exhibited the nanocoral structure. The synthesis of large-area and uniform nanocoral structures is repeatable. The nanocoral films exhibited higher photocurrents, most likely due to enhanced carrier transport properties, as evidenced by the sharp transitions between dark and photocurrent obtained during chopped light experiments.

We have also started to synthesize CoAl₂O₄ thin films, mentioned in the theory report, from Al₂O₃ and Co₃O₄ targets.

Conclusions

- InGa_N materials from NREL and LANL were characterized and demonstrated some promising results; stability of the initial films was questionable.
- Silicon nitride films were characterized; preliminary data indicated a tunable indirect transition band gap and the material could be capable of PEC; these films might be a stable coating if a pinhole free deposition could be achieved.
- Electrodeposition for CuGaSe₂ film formation showed success in the deposition of highly ordered Cu₃Se₂.

- Theory was used to predict some promising oxide compositions that were synthesized and characterized; the stability and carrier transport properties hamper the PEC performance of these materials despite their ability to absorb visible light.
- Synthesizing highly nanostructured ZnO improved the transport properties and might be useful in the synthesis of future oxide materials that have more appropriate band edge positions and stability.

Future Directions

Continue to synthesize and characterize nitride materials (GaNP, GaInPN, InGa_N, Si_N) for higher efficiencies and longer lifetimes; investigate thin-film materials as low-cost water-splitting systems.

Evaluate additional PEC semiconductor candidates in collaboration with others.

- Develop coatings that act as catalysts and provide corrosion protection in PEC systems.
- Develop and evaluate multi-junction structures for high efficiency.
- Continue to use theory to identify promising oxide semiconductor candidates for synthesis and characterization.

FY 2008 Publications/Presentations

Papers

1. Kwang-Soon, A.; Yanfa, Y.; Sudhakar, S.; Deutsch, T.; Turner, J.; Al-Jassim, M. "Enhanced photoelectrochemical responses of ZnO films through Ga and N codoping." *Appl. Phys. Lett.* Vol. 91, p. 231909 (2007).
2. Kwang-Soon, A.; Sudhakar S.; Deutsch, T.; Chun-Sheng J.; Yanfa Y.; Al-Jassim, M.; Turner, J. "Enhancement of photoelectrochemical response by aligned nanorods in ZnO thin films." *Journal of Power Sources*. Vol. 176, p. 387 (2008).
3. Sudhakar, S.; Kwang-Soon, A.; Yanfa Y.; Deutsch, T.; Chrastowski, K.M.; Turner, J.; Al-Jassim, M. "Carrier concentration and tuning of band gap-reduced p-type ZnO films by codoping of Cu and Ga for improving photoelectrochemical response." *J. Appl. Phys.* Vol. 103, p 073504 (2008).
4. Kwang-Soon, A.; Deutsch, T.; Yanfa Y.; Chun-Sheng J.; Perkins, C.; Turner, J.; Al-Jassim, M. "Synthesis of band gap-reduced p-type ZnO films by Cu incorporation." *J. Appl. Phys.* Vol. 102, p. 023517 (2007).
5. Kwang-Soon, A. Yanfa Y.; Se-Hee, L.; Deutsch, T.; Turner, J.; Perkins, C.; Al-Jassim, M. "Photoelectrochemical Properties of N-incorporated ZnO films Deposited by Reactive RF Magnetron Sputtering" *J. Electrochem. Soc.* Vol. 154, p. B956 (2007).

6. Turner, J.A.; Ghirardi, M.L.; Evans, R.J.; Blake, D. "Renewable hydrogen production." *Int. J. of Energy Res.* Vol. 32, p. 379-407 (2008).

Presentations

1. "Photoelectrochemical Characterization of InGaN Semiconductors for Hydrogen Generation from Sunlight and Water." Presented at the 212th meeting of the Electrochemical Society, October 7-12, 2007. Washington, D.C.

2. "Materials Issues for Photoelectrochemical Water Splitting: Chalcopyrite Thin-Films and III-V Nitrides." Presented at the International Symposium on Materials Issues in a Hydrogen Economy, November 12, 2007. Richmond, Virginia.

3. "InGaN Semiconductors for Photoelectrolysis." Presented at the 235th American Chemical Society National Meeting and Exposition, April 7, 2008. New Orleans, Louisiana.

4. "Materials Issues for Photoelectrochemical Water Splitting: Searching for the "Holy Grail." Presented at the American Chemical Society meeting, 2nd Symposium on Hydrogen from Renewable Sources and Refinery Applications, April 6, 2008. New Orleans, Louisiana.