Jeff Head received his B.S. in chemistry from Colorado State University in the spring of 2006. As an undergraduate Jeff worked with Dr. Bruce Parkinson on a combinatorial analysis of metal oxides capable of driving the water-splitting reaction for hydrogen production. Before and after his senior year at CSU Jeff completed two Science Undergraduate Laboratory Internships (SULI) at the National Renewable Energy Laboratory (NREL). While at NREL the focus of his studies was to carry out the photoelectrochemical characterization of various nitride compounds. Specifically, the goal of the research was to determine the water-splitting capabilities of the compounds with light as the only energy input. Advising him on the project was Dr. John Turner (NREL). Jeff is currently pursuing graduate studies in analytical chemistry at the University of Arizona for his Ph.D. under the direction of Dr. Neal R. Armstrong.

John A. Turner, Ph.D., is a Principal Scientist at NREL. He received his B.S. degree from Idaho State University, his Ph.D. from Colorado State University, and completed a postdoctoral appointment at the California Institute of Technology before joining the Laboratory. His research is primarily concerned with enabling technologies for the implementation of hydrogen systems into the energy infrastructure. This includes direct conversion (photoelectrolysis) systems for hydrogen production from sunlight and water, advanced materials for high temperature fuel cell membranes, and corrosion protection for fuel cell metal bipolar plates. Other work involves the study of electrode materials for high energy density lithium batteries and fundamental processes of charge transfer at semiconductor electrodes. He has twice received the Midwestern Research Institute President's Award for Exceptional Performance in Research. In addition, he has received the Hydrogen Technical Advisory Panel award for Research Excellence, an Idaho State University Outstanding Achievement Award (2006), and two Outstanding Mentor Awards from the U.S. Department of Energy for his work with undergraduate students. He is the author or co-author of over 90 peer-reviewed publications in the areas of photoelectrochemistry, fuel cells, batteries, general electrochemistry and analytical chemistry.

ANALYSIS OF THE WATER-SPLITTING CAPABILITIES OF GALLIUM INDIUM PHOSPHIDE NITRIDE (GaInPN)

JEFF HEAD AND JOHN TURNER

ABSTRACT

With increasing demand for oil, the fossil fuels used to power society's vehicles and homes are becoming harder to obtain, creating pollution problems and posing hazard's to people's health. Hydrogen, a clean and efficient energy carrier, is one alternative to fossil fuels. Certain semiconductors are able to harness the energy of solar photons and direct it into water electrolysis in a process known as photoelectrochemical water-splitting. P-type gallium indium phosphide (p-GaInP2) in tandem with GaAs is a semiconductor system that exhibits water-splitting capabilities with a solar-to-hydrogen efficiency of 12.4%. Although this material is efficient at producing hydrogen through photoelectrolysis it has been shown to be unstable in solution. By introducing nitrogen into this material, there is great potential for enhanced stability. In this study, gallium indium phosphide nitride $Ga_{1-y}In_yP_{1-x}N_x$ samples were grown using metal-organic chemical vapor deposition in an atmospheric-pressure vertical reactor. Photocurrent spectroscopy determined these materials to have a direct band gap around 2.0eV. Mott-Schottky analysis indicated p-type behavior with variation in flatband potentials with varied frequencies and pH's of solutions. Photocurrent onset and illuminated open circuit potential measurements correlated to flatband potentials determined from previous studies. Durability analysis suggested improved stability over the $GaInP_2$ system.

INTRODUCTION

Today humans collectively consume the equivalent of approximately 13 terawatts of energy; 85% of that comes from fossil fuels that release carbon dioxide, the primary greenhouse gas, into the atmosphere [1]. Moreover, pollution from fossil fuels used in society today creates many environmental and health problems. In addition, global warming is thought to be directly linked to the exponentially increasing anthropogenic carbon dioxide concentrations in the atmosphere that has been taking place over the past 200 years [2]. Several renewable energy sources exist that are capable of providing a cleaner form of energy from sun and wind power. For example, hydrogen is a clean and efficient energy carrier and has great potential when coupled to renewable energy resources. Various renewable technologies, such as biomass and geothermal power, can produce hydrogen fuel for use when it is not sunny or windy.

One of the most efficient ways of producing hydrogen is using sunlight to directly split water into hydrogen and oxygen on semiconductor surfaces [3]. An electric potential difference of at least 1.23V is required to split water into hydrogen and oxygen. Typically, a cathodic overpotential of 100mV and an anodic overpotential of 200mV are also required, so a band gap of at least 1.53eV is necessary for splitting water. It is important to take note that as band gap increases the portion of the solar spectrum the semiconductor can absorb diminishes [4]. In addition to having an adequate band gap, the semiconductor should exhibit stability in solution. Another key requirement relates to the energetic positions of the valence and conduction band edges at the solution interface.

Specifically, the energy bands must encompass the potentials at which the following half reactions occur:

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad -0.56\text{V (vs. Ag/AgCl)} \qquad (1)$$

$$2H_2O \rightarrow O_2 + 4e^{-} + 4H^{+} \quad 0.67\text{V (vs.Ag/AgCl)} \qquad (2)$$

The potentials associated with (1) and (2) will vary according to the Nernstian dependence on solution pH. The values given above are for a pH 6 electrolyte.

Semiconductors are classified as either n-type or p-type. Semiconductors in which the majority charge carriers are electrons are n-type whereas those in which the majority charge carriers are holes are p-type [5]. Oxygen evolution takes place on the surface of n-type materials and hydrogen evolution takes place on the surface of p-type materials. Preliminary characterization of semiconductors is carried out using open circuit potential measurements, photocurrent measurements, and Mott-Schottky analysis [6]. In estimating the location of the band edges one must factor in the Fermi level of the material, which for n-type materials lies just below the conduction band, and for p-type materials lies slightly above the valence band, as seen in Diagram 1.

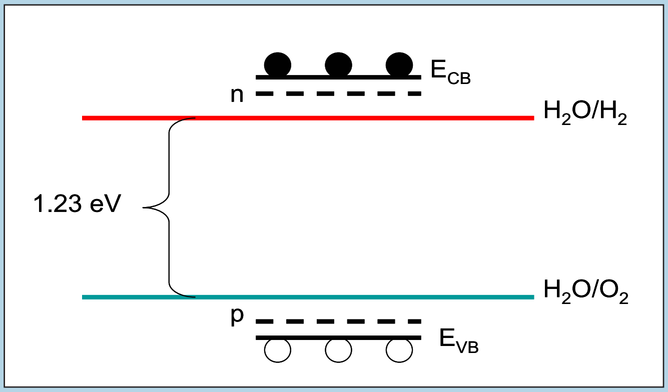

Diagram 1. Location of Fermi levels (dotted lines) for both p-and n-type semiconductors with respect to the water redox potentials.

The flatband potential, E_{fb}, the potential at which there is no net transfer of charge, and hence no band bending, or the energy of the Fermi level, which is the level at which the electrons are located, when the bands are flat, can be estimated from Mott-Schottky plots [5], based on the following equation:

$$\frac{1}{C^2} = \frac{1.41x10^{32}}{\varepsilon N_D}\left[E - \left(V_{fb}\right)\frac{kT}{e}\right] \qquad (3)$$

where C is the capacity of the space charge layer, ε is the static dielectric of the semiconductor (assumed to be 10), e is the electronic charge, N_D is the doping density, and E is the electrode potential [5]. Plotting the inverse square of capacitance versus voltage will give a linear plot with x-intercept equal to the flatband potential and a slope inversely proportional to the doping density. Similarly, measuring the illuminated open circuit potential can give the location of the Fermi level at flatband conditions.

Current studies show that when p-$GaInP_2$ is grown in tandem on a p/n GaAs substrate, water-splitting is successful with 12.4% solar-to-hydrogen efficiency [8]. Although this system exhibits efficient photoelectrolysis, studies show that it is susceptible to photoinduced corrosion, rendering it useless after several hours of irradiation [7]. A possible solution to the instability of these materials in solution is the introduction of nitrogen into the system.

Through metal-organic chemical vapor deposition (MOCVD), various ratios of gallium indium phosphide to nitride can be achieved when grown on a gallium phosphide substrate. The goal of this research is to isolate a stable epilayer material capable offering protection to a water splitting photoelectrode.

METHODS

Preparation of Samples

Gallium indium phosphide nitride samples were grown by metal-organic chemical vapor deposition (MOCVD) in an atmospheric-pressure vertical reactor. Zinc-doped gallium phosphide substrates were used as the growth template at 650°C. Triethylgallium, nitrogen trifluoride, trimethylindium, and phosphine sources were used, with hydrogen as the carrier gas (Triethylgallium and trimethylindium were OptoGrade from Rohm and Hass Electronics, the phosphine was 99.9999% from Air Products and nitrogen trifluoride was 99.99% from Air Products). X-ray diffraction (XRD) measurements of the samples were taken to determine the lattice parameters used to estimate compositions. The XRD pattern was measured by means of a four-circle Scintag X-1 diffractometer (Thermolab) with a copper Kα anode source. Once grown, electrodes of the samples were constructed using copper wire and epoxy. Samples were cleaved using a diamond scribe and lens paper and were mounted to coiled copper wire pieces within glass tubing using silver paint. The colloidal silver liquid was obtained from Ted Pella, Inc. Samples were then dried at 80°C for approximately 20 minutes. Edges of the semiconductor and exposed copper wire were then covered with HYSOL 9462 epoxy and left to dry overnight. After 24 hours the electrodes were again placed in the oven at 80°C for 2 hours. The 9462 epoxy was then covered with HYSOL E-120 epoxy, which was left to dry at room temperature for 3 hours, followed by being placed in the oven at 80°C for 2 hours. Surface areas of the electrodes were determined with a photocopy technique which compared the ratio of the photocopy area mass to that of a standard 1 cm^2 cutout [9].

Photocurrent Spectroscopy

A Stanford Research Systems chopper model SR540 along with a Stanford Research Systems Lock-in amplifier model SR830 DSP, and a PAR Potentiostat/Galvanostat Model 263A was used for photocurrent spectroscopy, along with Tungsten light source model LPS-220 at 75 Watts from Photon Technology International PTI. The experiments were performed in a glass cell with a borosilicate front face. The working electrodes were submerged in hexaammineruthenium (III) chloride in pH 2 buffer with a platinum counter electrode, and silver/silver chloride reference electrode, and scanned from 350 to 700nm using a 345nm filter to block second order diffraction.

Various electrochemical measurements were taken using GaInPN as the working electrode, along with a platinum counter electrode, and a silver/silver chloride reference electrode. This configuration was in a three port glass cell containing separate solutions of 3M H_2SO_4 (J.T. Baker), pH 2-pH 12 buffer (Hydrion Buffer Kenvelopes 280-7.00), and 1M KOH (J.T. Baker).

Cyclic Voltammetry

Using a potentiostat and frequency response analyzer (Solartron 1286 electrochemical interface/SI 1260 Impedance/Gain-Phase Analyzer), cyclic voltammetry scans were taken in the dark and light (100mW/cm^2), to see if the material passed anodic or cathodic photocurrent. Mott-Schottky analysis was carried out to determine flatband potentials as well as doping densities. Intensely illuminated open circuit potential measurements were taken using a DC power supply with a tungsten bulb at 10A (Oriel Corporation Model 66183 OSRAM Tungsten Bulb) for determining flatband positions.

Platinum Catalyst Surface Treatments

Platinum catalyst surface treatments were carried out using a two electrode technique of shorting the counter electrode, CE, and reference electrode, REF, leads connected to a platinum counter electrode, where samples were etched with concentrated sulfuric acid for approximately 20 seconds. Samples were then electroplated using a current relative to their surface areas in yellow chloroplatinic acid solution. These scans allowed for measurement of the photocurrent onset, another technique used to determine flatband potentials.

Durability Analysis of the Electrodes

Durability analysis of the electrodes was carried out using platinized electrodes and a DC powered lamp with a neutral density filter to attenuate the light intensity. After all the electrochemical data was collected the electrodes were disassembled for profilometry analysis to determine the amount of etching of the sample. Durability solutions were saved for future inductively coupled proton mass spectrometry, ICP-MS, analysis.

Software

Cyclic voltammetry, open circuit potential measurements, platinization, and durability measurement analyses were carried out using CorrWare2 software, and Mott-Schottky analysis was carried out using Zplot software from the vendor Scribner Associates International.

RESULTS

Samples were grown using metal organic chemical vapor deposition at 608 torr for 1 hour which resulted in 1µm thick materials of approximately 4cm^2. The substrate was p-type zinc doped gallium phosphide which served as the template for single crystal epilayer growth. X-ray diffraction measurements of atomic spacing resulted in estimated compositions of $Ga_{.95}In_{.05}N_{.025}P_{.975}$ (MF933) and $Ga_{.96}In_{.04}N_{.024}P_{.976}$ (MF932).

Once the samples were manufactured into electrodes, photocurrent spectra of the materials were taken and the tungsten lamp spectra was divided out [11] giving a normalized photocurrent. The direct band gap of the sample was estimated using a plot of the photocurrent squared vs. photon energy, as shown in Figure 1. The x-axis intercept of the linear portion of this curve gives the figure of merit. Out of thirteen electrodes tested, the band gap varied only slightly, from 1.99 to 2.01eV (Table 1).

In a solution of 3M H_2SO_4 with a working, counter, and reference electrode, potential as a function of current resulted in a wide shift in cathodic current when illuminated, as seen in Figure 2. For both sample compositions the current shifted an order of magnitude upon illumination. Minimal shifts occurred when tests took place in pH's ranging from 2-12, and 1M KOH.

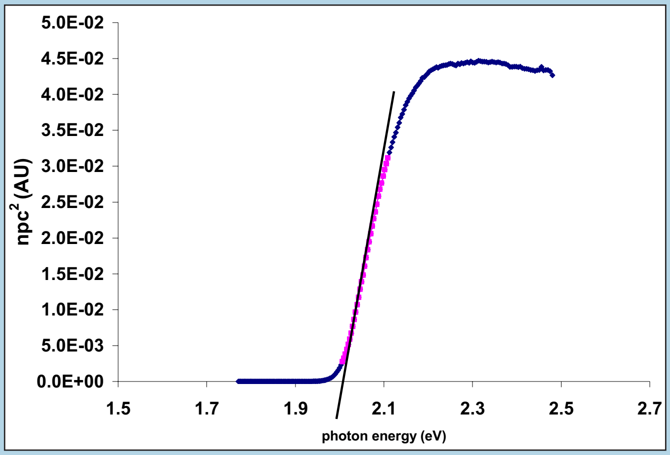

Figure 1. Band gap plot of Ga.96In.04N.024P.976 from 500 to 700nm in Hexaammineruthenium (III) Chloride with a 495nm filter with extrapolated intercept from normalized photocurrent squared versus photon energy (eV).

Material	Direct Band Gap (eV)
Ga.96In.04N.024P.936	
1	2.00
2	2.00
3	2.00
4	2.00
5	2.00
6	2.01
7	2.01
Ga.95In.05N.025P.975	
1	2.00
2	2.00
3	1.99
4	1.99
5	1.99
6	2.00

Table 1. Summary of band gap values for each respective composition with numbered electrodes tested with an error of ± 0.01eV.

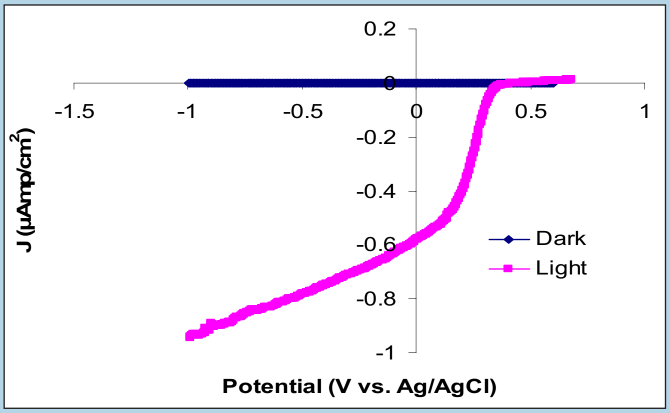

Figure 2. I-V plot in 3M H_2SO_4 of $Ga_{.96}In_{.04}N_{.024}P_{.976}$ in dark and light conditions with a fiber optic lamp at 0.100W/cm^2.

Mott-Schottky analysis was performed on each sample in 3M H_2SO_4 while varying the frequency between 1000 and 20,000Hz in the dark and light. All plots obtained from analysis revealed doping densities on the order of 10^{13} to 10^{16}/cm^3, with varied aphysical x-intercepts, and all negative slopes, indicative of p-type behavior.

Illuminated open circuit potential, OCP, measurements were taken in a range of solution pH's and the values are assumed to be close to the flatband potential (Figure 3). Photocurrent onset measurements on platinized electrodes were also used to estimate the flatband potential (Figure 3). The difference between the two measurements is attributed to the overpotential of hydrogen evolution from the photocathode. Both techniques demonstrated a steady increase in (flatband) potential with an increase in pH, as is typically observed in semiconductors.

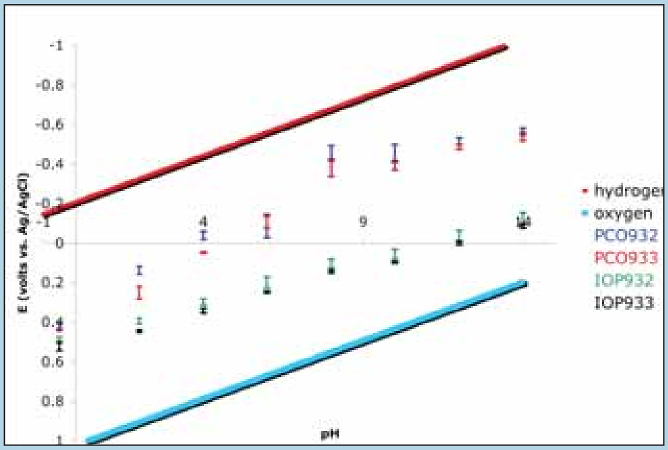

Figure 3. Illuminated open circuit potential (OCP) and photocurrent onset (PCO) measurements in pH values ranging from -0.5 to 14.

Durability analysis was performed in 3M sulfuric acid with Triton X-100 in a two-electrode cell with a platinum black counter electrode. A DC lamp was used with a water filter and neutral density filter to attenuate light to AM1.5 [10] intensity. Samples passed a cathodic current of 5mA/cm^2 for 24 hours using the solarton as a galvanostat. Electrodes were disassembled and etching was probed with a profilometer with an average depth of .13µm. Solutions were saved for future ICP-MS elemental analysis.

DISCUSSION AND CONCLUSIONS

The linear portion in the plot of normalized photocurrent squared vs. photon energy indicates a direct transition is present in these materials. The extrapolated intercept from this line results in a direct band gap of 2.00 ± 0.01eV (Figure 1). The results are tabulated in Table 1. GaInPN exhibits an appropriate band gap to drive the water-splitting reaction.

The sign of photocurrent observed in I-V scans can indicate whether a semiconductor is p-type or n-type (Figure 2). For p-type semiconductors, cathodic photocurrent arises at potentials negative of the flatband potential because of the orientation of the electric field in the space charge region. This behavior was observed inferring that these GaInPN materials are p-type despite being grown without the intentional introduction of dopants. In Figure 2 photocurrent onset can be observed near a positive potential of ~0.4V, where during the scan bubble evolution took place on the surface of the working electrode suggesting hydrogen evolution.

Mott-Schottky analysis is another good indicator of p- and n-type semiconductor characteristics. The slope of an M-S plot (1/C^2 vs. applied potential) can reveal whether the material is p-type (negative slope) or n-type (positive slope) [5]. All electrodes tested displayed the suggested p-type negative slope (Figure 5). However, x-intercept values varied from 40 to 0.4V, casting doubt on the ability of this technique for flatband potential measurements. For example, looking at Figure 5, an x-intercept of 0.33V suggests a valence flatband potential of 0.33V.

Illuminated open circuit potential measurements give a good approximation of the location of the Fermi level of the material. Photocurrent onset, which looks at photocurrent squared vs. potential of platinized electrodes, also gives a good idea of the valence flat band potential in addition to the overpotential of hydrogen evolution. The illuminated open circuit potential measurements lie more positive than the photocurrent onset measurements but the Fermi level is too negative to allow water-splitting. Even though the band gap of this material is sufficient for water-splitting and the conduction band lies more negative of the reduction potential, the valence band does not lie more positive than the oxidation potential. This suggests that GaInPN is not capable of splitting water when grown on a GaP substrate.

Durability analysis was carried out as described above. In this study a (cathodic) current of -0.408 to -0.577µA was applied resulting in a current density of 5mA/cm^2. The solution was collected for future ICPMS and semiconductor materials were profiled for depth analysis, as seen in Figure 4. The average depth for all material compositions was .13µm, suggesting a corrosion rate of .13µm/24hrs. This is a significant improvement over p-$GaInP_2$, which has a corrosion rate of 1-2µm/24hrs. This result suggests that the addition of nitrogen enhances the stability of $GaInP_2$.

In conclusion, gallium indium phosphide nitride was studied for its water-splitting and corrosion-resistance capabilities. The results of this study suggest that GaInPN grown undoped on a Zn doped GaP substrate, exhibits p-type semiconductor characteristics

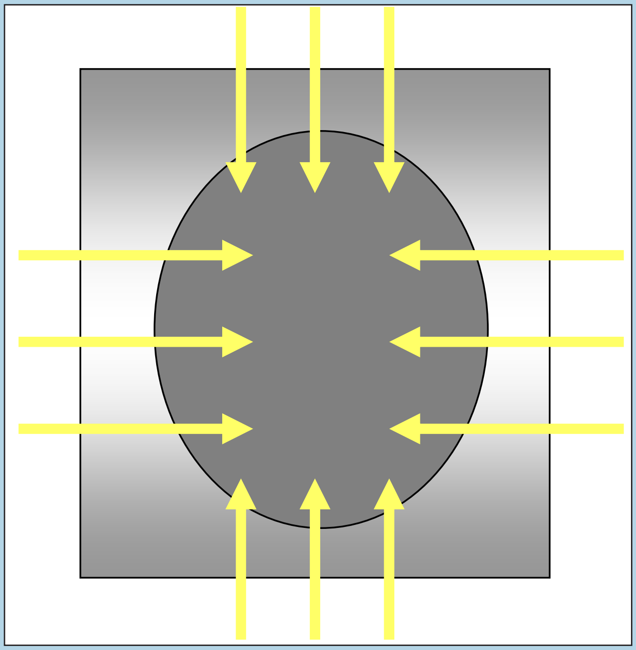

Figure 4. Profilometry scans of typical electrode material for depth analysis with stylus scanning in various locations of the semiconductor material after durability analysis.

with a band gap sufficient to split water, but unfortunately has band edges which lie too negative of the redox potentials for water-splitting to occur. Durability analysis suggests that the addition of nitrogen enhances the stability of the $GaInP_2$ epilayer. Other work currently in progress is looking at GaInPN silicon substrates in a tandem configuration. Future research might involve varying the compositional ratios of each element present. These novel materials may result in a semiconductor that meets the requirements for a photocathode.

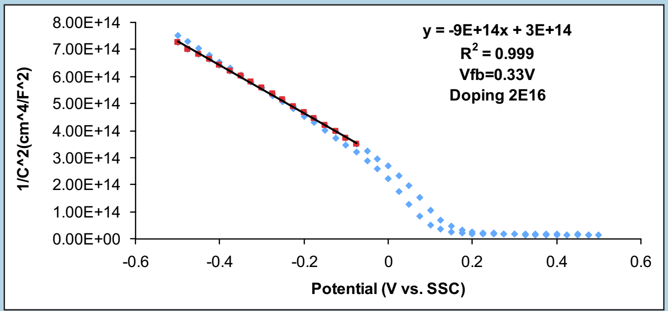

Figure 5. Mott-Schottky scan of GaInPN under illumination in 3M Sulfuric Acid at an applied potential of 20KHz.

ACKNOWLEDGMENTS

This research was conducted at the National Renewable Energy Laboratory in Golden, Colorado. I would like to thank the U.S. Department of Energy, Office of Science for the opportunity to participate in the SULI program for a second term in order to further my knowledge and appreciation of photoelectrochemistry and its applications in renewable energies. I would like to thank Dr. John Turner for inviting me back for a second summer to work in the Turner lab and carry out various photoelectrolysis experiments. I would also like to thank Dr. Todd Deutsch for his expertise in this area of research and for taking the time to further instruct me on the concepts applied in this study. I would also like to thank Dr. John Geisz for growing my samples, and finally I would like to thank my other coworkers in the Hydrogen, Fuel Cells, and Infrastructure Technologies program at NREL.

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[9] The photocopy technique involves using a copying machine as a magnifier. The copy machine is set at a specific

magnification and a copy is made of a piece of graph paper. The electrode whose area is to be measured is then copied at the same magnification. A $1cm^2$ piece of the copied and magnified graph paper cut from the page and the outline of the sample area is cut from the photocopied sample page. Weighing both and taking the ratio then provides an accurate measurement of the sample area.

[10] AM1.5 is Air Mass 1.5 and comes from the ASTM G173 spectra standard and represents the terrestrial solar spectral irradiance incident on an inclined plane at 37° tilt toward the equator, facing the sun (i.e., the surface normal points to the sun, at an elevation 48.81° above the horizon). These conditions are considered to be a reasonable average for the 48 contigous states. The tilt angle selected is approximately the average latitude for the contigous U.S.

[11] The intensity of the light coming from the lamp/monochromator combination is not constant throughout the spectral range of interest. To correct the photocurrent for these intensity variations incident on the sample as a function of wavelength, the output spectrum from the monochromator (as measured with a thermopile with a flat response) is divided into the response of the sample. This of course assumes that the response of the sample is linear with light intensity, which over this intensity range is expected to be true for all samples. Note this is not a background correction, but rather an intensity correction.