

Liquid-Semiconductor Surface Interactions of Silicon in a
Double Liquid Layer Solar Cell

A Major Qualifying Project Report

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Abstract

Semiconductor liquid junctions probe fundamental properties relevant to solar energy conversion, but questions remain for morphologies where liquid junctions make both the front and the back contact to a semiconductor. We designed double liquid layer reservoirs that sandwich silicon crystals in order to observe the effects of multiple liquid-semiconductor contacts on the band bending behavior on the silicon surface. Open circuit voltage was found in order to be able to construct a Schottky band bending diagram for the different redox couple liquid layer pairings with the silicon crystal type being varied between n-type, p-type, and intrinsic silicon.

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I would lastly like to thank professor Ronald Grimm for advising the project, for keeping new ideas flowing as the project progressed, and for fostering a research environment that promoted a pursuit of knowledge on a subject that isn't widely or easily taught.

1. Introduction

Solar cell research has been booming in the last few years due to a growing need for renewable energy and new lines of research are being explored all the time. Figure 1 shows a chart of the immense amount of research being done between 1975 to today in the field of solar cell efficiencies. These cells use the energy from the sun’s light to excite electrons in their structures and create voltage which results in energy.

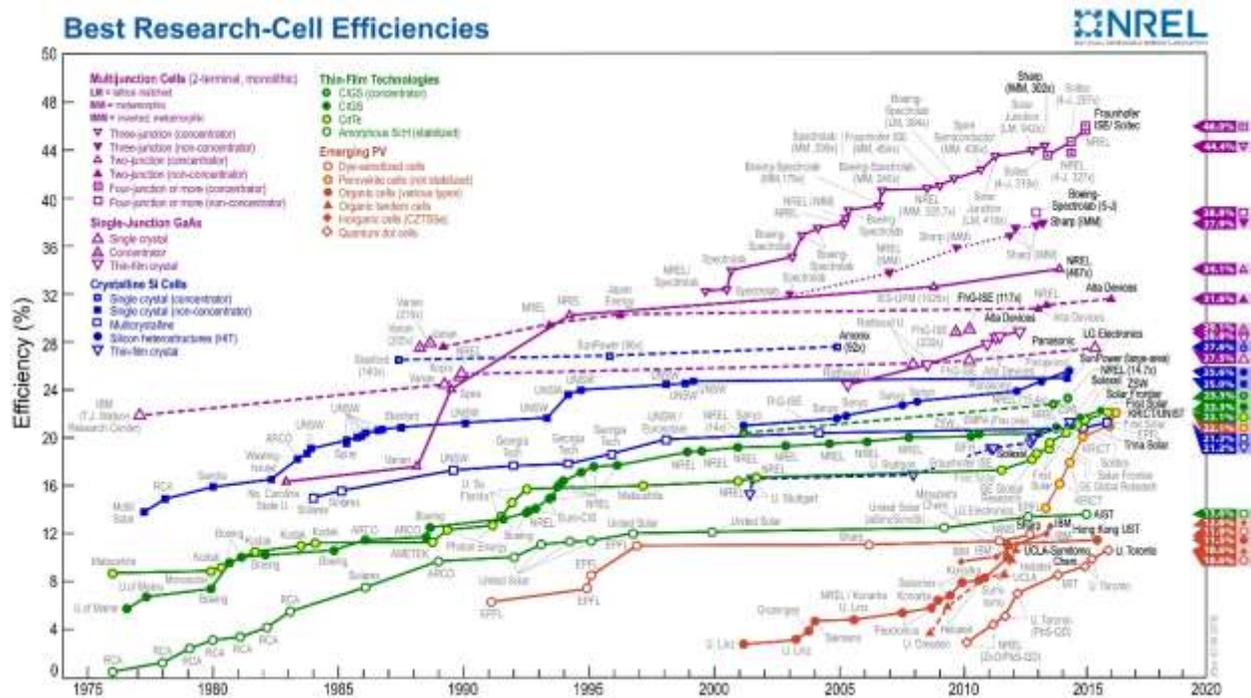


Figure 1 Solar Cell Efficiency Research^[1]

The aim of this project was to begin research in a previously untouched area of this emerging field. The open circuit voltage properties and thus the semiconductor band bending properties of solar cells using a single liquid redox layer have been previously extensively researched for silicon. The behavior for single liquid layer cells can be seen in Figure 2.

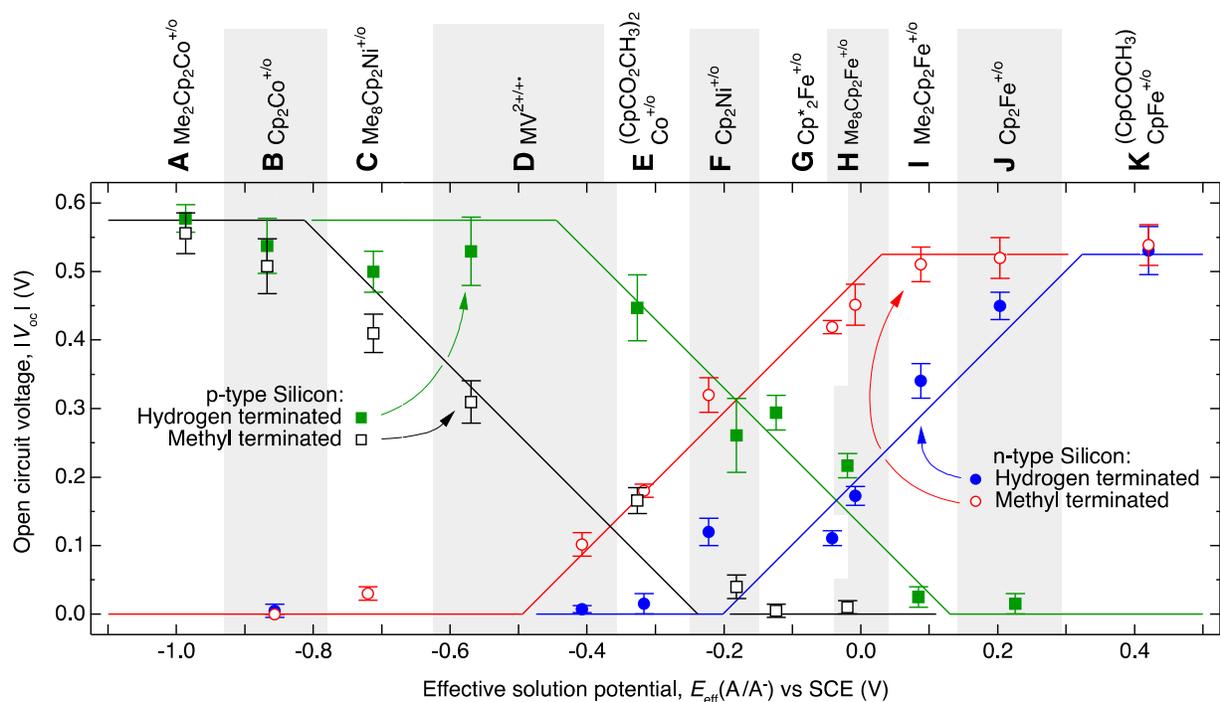


Figure 2 Single Liquid Layer Electrode Behavior^[2]

We set out to study what properties this same semiconductor displayed when the metal back contact of a normal single liquid layer cell was replaced with a second liquid redox couple layer.

We believed that the second liquid layer would affect the band bending diagram for the silicon semiconductor and that Fermi level pinning would be affected by the additional layer.

Figure 3 shows a possibility of band behavior under these new conditions using

decamethylferrocene^{0/+} as the front contact and Ferrocene^{0/+} as the back contact with each E_0 line representing the potential energy of the redox couples and the E_f representing the Fermi level of the n-type silicon wafer. $E(CB)$ and $E(VB)$ represent the energy of the conduction band and the energy of the valence band respectively.

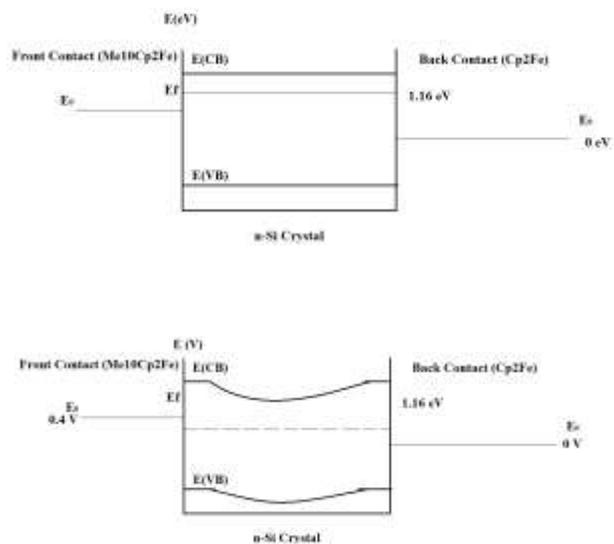


Figure 3 Hypothesis on Band Bending Behavior

In order to test this hypothesis, electrodes were constructed to allow the semiconductor wafer to be sandwiched between two different liquid redox couples. These electrodes were hooked up to a potentiostat and a monochromatic light beam was shone through the cell. The open circuit voltage (V_{oc}) was measured in a dark and light exposed environment.

2. Background

2.1 Semiconductor Types

2.1.1 Why a Semiconductor?

Semiconductors are solids with electrical characteristics between that of a metal and an insulator. Semiconductors are useful in electrode fabrication because they allow us to adjust electrical properties in order to monitor benefits or downfalls to changes in the overall cell. This property comes from the fact that, as seen in Figure 4, the conduction and valence bands of a semiconductor do not overlap, but the gap between them is small enough that an excited electron can make the jump between the bands.

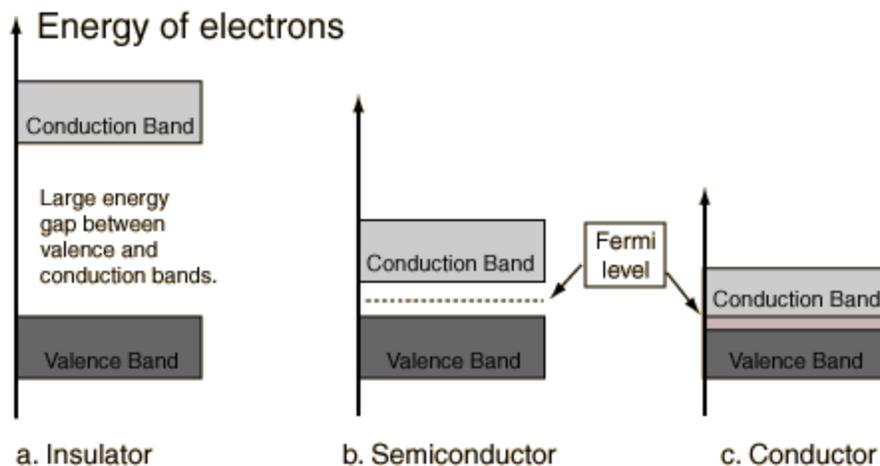


Figure 4 Semiconductor Band Representation^[3]

The valence band in a material is the highest energy band that non-excited electrons can exist in. The conduction band in a material is the lowest range of unoccupied states when no excitation of electrons has occurred. The space in between these bands is known as the band gap. The conduction and valence bands are the closest bands to the Fermi level of a material. A Fermi level represents the total chemical potential energy for the electrons in a material.

2.1.2 Dopant Effects on a Semiconductor

In this project we focused on three types of silicon semiconductor: n-type, p-type, and intrinsic. Intrinsic silicon is a non-doped version of the semiconductor. Nothing has been added or changed in an intrinsic wafer and these wafers present as pure of a lattice structure for that particular semiconductor crystal as possible. Doping a semiconductor is the process of adding a flaw in the lattice structure in order to shift the semiconductors Fermi level. To create an n-type silicon you would need to introduce an element with more valence electrons than silicon to the lattice structure. This adds more electrons to the lattice of silicon and creates an environment within the semiconductor where excess electrons are present. Alternatively to create a p-type silicon, an element with fewer valence electrons would need to be added. This process adds electron holes to the lattice of silicon. These changes can be seen in Figure 5.

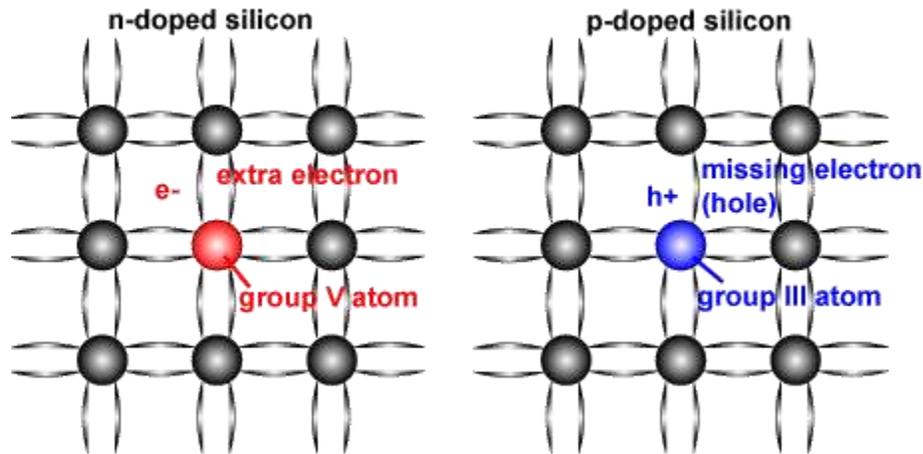


Figure 5 n-type and p-type Silicon Doping^[4]

In n-type semiconductors, the extra electrons tend to take up more energy states which causes the Fermi level to shift towards the conduction band to account for the additional energy bands being used. In p-type semiconductors, the extra electron holes tend to lead to less energy levels being

used. This shifts the Fermi level down towards the valence band. This principle can be seen in Figure 6.

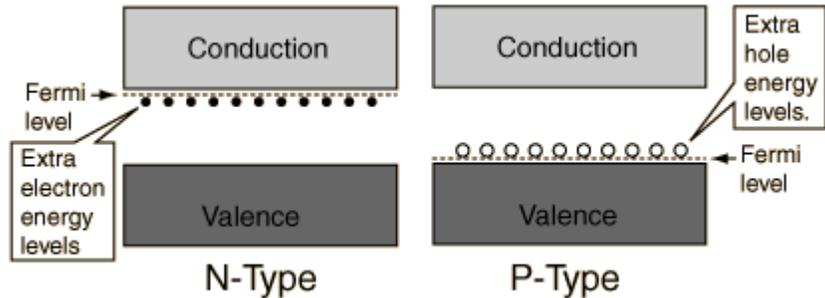


Figure 6 Dopant Effects on Fermi Level^[5]

2.1.3 Band Bending Behavior and Fermi Levels

As previously stated, a semiconductor's Fermi level is a representation of the chemical potential energy of the electrons in a solid. In other words, the Fermi level represents a barrier that, when the semiconductor is at 0K, electrons cannot pass even in an excited state.

A phenomenon called band bending occurs in semiconductors when a liquid redox couple is introduced to the semiconductor. The Fermi level of the solid will shift to accommodate a charge transfer by the redox couple. A visual representation of this can be seen in Figure 7.

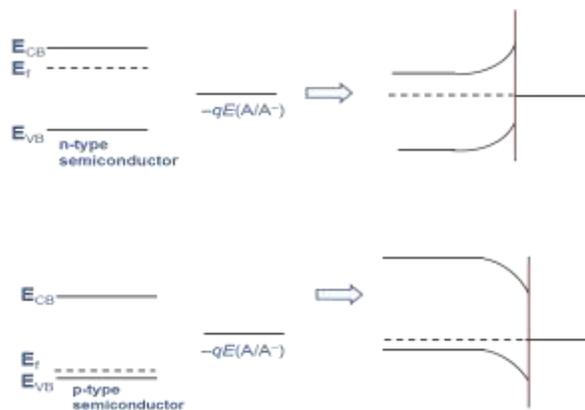


Figure 7 Band Bending Diagram^[6]

As can also be seen in Figure 7, the conduction band and the valence band will shift to maintain the relative distance between the Fermi level and the bands. The shifting occurs due to the electrical potential of the liquid layer dictating the energy states of the excited electrons which will not fall or raise in energy levels thus making the chemical potential of the semiconductor the same as that of the liquid layer.

2.2 Photoelectrochemical Cells

Photoelectrochemical cells, a common setup shown in Figure 8, works by exciting the electrons in the semiconductor so that they are mobile and transfer into the liquid layer. The electrons are attracted by the neutral component of the redox couple which turns it into the negative component of the redox couple. The other neutral molecules in the liquid layer will try to pick up the extra electrons in the negatively charged molecules thus causing the charge to transfer and causing a cycle of reduction and oxidation to occur in the liquid layer.

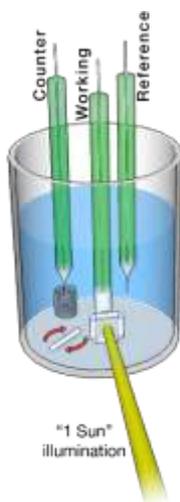


Figure 8 Photoelectrochemical Cell^[7]

The photoelectrochemical cell in Figure 8 shows a stir bar to ensure that the redox couple stays mixed, a counter electrode which carries a current into the cell, a reference electrode that allows for testing of an electrical potential of the cell without passing current through the working electrode, an illumination beam that is the equivalent of 1 sun, the liquid front contact, and the working electrode which is the silicon semiconductor connected in the back to a metal contact.

By hooking up the working, reference, and counter electrodes to a potentiostat, current, voltage, and fill factor can be monitored.

2.3 Liquid Layer Contacts

Liquid contacts are more efficient in solar cell batteries because they rely on free roaming electron and electron hole carriers to exchange a current between the liquid and the semiconductor. A junction of multiple semiconductors requires compatible lattice structures in order to ensure efficient carrying of holes and electrons. This extends to why multiple liquid layers are being examined as a possibility in solar cells. If liquids make such efficient charge carriers, then having liquid layers on either side of the semiconductor should make for an overall increase in charge carrier efficiency.

3. Design

Two different electrodes were designed and implemented in the process of this project. The first design was that of just the working electrode in a 3-electrode system (working, counter, reference) and consisted of a long rod that housed the semiconductor wafer as well as the liquid back contact. The second design was of a full cell which consisted of two cuvettes, each housing a liquid redox contact, the semiconductor wafer in the center and reference and counter electrodes in each redox solution.

3.1 Electrode Version 1

The first version of a multi-liquid layer electrode was made from Delrin® which is a stiff polymer resembling plastic as we didn't want anything made of metal outside of the actual metal contact which was present as well as the liquid back contact. The components of the electrode were:

- Hollow Delrin® rod
- Stainless steel plug with a well to fit inside of the rod and act as a stage for the liquid back contact and the semiconducting wafer
- The semiconducting wafer
- An o-ring to promote a tight seal of the cap onto the rod
- A cap with grooves and an opening in the top to allow light to shine through to the semiconducting wafer that screwed onto the rod
- A small metal spring to give the stainless steel plug a small amount of force towards the cap to, again, create a tighter seal
- The metal wire connected to the spring and to the potentiostat

A 3-D model of the design can be seen in Figure 9.

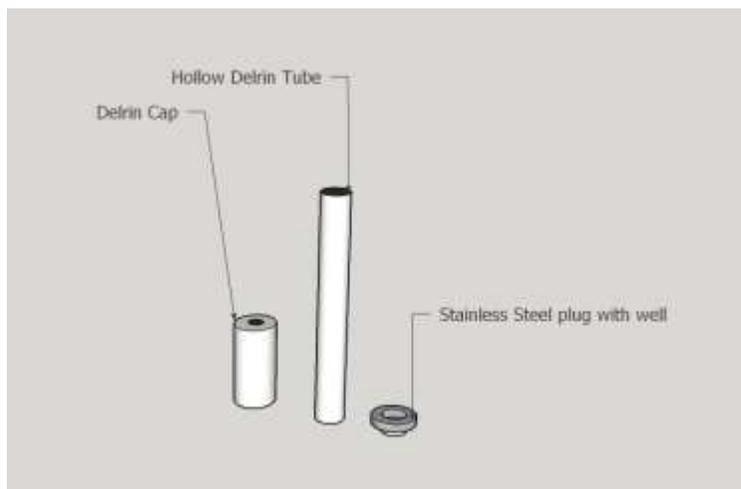


Figure 9 3-D Model of Electrode Design 1

This electrode acted as the working electrode in a 3-electrode system as depicted in Figure 8.

3.2 Electrode Version 2

The second version of a multi-liquid layer testing apparatus that was designed was made as a whole cell instead of just the working electrode. The second design consisted of:

- Two quartz cuvettes to house the liquid contacts on either side of the semiconducting wafer
- Two pieces of Viton® gasket used to create a seal in between the cuvette and the wafer on either side
- A glass holding piece to hold the cuvettes in the hood
- Stir bars in both cuvettes to keep the redox solution from separating
- Caps for each of the cuvettes that hold counter and reference electrodes for each redox solution
- A custom clamp to hold the cuvettes steady during testing

A 3-D model of the design is shown in Figure 10.

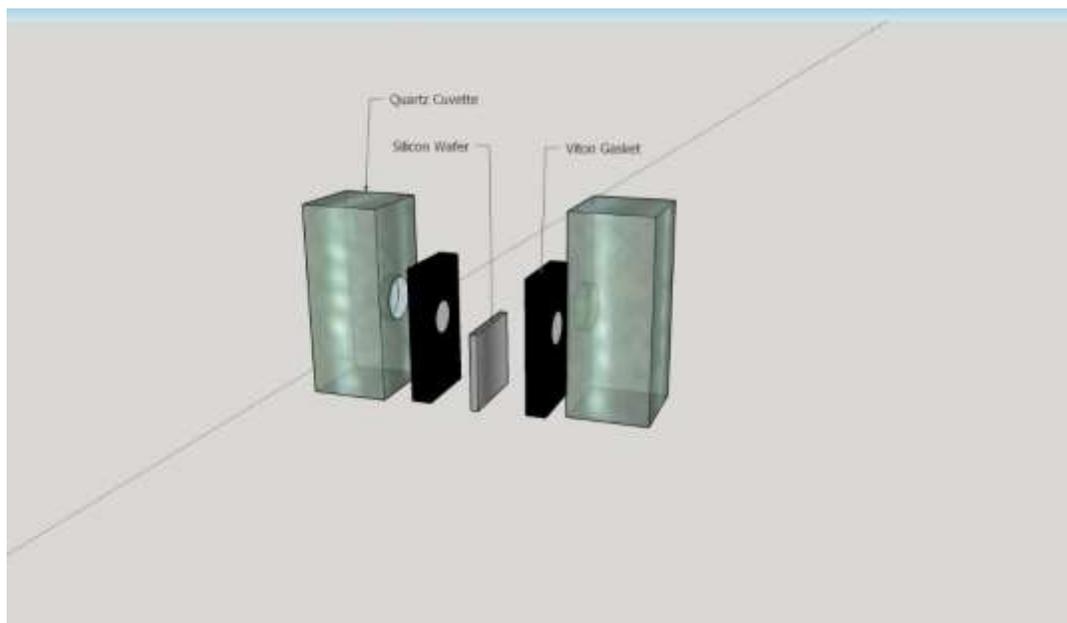


Figure 10 3-D Model of Electrode Design 2

4. Experimental

4.1 Testing With Electrode Version 1

To set up our first iteration of the electrode, a full 3 contact cell needed to be set up in an oxygen free glovebox. All of the items would be “pumped in” meaning that they would be placed in a chamber on the side of the glove box that extracted the oxygen from the chamber in order to not contaminate the environment of the glovebox. To set up the cell we needed a piece of glassware that had a beaker-like bottom with 3 openings in the top to accommodate the three electrodes, a stir bar, the three electrodes, the working electrode semiconducting wafer that had been very recently etched with HF in order to remove any oxidation on the surface of the wafer, and the materials to make the liquid redox contact.

The liquid contact was made by combining lithium perchlorate (electrolyte), acetonitrile, and the two components of the redox couple (ferrocene/ferrocenium, cobaltocene/cobaltocenium, decamethylferrocene/decamethylferrocenium, and decamethylcobaltocene/decamethylcobaltocenium). A small droplet of a redox couple was placed on the stainless steel plug, the silicon wafer was placed on top of the liquid layer, the o-ring was secured on top of the semiconductor, and the cap was fit over the rod and placed upside down into the liquid front contact which was poured into the glassware which was suspended, using a clamp setup in the glovebox, over a magnetic motor that caused the stir bar to rotate inside the glassware. This was all placed over a glass window on the floor of the glove box that allowed the 1-sun monochromatic light beam to shine in and through the bottom of the cell. The potentiostat was connected to the three electrodes and fed data to the Igor program which created a graph of the data.

The open circuit voltage and the circuit voltage curve was first taken in a completely dark environment. Then a test was done where the environment started dark, then after 2 seconds of data collection, the light beam was turned on and data collection continued through the energy shift.

4.2 Testing With Electrode Version 2

The second iteration of liquid contact testing apparatus was more of a complete cell so only it needed to be pumped into the hood. The cell was assembled by placing one of the Viton® gaskets (with a hole punched in the middle) next to one of the cuvettes so that the holes in each matched up with the other. The semiconducting wafer was placed next to that, and the process repeated on the other side. A custom clamp was made to secure the cuvettes into place to avoid leakage.

Two different redox couples were added to each of the cuvettes. We tested couples of ferrocene^{0/+} / decamethylferrocene^{0/+} and cobaltocene^{0/+} / decamethylcobaltocene^{0/+}, alternating which was the front and back contact and switching out the semiconductor type. The caps containing the counter and reference electrodes were placed on top of the cuvettes and everything was hooked up to the potentiostat.

The open circuit voltage and the circuit voltage curve was first taken in a completely dark environment. Then a test was done where the environment started dark, then after 2 seconds of data collection, the light beam was turned on and data collection continued through the energy shift.

5. Results & Discussion

Apparatus one was tested using an n-type Si wafer with a ferrocene^{0/+} front contact and cobaltocene^{0/+} back contact. Table 1 shows the open circuit voltages that were obtained from these tests.

Front Contact	Back Contact	Si Type	V _{OC} (mV)
Cp ₂ Fe	Cp ₂ Co	n	-85
Cp ₂ Fe	Cp ₂ Co	n	-368
Cp ₂ Fe	Cp ₂ Co	n	-75
Cp ₂ Fe	Cp ₂ Co	n	-194
Cp ₂ Fe	Cp ₂ Co	n	-69
Cp ₂ Fe	Cp ₂ Co	n	-51
Cp ₂ Fe	Cp ₂ Co	n	-62
Cp ₂ Fe	Cp ₂ Co	n	-7

Table 1 Apparatus 1 Voc Testing Results

The V_{OC} values obtained are not reproducible. There are several possible causes for this. The most probable reason that issues arose was the seal of the cap on the electrode. We believe that the cap was not sealed onto the electrode tightly enough which caused the front liquid contact to leak into the electrode and mix with the back liquid contact causing the redox properties of the liquids to cease and thus rendering the system unusable.

Another cause for problems in this electrode was the size of the parts that we were working with in the glovebox. The parts of the electrode that we needed to handle were very small and hard to handle through 3 sets of gloves. This led to setup of the electrode being a,

sometimes, messy and lengthy process. With the stainless steel plug being so small, the amount of liquid back contact was found to almost be negligible and was hard to control and keep track of so by the time the electrode was successfully assembled and put into the cell, the back contact may have fallen off of the plug.

These downfalls of the electrode led to the design of the second testing apparatus.

The second apparatus was tested using n-type, p-type, and intrinsic silicon wafers and with varied front and back contacts. The results from these tests can be seen in Table 2.

Back	SC	Front	Voc (mV)	Trial 2	Trial 3
Cp2Fe	n-Si	Me10Cp2Fe	206	96	
Me10Cp2Fe	n-Si	Cp2Fe	-321	-183	-252
Cp2Fe	p-Si	Me10Cp2Fe	-204		
Me10Cp2Fe	p-Si	Cp2Fe	27		
Cp2Fe	i-Si	Me10Cp2Fe	176		
Me10Cp2Fe	i-Si	Cp2Fe	-178		
Cp2Co	n-Si	Me10Cp2Co	-131	-187	-151
Me10Cp2Co	n-Si	Cp2Co	-139	128	158
Cp2Co	p-Si	Me10Cp2Co	59	136	29
Me10Cp2Co	p-Si	Cp2Co	274	261	

Cp2Co	i-Si	Me10Cp2Co	127	-274	-323
Me10Cp2Co	i-Si	Cp2Co	102	123	85

Table 2 Apparatus 2 Voc Testing Results

These results are not reproducible at this time, however, this apparatus is showing more promise.

The issues that we ran into with the second testing apparatus were mostly due to the fragility of the quartz cuvettes. In order to drill holes into the cuvettes, a very specific procedure needed to be followed. This made the cuvettes complicated to fix were problems to arise and ultimately costed time when cracks occurred in the cuvettes. Because we were introducing holes to glass, it created a weak point in the cuvettes and ended up causing cracks in the system. These cracks lead to leaks and made the system unusable for a while.

The second set of cuvettes were annealed in order to strengthen the glass and there have not been any problems with cracks since the annealing was performed.

6. Conclusion

We believe that we have created an apparatus that can be used to test the effects of a liquid front and liquid back contact in a three-electrode solar cell. The results from the testing so far have not been reproducible and therefore no conclusions on the band bending properties of the semiconductor wafer can be made.

The future goals for this project and the research group include getting reproducible results from this system. Once those results are obtained, the next step is try to vary things in the cell. The group is hoping to test multiple surface treatments on the Si crystals including methylation and hydrogenation and they are looking to switch up the redox couples and their placement as either front or back contact. The ultimate goal of the project is to be able to test perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) crystals that are grown by the research group in order to better understand their properties and to contribute to the growing field of perovskite solar cell research as can be seen in Figure 1 by improving current perovskite solar cells.

References

- [1] National Center for Photovoltaics. (2016, April 20). Retrieved April 23, 2016, from <http://www.nrel.gov/ncpv/>
- [2] Grimm, R.L. et al., *J. Phys. Chem. C* **2012**, *116*, 23569
- [3] Band Theory of Solids. (n.d.). Retrieved April 10, 2016, from <http://hyperphysics.phy-astr.gsu.edu/hbase/solids/imgsol/band2.gif>
- [4] Doping. (n.d.). Retrieved April 10, 2016, from <http://www.pveducation.org/pvcdrom/pn-junction/doping>
- [5] The Doping of Semiconductors. (n.d.). Retrieved April 15, 2016, from <http://hyperphysics.phy-astr.gsu.edu/hbase/solids/dope.html>
- [6] Lewis, N. S. *J. Electrochem. Soc.* **1984**, *131*, 2496
- [7] Photoelectrochemistry overview. (n.d.). Retrieved April 15, 2016, from <http://cbc41.wpi.edu/research/pec/>

Further Reading

- Lewis, N. S. (1984). A Quantitative Investigation of the Open-Circuit Photovoltage at the Semiconductor/Liquid Interface. *J. Electrochem Soc.*, *131*(11), 2496-2503.
- Lewis, N. S., Grimm, R. L., Bierman, M. J., O'Leary, L. E., Strandwitz, N. C., & Brunshwig, B. S. (2012). Comparison of the Photoelectrochemical Behavior of the H-Terminated and Methyl-Terminated Si(111) Surfaces in Contact with a Series of One-Electron, Outer-Sphere Redox Couples in CH₃CN. *The Journal of Physical Chemistry*, 23569-23576.
- Lewis, N. S., Tan, M. X., Kenyon, C. N., & O. K. (1997). Behavior of Si Photoelectrodes under High Level Injection Conditions. 1. Steady-State Current-Voltage Properties and Quasi-Fermi Level Positions under Illumination. *The Journal of Physical Chemistry*, 2830-2839.
- Lewis, N. S., Tan, M. X., Laibinis, P. E., Nguyen, S. T., Kesselman, J. M., & Stanton, C. E. (1994). Principles and Applications of Semiconductor Photoelectrochemistry (K. D. Karlin, Ed.). *Progress in Inorganic Chemistry*, *41*, 21-144.
- Sivula, K., Guijarro, N., & Prevot, M. S. (2015). Surface Modification of Semiconductor Photoelectrodes. *Phys. Chem. Chem. Phys.*, *17*, 15655-15674.