Project Plan

SENIOR DESIGN GROUP MAY 14-03

Client: ISU Nanolab, Dr. Sumit Chaudhary and John Carr

DESIGN AND IMPLEMENTATION OF A CRYOGENIC ELECTRICAL CHARACTERIZATION SYSTEM FOR ORGANIC PHOTOVOLTAICS

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SYSTEM OVERVIEW

The purpose of this document is to describe the design process and final results of the May14-03 Senior Design Group. Our project is the design of an experimental setup for characterizing defect states in organic photovoltaic cells.

MOTIVATION

Photovoltaic cells are considered to be one of the most promising technologies for future sustainable energy production. Currently, the market is dominated by inorganic semiconductor photovoltaics, which have a low photon absorption coefficient. Organic photovoltaics have recently received much attention due to their high photon absorption, but full-scale distribution has been limited by an inability to convert excited electrons into useable current flow. One of the reasons for this obstacle is the existence of electron and hole trapping states or recombination centers within the materials, created as a result of defects. In order to better understand the defect states, several different methods known as trap-level spectroscopy (TLS) can be used.

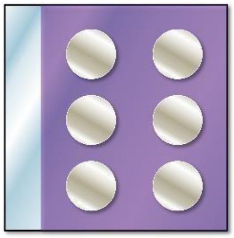
One of these methods is known as non-isothermal thermally stimulated current (TSC) measurement. In these tests, the sample is cooled to a temperature such that electrons in trapping states are no longer able to escape due to thermal energy, and then excited with a voltage or optical pulse to fill those trapping states. The sample is then heated slowly back to room temperature, and the current through the device is measured. As the temperature rises, the defect states slowly and selectively depopulate based on their trapping energies and density. Various curve fitting models, as well as an understanding of the material structure will allow the determination of the most prominent trapping mechanisms.

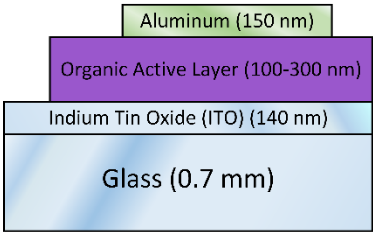
The purpose of this senior design project is to design an automated test-setup to support and streamline ongoing research efforts in the field of organic photovoltaics.

FUNCTIONAL DECOMPOSITION AND BACKGROUND

This design project was not intended to create an entire new system from scratch. Instead, the group was task with solving a technological problem by improving and extending existing equipment. The basic functionality of the required system was already in place, but did not satisfy the client's needs. The following sections describe the required functions of the system. All of the components, including the cryostat, LN_2 and atmospheric vacuum pumps, variable transformer, and temperature controller, were already owned by the client, and this setup is the starting point of this design project.

SAMPLES UNDER TEST





The research lab operated by our client has a fairly standardized method of fabricating organic solar cell samples for testing. The samples are built on square slides of glass which measure 1 inch on each side and are 0.7 mm thick. The glass slides are purchased pre-deposited with a layer of indium tin oxide (ITO), a commonly used, conductive, optically clear oxide for the creation of the bottom electrode. Then, between 100 and 300 nm of the active organic layer, bulk heterojunction poly-3-hexylthiopene (P3HT) is applied to the surface in an environmentally-controlled glove box, leaving a thin strip of bare ITO along one edge to allow electrical contact to the bottom electrode. The top electrodes are composed of 100-150 nm aluminum films prepared by sputtering. As both the P3HT and aluminum layers are very thin, the cells are very fragile and easy to puncture from above. Also the glass is fragile and will crack under too much applied pressure, even on the ITO tab.

SAMPLE TEMPERATURE CONTROL

In order to accurately control the heating and cooling cycles for the sample, a simple vacuum cryostat will be used with a Dewar flask filled with liquid nitrogen (LN_2). The top surface of the cryostat is a flat circular copper stage, on which the sample will be placed. A simple vacuum pump powered by a variable transformer will pull nitrogen out of the flask and up into a copper head, cooling the sample down. In order to achieve stable and repeatable temperatures, a heating coil is also included in the cryostat assembly. The temperature is monitored internally and the heater is supplied with variable power by a Model 331 Cryogenic Temperature Controller from Lakeshore Cryotronics.

This system, while basically functional, had the limitation that the sample could not be brought down to the required temperature of 80 K.

SAMPLE TEMPERATURE MONITORING

In the initial implementation of the system, there was no way to accurately determine the temperature of the photovoltaic sample itself. In order to be successful, the system must provide accurate and reliable measurement of the sample temperature in real time.

ELECTRICAL CONTACT

In order to measure the thermally stimulated currents in the photovoltaic cells, reliable electrical contact must be made inside the vacuum chamber, but the contact must be soft enough to avoid damaging the cells. The contact probe must also have a low thermal mass in order to avoid altering the temperature of the cell at the contact point. The old system had a large, spring-loaded device which, while capable of making very soft contact, was proven to have far too large of a thermal mass

THERMAL ISOLATION

In order to minimize convective heating of the sample, the entire cryostat head and assembly is encased in a vacuum chamber. The chamber itself, however, provides only minimal thermal insulation from the ambient temperature in the laboratory, so a layer of insulation will be required.

CURRENT MEASUREMENT

The system must be able to reliably and accurately measure very low currents in the sample. This functionality requires not only a high-end ammeter or source measurement unit, but also a significant amount of effort in shielding and noise management.

AUTOMATION SOFTWARE

A software-based control system was the only system which had to be designed from scratch. The software must be able to collect and export data, as well as to control the heating and cooling cycles of the sample.

SPECIFICATIONS

The new systems designed by this project as well as the improvements to the existing systems will all be expected to meet the following criteria.

VACUUM CHAMBER SYSTEM

- Chamber must be able to reduce the sample temperature to 80 K
- Must include a temperature sensor for real-time monitoring of the sample temperature
- Any improvements or additions to the efficiency of the system must fit inside the existing enclosure
- The cold shroud enclosure must be easily and quickly removable by one person using one tool or less
- A cold trap or other improvement must not interfere with electrical contact to the sample
- Requires a vacuum electrical feedthrough to enable the connection of enough wires to fulfill all measurement needs

THERMAL INTERFACE MATERIAL

- Must be conformal to ensure good thermal contact

MEASUREMENT SETUP/CONTROL SOFTWARE

- Must enable all measurements to be made through GPIB interface
- Must encompass full automation of cooling, excitation, heating, and data collection
- Must be able to detect and suggest solutions to flaws in hardware setup or set-points
- Must elegantly and safely recover from software or hardware errors
- Measurement of thermally stimulated current must have resolution measured in fA
- Must record logs of all data in an organized and readable file format
- Log files must include date, time, setpoints used, information about the samples, and other important details deemed necessary by the client

EXPERIMENT DESIGN

- Hardware and software should support a customizable temperature profile for modified TSC methods such as thermal cleaning, fractional emptying, and reversibility cycles.
- Software must calculate an optimal power setting for the LN2 pump such that a single setting can be used for the duration of the test

DETAILED DESIGN PROCESS

The purpose of this section is to describe the design decisions made over the course of this project.

TEMPERATURE MEASUREMENT SYSTEM

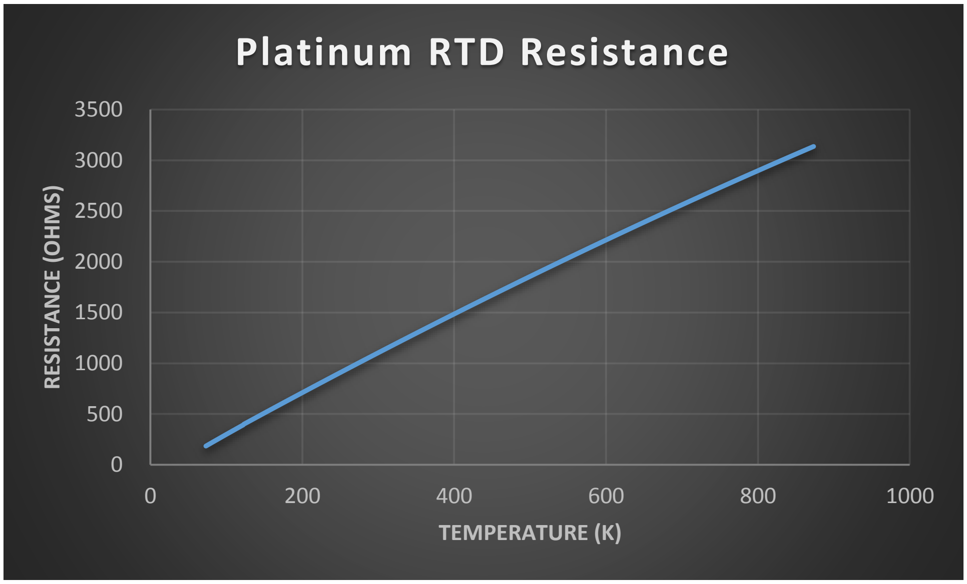
The Lakeshore device has two built in temperature sensors, both within the cryostat. Due to non-ideal effects of within the vacuum chamber, however, the temperature of the copper cryostat itself is not necessarily the same as that of the device under test. In order to accurately determine the temperature of the device, it is necessary to implement a method of real-time temperature measurement directly on the surface of the sample. Such a device must be small in order to minimize thermal mass, must be operational down to or beyond 80 K (-193 °C), and would ideally have a linear response with temperature. Several different technologies were considered to fulfill this need.

The first, and easily the cheapest solution considered was a semiconductor thermistor. These devices are readily available in easy-to-use, small packages. While most models available are designed for room temperature use, some specialized thermistors are available which operate in the required temperature regime. The major drawback to all of these devices, however, is that their temperature-resistance dependence is highly non-linear and follows the Steinhart-Hart equation:

$$\frac{1}{T} = A + B\ln(R) + C\ln^3(R)$$

While these devices would fulfill the need, however, a linear solution would be more desirable. Another, more linear technology which was considered was a thermocouple. Thermocouples consist of two dissimilar metals placed in contact with each other. When two such junctions are held at different temperatures, a measureable voltage is developed with a linear response. Thermocouples have historically been used many applications requiring a wide temperature range. We decided, however, that the requirement of a reference junction as well as the requirements of using specialized thermocouple wire to hook it up were both grounds enough to avoid this solution.

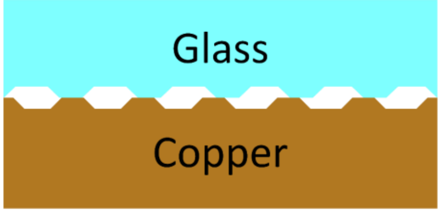
The final solution we decided to use was a platinum resistive temperature detector (RTD). These devices are simply a carefully specified sample of platinum, which shows a very linear temperature response over a high range. Platinum RTDs have recently been replacing thermocouples in all but the highest temperature applications. Our specific device is a PPG102A6 from US Sensor, which has an approximate linear temperature coefficient of resistance (TCR) of 3850



ppm over a temperature range of -200°C to 600°C. This device is specified to exhibit 1 kΩ (R_0) of resistance at 0°C (T_0) and the temperature can be calculated using the following formula:

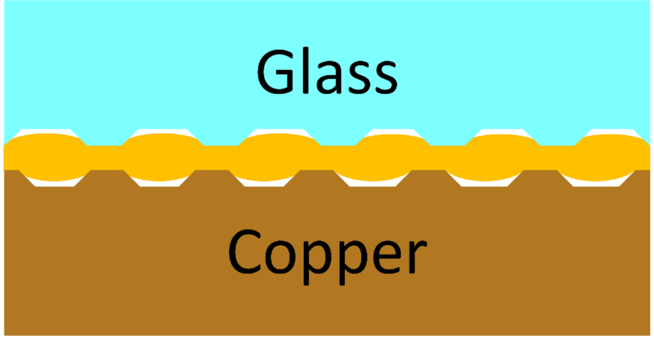
$$T = 31.483 + 0.22R + 2.83 \times 10^{-5} R^2 - 6.62 \times 10^{-9} R^3$$

THERMAL INTERFACE



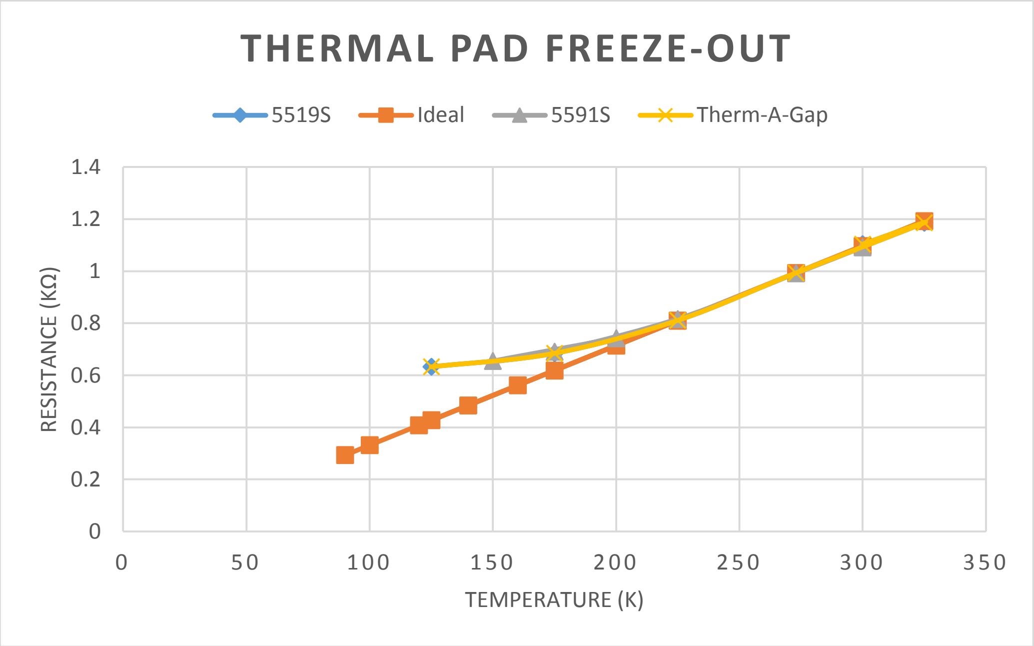
The roughness of the cryostat means that it doesn't touch the sample that much, even though both surfaces were designed to be completely flat. And since there is no air to transfer heat through convection, and radiation is almost nothing at these temperatures, we need to create a better interface between the cryostat and the sample. Several methods have been tried.

THERMALLY CONDUCTIVE PADS



Traditionally, a thermal pad is a thermally conductive, electrically isolating pad to put between a heat source and a cooler. It is meant to replace the slightly better, but more messy thermal paste. This is easy to come by if the purpose is to get heat away from an active chip or transistor, but won't work as well with low temperatures, because the material tends to freeze.

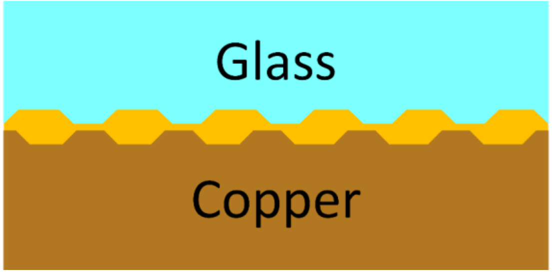
The pads that we did use all had a soft side that looks like paste and a side covered in plastic. They are about half an mm thick. The chart below shows the non-ideal characteristics of all the three thermal pads tested: the 5591S and 5519S from 3M and the Therm-A-Gap pad from Parker Chomerics.



ENCAPSULATION IN CRYOGENIC EPOXY

Another idea was to cover the entire sample in an epoxy with high thermal conductivity. The epoxy will dry for 18 hours, the purpose is not to actually glue the sample to the cryostat. There are two sides to this idea. One is that that this saves us the mess of using grease, because the epoxy is softer and more flexible than glass (at least at room temperature, it might harden at lower temperatures). Another way to use this is to conduct heat away from the top side of the sample, around the edges and to the cryostat. While this works great with just samples of glass, it also has an undesired reaction with the solar cell. The epoxy used is a two component, low viscosity epoxy encapsulant; Stycast 1266.

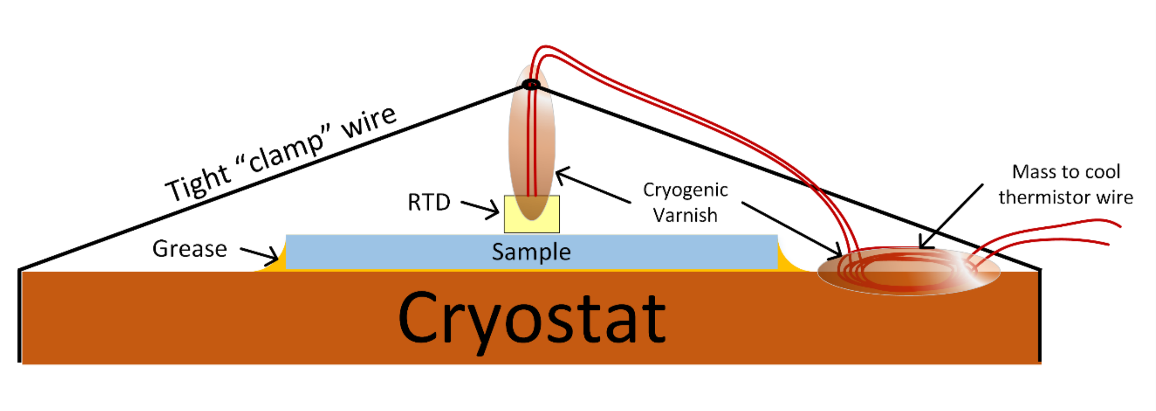
THERMALLY CONDUCTIVE CRYOGENIC VACUUM GREASE



To reduce the thermal resistance from the sample to the cryostat, we need to use a thermal paste of some sort. Turns out, they are not available for temperatures down to 80 K, because the market for this isn't very big. Furthermore, it needs to be useable at very low pressure. A vacuum grease is an acceptable but not perfect substitute. This grease, Apiezon N, is designed to seal lids for container that are under vacuum. It is also designed to work down to 4 K. It isn't ideal though, because it has a thermal conductivity of only 0.194 $W \cdot m^{-1}K^{-1}$,, so that means we have to use absolutely as thin a layer as possible.

Because of the vacuum, however, thermal conductivity isn't quite as important as the thermal interface itself. Glass has approximately the same thermal conductivity as the grease, copper has up to 400 $W \cdot m^{-1}K^{-1}$, and vacuum has less than 0.002 $W \cdot m^{-1}K^{-1}$, and since the cryostat, grease and glass isn't that thick compare to the vacuum around it, nearly all the temperature difference is across the vacuum.

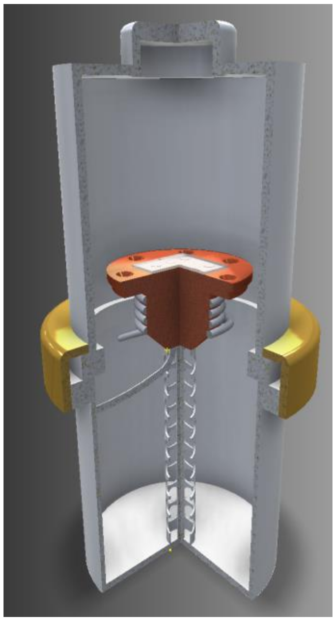
ELECTRICAL CONTACT INTERFACE

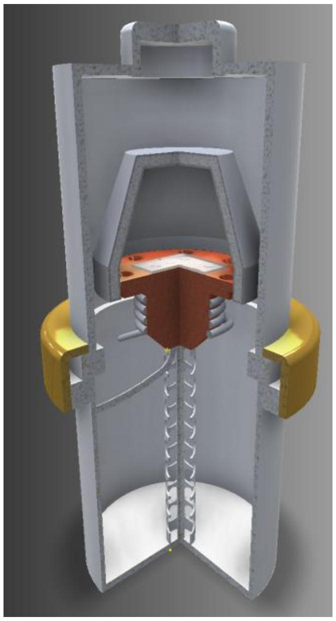


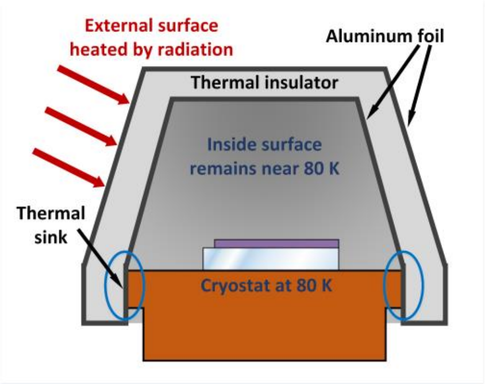
One of the main challenges of our project has been to reduce thermal coupling between the sample and the outside, while maintaining good conduction with the cryohead. This requirement motivated us to adopt a probe/clamping system as electrical contacts. However since the solar samples are very thin, we need to design the clamp and probe such that it applies enough force on the sample to enhance thermal conduction with the copper head, without creating enough stress to the device. In fact our vacuum insulation pump transmits vibrations to the sample during test runs and we had to incorporate those considerations into our design of the electrical contact interface. At first we have chosen a relatively bulky probe with a smooth pin connected to the aluminum contacts of the sample. This system provides the advantage of providing enough contact force to the sample while minimizing damage. However as we ran simulations we noticed that the thermal mass of the system was reducing the thermal efficiency of the system. The lowest thermal mass we could create was to use a thin wire as a kind of clamp, where the tension in the wire will pull the sample down onto the surface. After so many other attempts, the wire clamp method was determined to be the best one.

COLD SHROUD

The cold shroud is a simple idea of adding a layer of insulation around the sample itself to cancel out any adverse radiative coupling between the external walls of the vacuum chamber and the sample itself. The prototype used for some basic tests consisted of materials which were readily available in lab—a Styrofoam cup and layers of aluminum foil. The rim of the cup was placed in thermal contact with the cryostat head, which gave any radiative heating effects a heat sink before that thermal energy could disrupt the measurement. Our final design consists of thicker layers of aluminum foil which would be able to support themselves, eliminating the need for a Styrofoam filler layer.







CHAMBER INSULATION

The chamber that houses the internal components of the system provides insulation from the room-temperature air found in the laboratory. The chamber itself houses components such as the solar cell, measurement probes, cold shroud and/or thermistors. As part of the on-going design process, the chamber, a thick cylindrical mass of metal, serves as a form of insulation in its current form. However, the chamber is currently being improved by adding further insulation along its inner walls by the use of several layers of aluminum sheet, along with a material for fiber reinforcement. The specifics for the fiber material are currently being researched; however, the overall design for the chamber insulation remains the same. The system's chamber insulation can be treated as a second form of thermal insulation, similar to a cold trap; however, it also serves as the primary line of defense between room temperature and cryogenic temperatures.

CURRENT MEASUREMENT SYSTEM

Thermally stimulated current tests are fairly simple to implement because they only require monitoring of the current through the device as the temperature changes. The measurement of those currents is complicated, however by the very low amplitude of those currents. Those currents are in the range of femtoamperes, and therefore require a high resolution ammeter. One of the tasks within this design project was to determine which instrument was the best choice, while still fitting within our client’s budget.

The first thing which was determined was that the circuit with the ammeter must also be able to apply an excitation voltage to the cell. In order to simplify the wiring and to cut down the number of instruments required for the system, the decision was made to find a source measurement unit (SMU) capable of both sourcing voltage and measuring high accuracy current. Keithley, a division of Tektronix, is widely considered to be one of the most popular producers of SMUs.

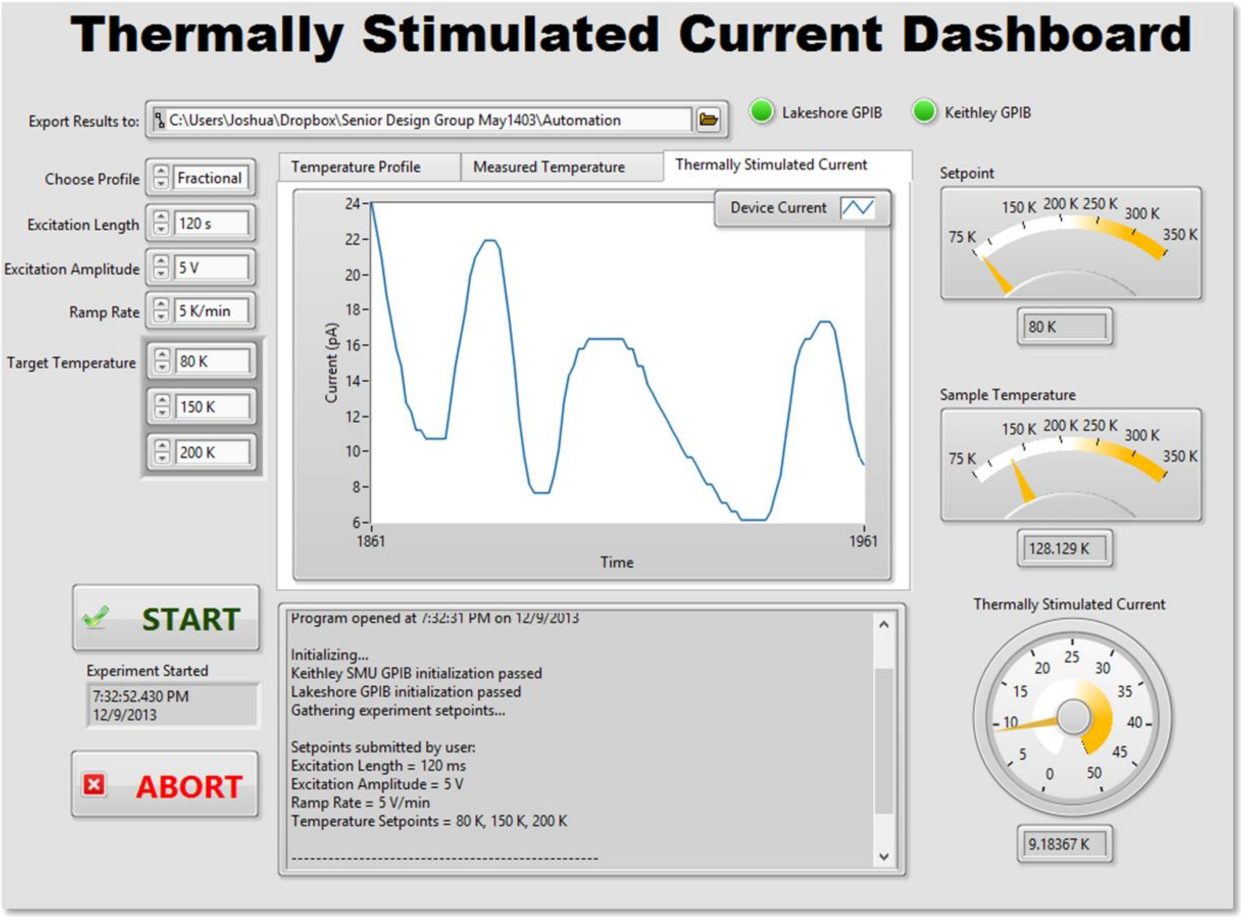
Measuring very low currents accurately becomes a serious problem in the face of noise, coupling, and leakage. Without careful consideration of these issues, it is very likely that those very low currents would become drowned out by noise and other effects. To combat this, we determined that a triaxial connection would be the best option between the sample and the instrument. This limited us to SMUs which are designed with such triaxial hookups.

With these criteria in mind, we examined Keithley’s SMU product line. All potential solutions are marked in the table. Based on the requirements of the project and the limitations of budget, we decided that the Model 2450 SMU would be the most cost effective choice.

Model	Min I	Max I	Min V	Max V	Read/sec	I Acc.	V Acc.	Chan.	Banana	Price
2634B	1 fA	10 A	100 nV	200 V	20K	0.020%	0.015%	1	No	$ 11,400
2635B	0.1 fA	10 A	100 nV	200 V	20K	0.020%	0.015%	1	No	$ 9,200
2602B	100 fA	10 A	100 nV	40 V	20K	0.020%	0.015%	2	Yes	$ 9,060
2612B	100 fA	10 A	100 nV	200 V	20K	0.020%	0.015%	2	Yes	$ 9,060
2601B	100 fA	10 A	100 nV	40 V	20K	0.020%	0.015%	1	Yes	$ 6,180
2611B	100 fA	10 A	100 nV	200 V	20K	0.020%	0.015%	1	Yes	$ 6,180
2604B	100 fA	10 A	100 nV	40 V	20K	0.020%	0.015%	2	Yes	$ 7,260
2614B	100 fA	10 A	100 nV	200 V	20K	0.020%	0.015%	2	Yes	$ 7,260
6430	10 aA	0.105 A	1 uV	200V	256	0.035%	0.012%	1	No	$ 13,000
2450	10 fA	1.05 A	20 mV	200 V	3,100	0.020%	0.012%	1	Yes	$ 5,400

AUTOMATION SOFTWARE

In order to control the heating and cooling, and to regularly collect and store data, a software-based automation program must be developed. The LabVIEW programming language was chosen because of its original intention of being used to communicate with and control laboratory instrumentation. The user interface can be seen in the large graphic below, and a flowchart of basic operation can be seen to the right on the next page. When a user initiates a TSC measurement session, they must define certain setpoints to define how the test will be conducted. After that, the cooling cycle will begin, in order to lower the temperature of the sample. Once the temperature has been reached and the sample has been soaked at that temperature for the user-defined duration, the program will instigate the excitation voltage pulse into the sample. Following this, the system will begin to warm the sample again with the defined temperature profile, and the thermally-stimulated currents will be measured. At the conclusion of the heating cycle, the data will be exported in a spreadsheet format with columns for time, temperature, and current.



Export Results to: C:\Users\Joshua\Dropbox\Senior Design Group May1403\Automation

Choose Profile: Fractional

Excitation Length: 120 s

Excitation Amplitude: 5 V

Ramp Rate: 5 K/min

Target Temperature: 80 K, 150 K, 200 K

Setpoint: 80 K

Sample Temperature: 128.129 K

Thermally Stimulated Current: 9.18367 K

Experiment Started: 7:32:52.430 PM 12/9/2013

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Program opened at 7:32:31 PM on 12/9/2013

Initializing...
Keithley SMU GPIB initialization passed
Lakeshore GPIB initialization passed
Gathering experiment setpoints...

Setpoints submitted by user:
Excitation Length = 120 ms
Excitation Amplitude = 5 V
Ramp Rate = 5 V/min
Temperature Setpoints = 80 K, 150 K, 200 K

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NEXT STEPS

The current system design has exceeded our previous expectations in terms of thermal insulation and TSC measurement reliability. Furthermore, current on-going research dictates the specific design changes that are being made, whether it be the type of fiber to be used for the chamber insulation or the vacuum feedthrough to be replaced. During the next upcoming weeks, the design project team will be compiling all available data taken from the results we have conducted so far on thermally conductive pads, the encapsulation by cryogenic epoxy, and so on. In this regard, we seek to refine our current system design and eventually implement the automated process for taking thermally stimulated current measurements on the sample cell.