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PHOTOELECTROCHEMICAL BASED DIRECT CONVERSION SYSTEMS FOR HYDROGEN PRODUCTION

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Abstract

With an eye towards developing a photoelectrochemical system for hydrogen production using sunlight as the only energy input, two types of systems were studied, both involving multijunction devices. One set of cells consisted of a-Si triple junctions and the other a $GaInP_2/GaAs$ tandem cell combination. Additional investigations were carried out on semiconductor surface modifications to move semiconductor band edges to more favorable energetic positions.

Introduction

An ideal renewable direct hydrogen production system would consist of an efficient light harvesting system and a highly catalytic water electrolysis system as a single monolithic device. This direct conversion system would decompose water directly upon illumination. For a one-step process to be viable, the light harvesting system must generate sufficient voltage to effect the decomposition of water, and the system also must be stable in an aqueous environment. Splitting water into hydrogen and oxygen requires a thermodynamic potential of 1.23 eV at 25 °C. Typical values of the overvoltage for the cathode and anode reactions are 100 mV and 250 mV respectively. An equivalent potential then, of at least 1.6 V is required for a water splitting system.

An illuminated semiconductor immersed in aqueous solution exemplifies such a direct conversion system. These systems have been the focus of a number of researchers for over 20 years. For a single gap semiconductor based direct conversion water splitting system, the fundamental requirement of at least 1.6 V implies a minimum bandgap of 1.8 electron volts. Surface catalysts would also be required in order to bring the overvoltage for the oxygen and hydrogen evolution reactions down to an acceptable level. An additional requirement is that the semiconductor band edges span both redox potentials of the hydrogen and oxygen evolution reactions.

The goal of this research is to develop a stable semiconductor based system that will split water directly. We are focusing our study of these systems in three basic areas: materials research, surface stability and catalysts. NREL's Photovoltaic and Basic Sciences Divisions provide a state of the art resource for new solid state materials that could be used in a direct conversion system. From a study of their materials, we have focused on gallium indium phosphide, $GaInP_2$, as an ideal material for our initial studies. Because its bandgap of 1.83 is ideal for photoelectrolysis, it is a promising semiconducting material for water splitting as a single bap material, and as a test system for our novel multi-junction designs. In general, we believe that semiconducting materials that have indium as a constituent have a greater opportunity for long-term stability in an aqueous environment. In aqueous solution, indium can form a conductive oxide layer that stabilizes the interface. If the surface of the semiconductor becomes damaged, indium ions, under the proper conditions, will form an oxide, ameliorating the surface. This self-healing of the interface will greatly increase the long-term stability of the system. Our work on $GaInP_2$ then is focused on its use as a direct conversion photoelectrochemical water-splitting system

Our past work on single crystal $GaInP_2$ has shown that while its bandgap is sufficient, its bandedges are from 100 to 400 mV more negative than would be ideal. For this material, our approach has been to study the feasibility of inducing changes in the surface to obtain a more energetically favorable situation, as well as engineering solid state designs to integrate a bias voltage to effect the water decomposition reaction. Additional studies include passivating and stabilizing the semiconductor surface, and colloidal platinum catalysts.

A possible low cost direct conversion system for water splitting is one based on amorphous silicon (α-Si). Amorphorous silicon multijunction devices consist of multiple layers of a-Si cells. These multi-layer cells provide higher efficiency than single junction cells and reduce the amount of photodegradation that is common to all a-Si devices. The combination of lower system cost and higher efficiency, represent an important area of research for hydrogen production systems. Further, manufacturing capability for α-Si systems is high, with current production capability of these type of devices at over 10 megawatts per year in the US alone. Our approach here is to work with an industrial collaborator to develop optimized α-Si systems designed specifically for water splitting.

Our discussion this year then will focus on a novel multi-junction concept to split H_2O, HBr and HI, corrosion of $GaInP_2$, surface modification studies, and α-Si multi-junction systems.

Discussion

Technical Approach and Results

Corrosion of III-V Materials

The results of our work with $GaInP_2$ showed that it susceptible to photo-induced corrosion, which can suppress constructive photo-driven redox processes after several hours of irradiation. Identification of solution compositions and additives that stabilize the semiconductor/electrolyte interface will be critical if a stable PEC-based, water-splitting system is to be developed. We have studied the stability of the p-$GaInP_2$ electrode in aqueous electrolytes of different pHs. To find the optimum operating conditions for the p-$GaInP_2$ photocathode, the electrochemical behavior of p-$GaInP_2$ was studied in 10 M KOH, 3 M H_2SO_4, and a phosphate buffer of pH=7. Of particular interest is the electrochemical behavior of the illuminated electrode under both open-circuit conditions and cathodic polarization where hydrogen evolution would occur.

Our results show that upon illumination, anodic processes increase. The effect of light on the anodic current density is greatest in 10 M KOH, less pronounced in neutral solution, and only slight in 3 M H_2SO_4. It should be noted, that under illumination the electronic transition of promoting an electron from the valance band to the conduction band is a bond-breaking transformation in these materials. The electron is promoted from a bonding orbital to an anti-bonding orbital. This bond breaking under illumination increases the susceptibility of the surface to corrosion, giving rise to an increase in the anodic current.

A potentiodynamic test in 3 M H_2SO_4 (Figure 1) showed the onset of the anodic current at ~-0.05 V, which is a much more positive potential than in 10 M KOH. The electrode was passive up to 0.25 V when anodic current density began rapidly increasing with potential. Upon illumination, the cathodic current density was almost constant with potential, indicating a light-limited photocurrent. Unlike what was observed in 10 M KOH, the onset of the anodic current was seen at ~0.180 V, which represents a shift to a more positive potential as compared to the dark. The anodic current densities were only slightly higher than those in the dark, but much lower than the anodic current densities observed for p-$GaInP_2$ in 10 M KOH solution.

The cathodic current density transients in 3 M H_2SO_4 are shown in Figure 2. At -0.15 V the transient showed a relatively low initial value of 20 mA/cm^2, which rapidly decayed with time. At -0.8 V, the initial cathodic current density was ~110 mA/cm^2 and remained almost constant throughout the experiment. A similar current-density transient was observed for a bias of -2.0 V. The current density of 120 mA/cm^2 observed in this experiment was almost the same as that observed in 10 M KOH at the same potential. This indicates the value of the light-limited saturated photocurrent density under the illumination intensity that was used.

In summary, this semiconductor is susceptible to corrosion in the dark in all investigated solutions. Upon illumination, anodic processes grow. Potentiodynamic tests revealed the onset of the anodic current at -1.55 V, -1 V, and -0.05 V in 10 M KOH, 3 M H_2SO_4, and a pH=7 phosphate buffer, respectively. In 10 M KOH, under cathodic polarization, the p-$GaInP_2$ electrode showed a photo-limited current density, however, the current slowly decreased with time due to precipitation of indium-enriched oxide. In neutral solution, the p-$GaInP_2$ is covered by a semi-insulating oxide film, and the observed cathodic photocurrent densities were much lower than those in 10 M KOH and 3 M H_2SO_4. For the p-$GaInP_2$ electrode in 3 M H_2SO_4, the anodic process can be inhibited under relatively low cathodic potentials, giving rise to a stabilized electrode and a stable photocurrent for hydrogen evolution. Our conclusion is that 3 M H_2SO_4 is the solution of choice for photoelectrolysis using p-$GaInP_2$ semiconductor electrodes.

Water Splitting using III-V Tandem Cells Configuration

The first successful direct electrolysis device based on a novel integrated monolithic PEC/PV device showed outstanding hydrogen production efficiency. The basic structure of the device is shown in figure 3. This device is patterned after the well known $GaInP_2$/GaAs p/n,p/n tandem cell device grown at NREL. The solid state tandem cell consists of a gallium arsenide (GaAs) bottom cell connected to a gallium indium phosphide ($GaInP_2$) top cell via a tunnel diode interconnect. Our device differs from the standard solid state tandem cell in that a PEC Schottky type junction has replaced the top p/n junction. This device then is a PEC Schottky barrier device, voltage biased with an integrated PV device. The top junction bandgap of the $GaInP_2$ at 1.83 volts is designed to absorb the visible portion of the solar spectrum and the bottom GaAs junction (bandgap of 1.42 eV) absorbs the near infrared portion of the spectrum transmitted through the top junction. Operationally, under illumination, electrons flow towards the surface and holes towards the back ohmic contact.

For this device configuration to work properly, the GaAs cell must provide sufficient voltage to overcome the bandedge mismatch between the $GaInP_2$ and the water redox reactions and also provide additional voltage to overcome any overvoltage losses from the hydrogen and oxygen evolution reactions.

A photocurrent voltage curve for the mixed PEC/PV device is given in figure 4. Note that the onset of hydrogen occurs before short circuit, indicating a spontaneous water splitting reaction . The efficiency (η) for hydrogen production is calculated using the equation η=(power out)/(power in). The input power is the incident light intensity of 100 mW/cm^2. For the output power, assuming 100% photocurrent electrolysis efficiency, the hydrogen production photocurrent of 11.2 mA/cm^2 is multiplied by 1.23 volts, the ideal fuel cell limit at 25 C. The hydrogen production efficiency calculated by this method is 13.7%.

Photoelectrolysis of HBr and HI Utilizing the Monolithic Combined PV/Photoelectrochemical Device.

We have also used this PV/PEC device to demonstrate the photoelectrolysis of HBr and HI. As expected, this system splits these acids directly upon illumination, using light as the only energy input. In addition, in contrast to water splitting, the device can simultaneously produce electrical energy. In this case, the device not only can produce chemicals, but also electrical energy. The HBr cell operating at zero bias and a light intensity of 380 mW/cm^2 showed a photocurrent density of 37 mA/cm^2 corresponding to 8.1% light to chemical conversion efficiency. The HI cell operating at zero bias and a light intensity of 106 mW/cm^2 showed a photocurrent density of 8.5 mA/cm^2 corresponding to a 2.6% light to chemical conversion efficiency.

Surface Modification Studies

The suppression of corrosion and the control of the energetics is of paramount importance for the development of a viable photoelectrochemical water splitting system. Based on our results on the corrosion of $GaInP_2$, we have initiated work towards the prevention/suppression of photocorrosion and photooxidation of this material. We are studying three parallel approaches, each involving semiconductor surface modification. These three approaches are: 1) adsorption of alkanethiols, 2) alkylation and 3) adsorption of transition metal ions. The adsorption of two transition metal ions, iron and vanadium, showed shifts in the energetics of the photocurrent onset of $GaInP_2$. The shift of the photocurrent for iron is shown in figure 5.

Amorphous Silicon Systems

There are two main technological problems that must be solved before an α-Si based system could operate as a photoelectrolysis device: 1) its bandgap is insufficient to effect the decomposition of water and 2) α-Si is not stable in contact with aqueous electrolytes, it decomposes within a few minutes. The first issue is easily addressed because current state-of-the art α-Si triple junction devices can have voltages greater than 1.8 volts (even up to 2.3v), which is sufficient for water splitting. Stabilized efficiency for these systems can be greater than 10%.

For this work we are partnering with Energy Conversion Devices to grow samples specifically for water splitting. For these samples, two areas of research were of interest to us: 1) a device structures that pushed electrons toward the semiconductor/electrolyte interface and 2) protective coatings for the surface that offered minimum light absorption, but stability at high and low pH. The reason we want electrons to be driven toward the semiconductor electrolyte interface is because we want hydrogen to be evolved from the illuminated surface. Of the two reactions involved in water splitting (hydrogen evolution and oxygen evolution), hydrogen evolution is the easiest, requiring the least amount a catalyst and it has the lowest overvoltage. We also expect that it will be easier to protect a surface under reducing conditions than under oxidizing conditions.

Growing a-Si multijunctions specifically for this purpose, involves growing the a-Si layers in reverse order than what is usually done for the solid state device. Instead of growing the layers in the order n-i-p, they need to be grown in the order p-i-n. We have contracted with ECD to grow this new design.

The results of our latest samples from the subcontract is shown in figure 6. Note that the efficiency for water splitting is rather low, and the curve shows that there is a good deal of series resistance with in the cell. Also, this samples did not have the a-SiC surface protective layer, so some of the resistance could be due to a surface oxide layer being formed. However, we are very encouraged with this result. ECD has raised the efficiency of this reverse design from around 4% to over 9% in less than a year (with very little funding). The PV efficiency is approaching that of the standard PV cells and this should translate to better photoelectrolysis efficiency. We expect a much improvement in this system in the coming year.

Plans for Future Work:

In general, our future work will involve: the identification of new materials and the growth of promising multi-junction systems including designing unique multi-junction systems focused specifically on water splitting; establishment of cooperative efforts to obtain samples or development of in-house growth capabilities; and lifetime testing and efficiency measurements for working systems. Since we have had good success with the III-V PV/PEC system, we intend to increase our efforts with our industrial collaborators to optimize the α-Si multi-junction systems for water splitting. We would like to bring the α-Si multi-junction systems up to the same level of excellence.

The subject of the interaction of colloidal catalysts with the various tandem cell surfaces is also a very important area for future work. More specifically, we will focus on continued investigation of the III-V material system concentrating on tailoring the tandem cell structure specifically for an aqueous environment and the energetics of the water splitting reaction. We will be evaluating various surface treatments to enhance stability and energetics. The semiconductor corrosion mechanisms will also be a point of study.

Major Barriers

In general, the major problems that must be addressed in order to produce a viable system are: stability of the semiconductor/electrolyte interface, and system energetics. Materials and catalysts must be found that protect the semiconductor surface, but allow electrons to pass through unimpeded. While we lack full understanding of the fundamental characteristics of the semiconductor/electrolyte interface, considerable progress has been made. For the a-Si multi-junction cells the design of the water-splitting cells must be optimized for maximum efficiency. For the III-V systems, to maximize their efficiency, materials and designs must be identified for lower voltage, higher current applications. Promising new systems currently under development may directly address this issue.

Figure Captions

Figure 1. Potentiodynamic curves for p-$GaInP_2$ in 3 M H_2SO_4. The E^0 for hydrogen evolution is indicated by the dashed line.

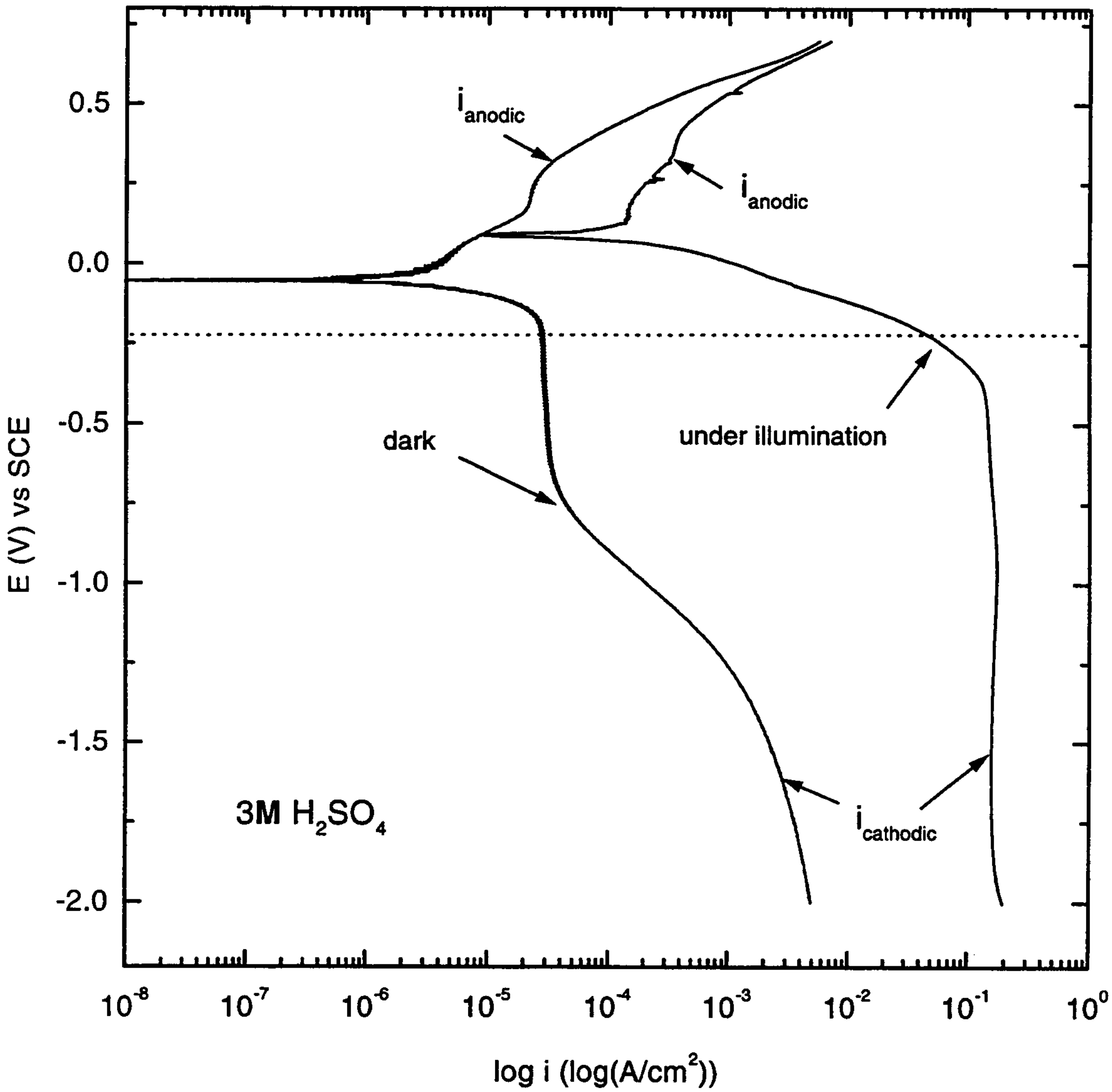
Figure 2. Cathodic photocurrent density transients for p-$GaInP_2$ in 3 M H_2SO_4.

Figure 3 Schematic of monolithic PEC/PV device

Figure 4. Current voltage characteristics for p-$GaInP_2$(Pt)/TJ/GaAs electrode in 3 M H_2SO_4 under white light illumination.

Figure 5. Current voltage characteristics for p-$GaInP_2$ electrode in 3 M H_2SO_4 under white light illumination with and without iron.

Figure 6. Current voltage curve for a-Si triple cell electrode in 3 M H_2SO_4 under white light illumination.



i_{anodic}
i_{anodic}
dark
under illumination
$i_{cathodic}$
3M H_2SO_4
0.5
0.0
-0.5
-1.0
-1.5
-2.0
E (V) vs SCE
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
log i (log(A/cm^2))

Figure 1

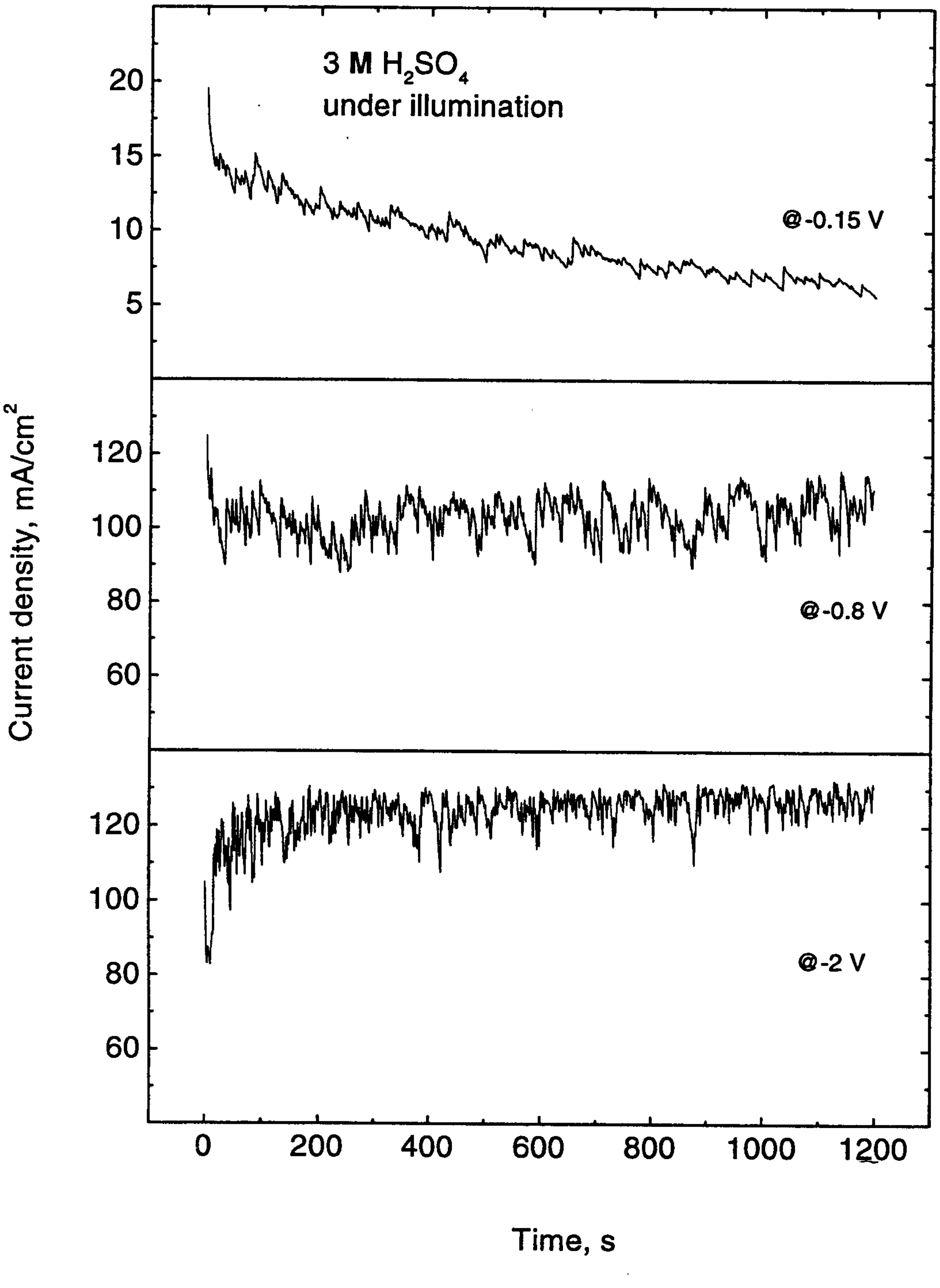

3 M H_2SO_4
under illumination
@-0.15 V
@-0.8 V
@-2 V
Current density, mA/cm^2
Time, s
20
15
10
5
120
100
80
60
120
100
80
60
0
200
400
600
800
1000
1200

Figure 2

Novel Monolithic PV/PEC Water Splitting Device

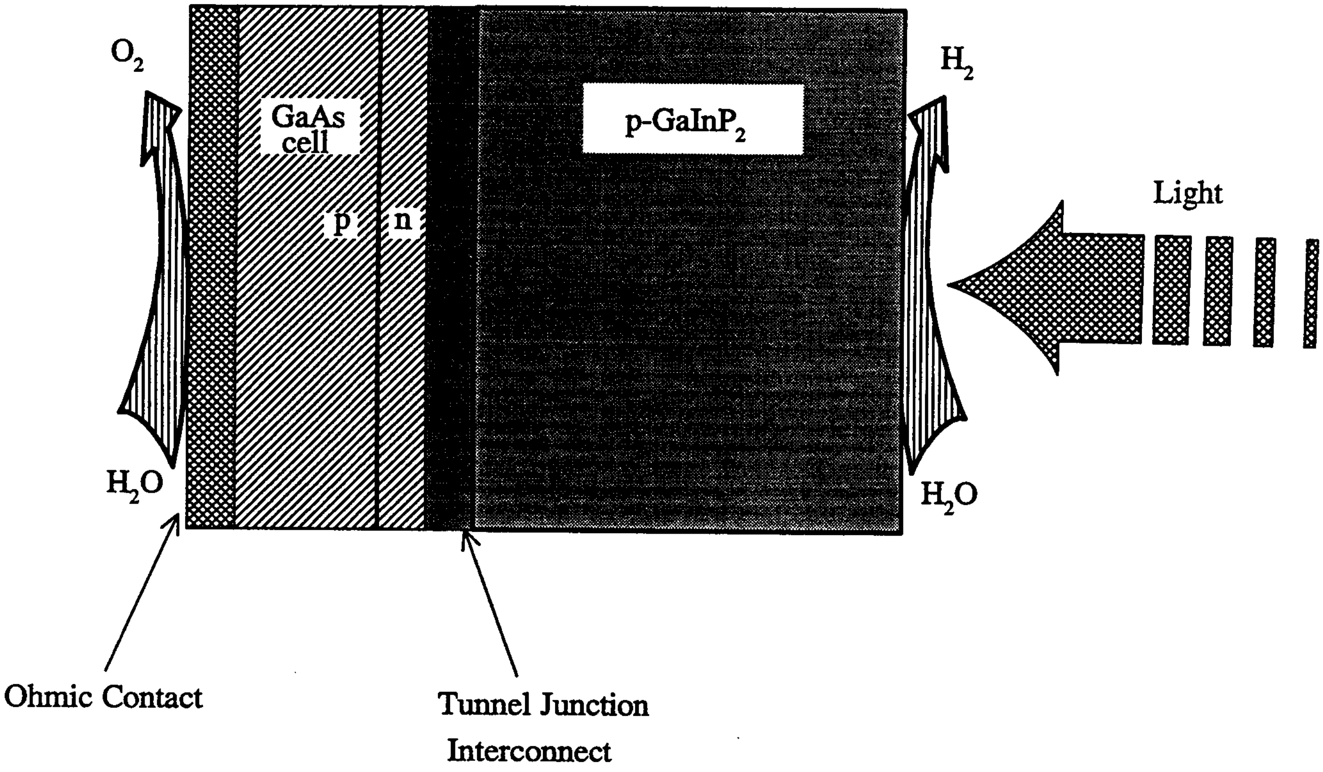


Figure 3

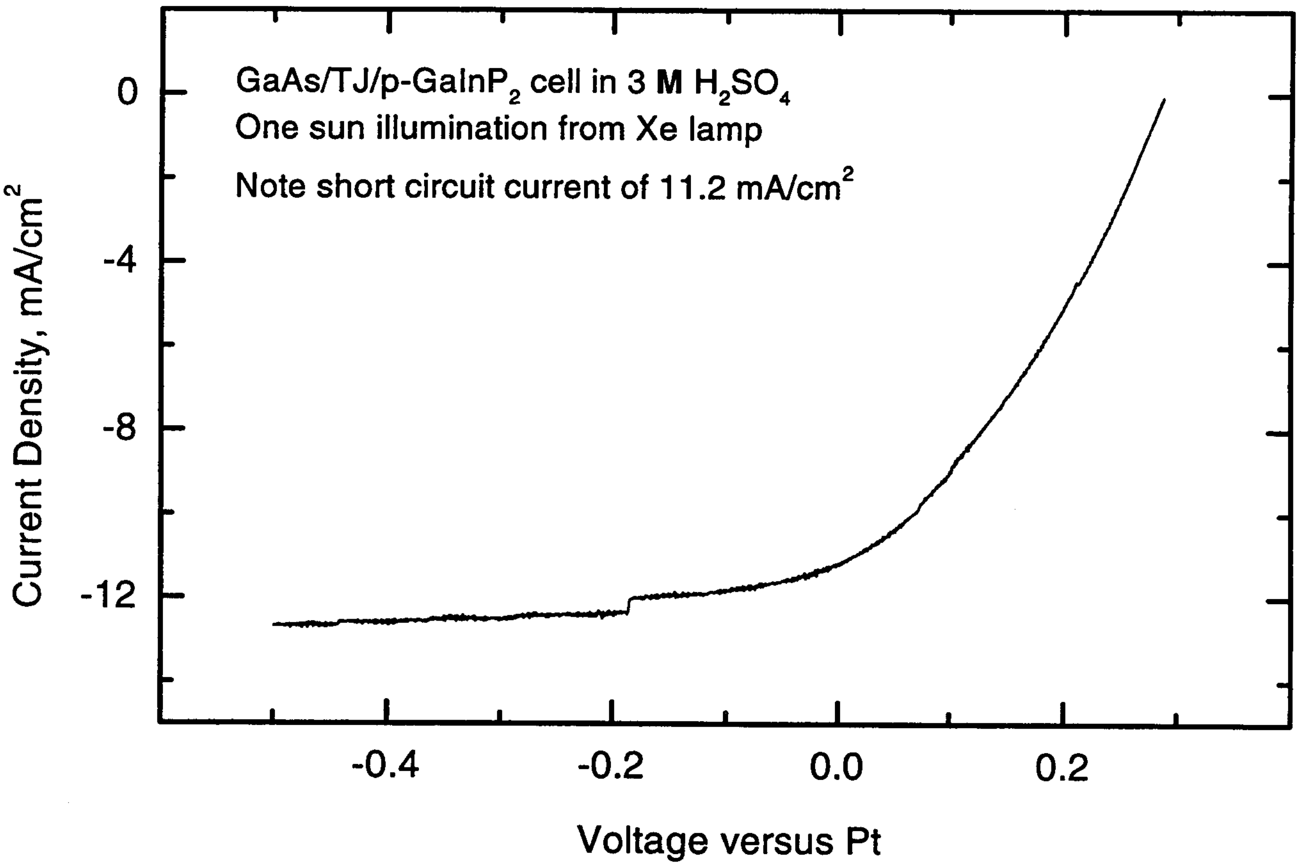

GaAs/TJ/p-GaInP₂ cell in 3 M H₂SO₄
One sun illumination from Xe lamp
Note short circuit current of 11.2 mA/cm²
Current Density, mA/cm²
0
-4
-8
-12
-0.4
-0.2
0.0
0.2
Voltage versus Pt

Figure 4

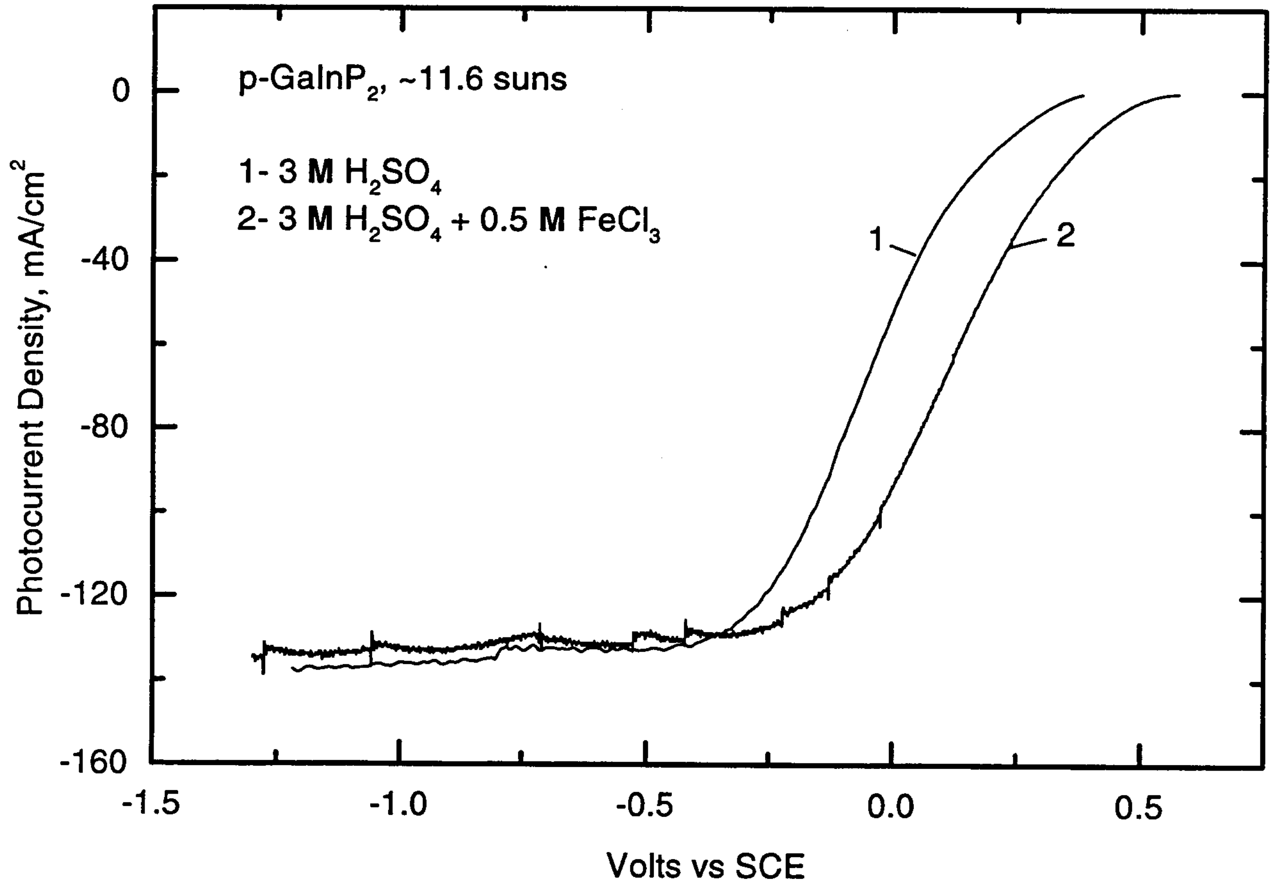

p-GaInP$_2$, ~11.6 suns
1- 3 M H_2SO_4
2- 3 M H_2SO_4 + 0.5 M $FeCl_3$
1
2
0
-40
-80
-120
-160
Photocurrent Density, mA/cm^2
-1.5
-1.0
-0.5
0.0
0.5
Volts vs SCE

Figure 5

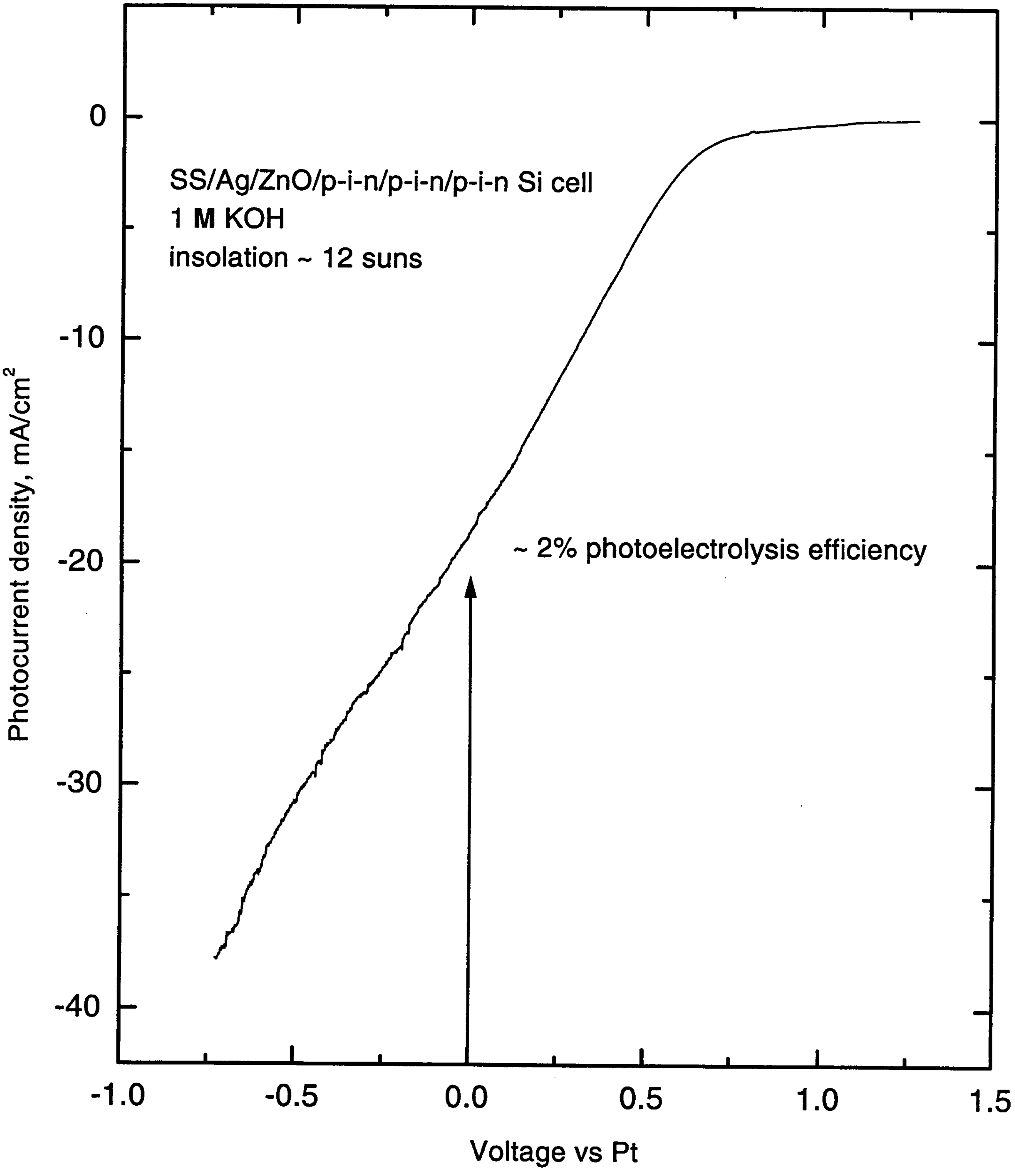

SS/Ag/ZnO/p-i-n/p-i-n/p-i-n Si cell
1 M KOH
insolation ~ 12 suns
~ 2% photoelectrolysis efficiency
0
-10
-20
-30
-40
Photocurrent density, mA/cm²
-1.0
-0.5
0.0
0.5
1.0
1.5
Voltage vs Pt

Figure 6