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Table of Contents

Executive Summary

There has long been a desire to replace the front-side silver contacts in silicon solar cells. There are two driving forces to do this. First, silver is an expensive precious metal. Secondly, the process to use silver requires that it be formulated into screen print pastes that need a lead-containing glass frit, and the use of lead is forbidden in many parts of the world. Because of the difficulty in replacing these pastes and the attendant processes, lead exemptions have granted to solar cells.

Copper has been the replacement metal of choice because it is significantly cheaper than silver and is very close to silver in electrical conductivity. Using processes which do not use lead, obviates it as an environmental contaminant. However, copper cannot be in contact with the silicon of the cell since it migrates through the silicon and causes defects which severely damage the efficiency of the cell. Hence, a conductive barrier must be placed between the copper and silicon and nickel, and especially nickel silicide, have been shown to be materials of choice. However, nickel must be sputtered and annealed to create the nickel silicide barrier, and copper has either been sputtered or plated. All of these processes require expensive, specialized equipment and plating uses environmentally unfriendly chemicals. Therefore, Intrinsiq proposed using printed nano nickel silicide ink (which we had previously invented) and printed nano copper ink to create these electrodes and barriers.

We found that nano copper ink could be readily printed and sintered under a reducing atmosphere to give highly conductive grids. We further showed that nano nickel silicide ink could be readily jetted into grids on top of the silicon cell. It could then be annealed to create a barrier. However, it was found that the combination of printed NiSi and printed Cu did not give contact resistivity good enough to produce efficient cells. Only plated copper on top of the printed NiSi gave useful contact resistivity, and that proved to five to ten times less conductive than the commercial silver grids. Even so, the NiSi layer was a very good barrier to copper migration, even under harsh environmental conditions. Additionally, both plated copper and printed copper could be soldered to.

While it may be possible to produce an all printed copper/nickel silicide top electrode for silicon cells, it was not easily demonstrated within the time and monetary constraints of the present project. Additionally, potential customers have told us that having to laser ablate the anti-reflection coating of cells to create a connection for NiSi, and the addition of two printing and annealing (sintering for copper) steps, adds too much expense to compensate for any potential cost savings from using copper. The cost benefits of copper have been further eroded by the facts that over the lifetime of this project, the cost of silver electrodes decreased due to manufacturers finding ways to use less and less silver, and inventing pastes which use less costly silver materials to begin with. All of these factors were considered and led to the decision to stop the program before actual manufacturing scale was attempted.

Background

The use of silver front-side contacts in silicon solar cells is ubiquitous. This is principally due to the ease of creation of the contacts in a manufacturing environment. Specially formulated pastes are screen printed onto the top of the anti-reflection coating (ARC) layer and fired for fractions of a minute in a conveyorized furnace at 800˚C. This process works because the pastes are specially formulated[1] using glass frit to "fire through" the ARC layer. The glass aids in the paste etching-melting through the SiN of the ARC so that some metal can make ohmic contact with the silicon layer underneath the ARC and conduct electrons to the bulk of the silver electrode on top of the ARC.

While this process is elegant in its simplicity, the glasses used in the frit must contain lead (Pb) which is banned from products in Europe and in the State of California. Attempts to remove lead have proven fruitless. Yet this process is so important for the solar industry, that California and Europe have both given exceptions for using Pb in solar cells. The second objection to these pastes is that they use silver which is an extremely expensive precious metal. In addition, silver can contribute as much as 50% of the cost of the cell itself.[2] Copper would seem a logical substitute for silver since it is 100 times less expensive and very similar to silver in its electrical conductivity. However, copper is known to migrate through the silicon of the cell, poisoning the p-n junction by creating deep level electron traps, and severely degrading the efficiency of the cell.[3]

To overcome this effect, various workers have interposed a nickel silicide barrier layer in between copper electrodes and the silicon. This is usually done by opening a grid pattern for the electrodes in the ARC by etching or laser ablating. Nickel can be sputtered into the opening and annealed to make NiSi[4], Ni can be electrolessly plated[5], or Ni in can be printed[6]. Copper can be sputtered or light induced plated on top of the nickel silicide.

It was our plan to simplify these processes by printing a nickel silicide ink into the opening, annealing, then printing a copper ink of top of the silicide and sintering. These processes could be sequenced into a continuous, rather than batch, manufacturing process to reduce the cost of the added number of processes compared to the number of processes used to make silver grids. Such process should be scalable and easily integrated into solar cell manufacturing lines. We had previously developed a method of making nickel silicide nanoparticles via a plasma method, and incorporating them into ink.[7]

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[1] J.D. Fileds, et al, Nature Communications, 7, 11143 (2016)

[2] Key Issues and Innovations in Photovoltaic Metallizaiton, Lux Research, 2012

[3] A. Kraft, C. Wolf, J. Bartsch, M. Glatthaar, Energy Procedia 67, 2015, p93, and M.C.Raval and C.S. Solanski, Journal of Solar Energy 2013 (2013)

[4] A. A. Marshall, MS Thesis, Rochester Institute of Technology, 2017

[5] A. Fosca, et al, Energy Procedia, Vol 38, 2013, p 713

[6] Y. Li, X. Li, J.P. Novak, US 2012/0142140

[7] R. Dixon, J. Pedrosa, K.M. Yu, and E. Yu, WO 2014/072918

Objectives

The primary objective of this program was to demonstrate a cost-effective alternative to silver contacts in silicon solar cells. The present silver processes are carried out in the far east, so a lower cost alternative should allow manufacturing of cells in the United States. By replacing the silver paste process with the less expensive and already developed nickel silicide and copper nano particle inks, the materials costs are reduced. In addition, these are additive printing processes that do NOT require vacuum deposition. The removal of lead makes the process palatable in California and the EU without having environmental exceptions. The tooling and labor costs are minimal and easily incorporated into the manufacturing line. The program is designed to, first, demonstrate the efficacy of the materials and process, then to show it to be scalable and integrable into solar cell manufacturing lines in a cost-effective manner.

Intermediate goals include creation of NiSi contacts through formation of a NiSi ink that can be inkjetted onto an etched ARC. This will be followed by inkjet printing a special copper inkjet ink. The possibility of plating copper will be investigated. The end result will be a composite NiSi/Cu contact. We also intended to demonstrate the performance of the resulting solar cell, but also a manufacturing process.

Project Results and Discussion

Report on D0, Intrinsiq Materials, January 16, 2015

The following information is being presented in fulfillment of the D0 deliverables from the Sunshot Printed Cu/NiSi Project Deliverables Table.

There are three general sets of baseline deliverables. In the first, D0.1, we are required to show that copper materials can be printed and sintered to give electrical and physical properties required for use as gridlines in silicon solar cells. D0.2 requires our construction of a test cell whose gridlines perform well enough to be used as a base structure for future testing. D0.3 requires feedback from knowledgeable solar cell companies that this copper over nickel silicide technology is potentially useful and feasible, and an assessment of tooling necessary to commercially implement. These deliverables, as taken from the Project Deliverables Table, are shown below.

D0.1 requires that at least 3 samples of copper ink printed onto glass pass electrical performance and adhesion testing. The parameters required to pass these tests are:

1. Bulk resistivity by the two point probe method less than 6.8 μΩ-cm
2. Adhesion as measured by the ASTM 3359 tape test of 4B or better

D0.2 requires at least 3 baseline test structures (hereafter called Si test structure) using the RIT process that includes implanted emitter, single layer SiN ARC, photolithographic etching of the ARC layer, and depositing a Ti-Pd-Ag conductor. Pass below:

1. Specific contact resistance: ρc </= 10^-4 Ohm-cm^2. Tested by TLM method.
2. Gridline resistivity by two point probe method </= 10^-5 Ohm-cm.

D0.3 Business Deliverables

1. Create a Target List of key companies that can utilize technology.
2. Contact 3 companies on the list with a description of the program and request feedback and input.
3. Obtain Feedback from process vendors regarding line tooling and identified program

D0.1 Results

Two kinds of samples were prepared for testing of this set of deliverables. The first was a series of lines with end pads, of copper printed onto glass, whose physical dimensions and electrical resistance could be measured. These were sintered in a tube furnace in a reducing atmosphere to create conductive traces as shown in Figure 1b. A cross sectional area measurement for one of these lines is shown in Figure 1a. One set of three samples was measured at Intrinsiq and one was sent to NREL. Bulk resistivities were calculated from the formula:

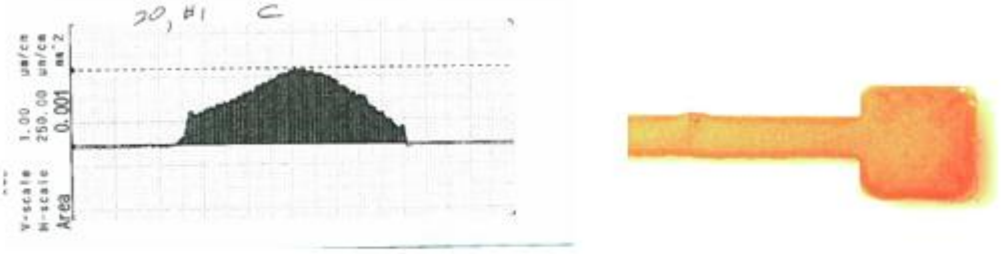
P (Bulk Resitivity, rho) = [R (Ohms) * Area (mm^2) / length (mm)] * 1 cm / 10 mm.

A comparison of the bulk resistivity data from Intrinsiq and NREL is shown Table 1.

Table 1. Test Structure Volume Resitivities

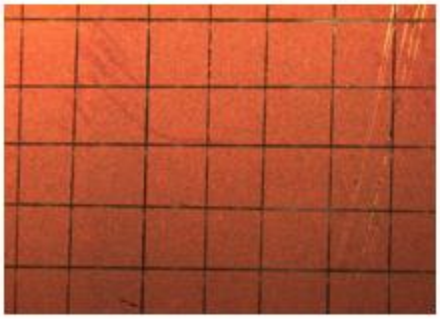
Sample Number	Intrinsiq Measured Values	NREL Measured Values
1	5.2	4.66
2	4.4	5.43
3	4.3	6.46

Figure 1. Testing Printed Copper Traces

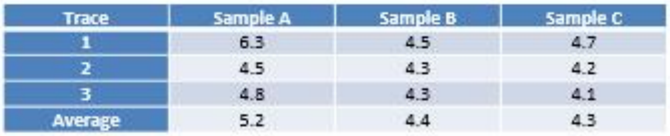


a. Profile and cross sectional area of an inkjet-printed nanocopper ink.

b. A printed, sintered trace



c. A tape tested sample scored 5B for adhesion

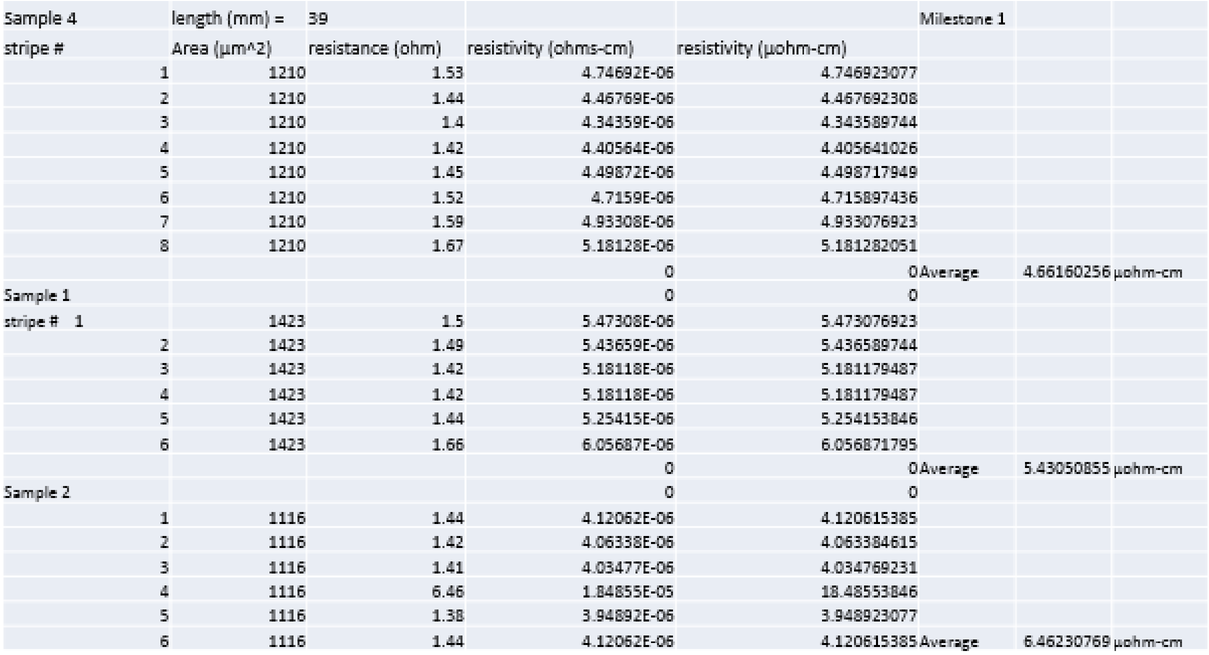


Trace	Sample A	Sample B	Sample C
1	6.3	4.5	4.7
2	4.5	4.3	4.2
3	4.8	4.3	4.1
Average	5.2	4.4	4.3

d. Bulk resistivities of nine printed samples (all values in µΩ-cm)

The units of bulk resistivity are µΩ-cm. The values of a number of lines used to calculate the averages in the table are shown for Intrinsiq in Figure 1d and for NREL in Figure 2. The Intrinsiq and NREL values are reasonably close and all are under the required minimum of 6.8 µΩ-cm, so this *milestone is passed*.

Figure 2. NREL Volume Resistivity Measurements on Inkjet Printed Test Structures



Sample 4	length (mm) =	39			Milestone 1		
stripe #	Area (µm^2)	resistance (ohm)	resistivity (ohms-cm)	resistivity (µohm-cm)			
1	1210	1.53	4.74692E-06	4.746923077			
2	1210	1.44	4.46769E-06	4.467692308			
3	1210	1.4	4.34359E-06	4.343589744			
4	1210	1.42	4.40564E-06	4.405641026			
5	1210	1.45	4.49872E-06	4.498717949			
6	1210	1.52	4.7159E-06	4.715897436			
7	1210	1.59	4.93308E-06	4.933076923			
8	1210	1.67	5.18128E-06	5.181282051			
			0	0	Average	4.66160256	µohm-cm
Sample 1			0	0			
stripe # 1	1423	1.5	5.47308E-06	5.473076923			
2	1423	1.49	5.43659E-06	5.436589744			
3	1423	1.42	5.18118E-06	5.181179487			
4	1423	1.42	5.18118E-06	5.181179487			
5	1423	1.44	5.25415E-06	5.254153846			
6	1423	1.66	6.05687E-06	6.056871795			
			0	0	Average	5.43050855	µohm-cm
Sample 2			0	0			
1	1116	1.44	4.12062E-06	4.120615385			
2	1116	1.42	4.06338E-06	4.063384615			
3	1116	1.41	4.03477E-06	4.034769231			
4	1116	6.46	1.84855E-05	18.48553846			
5	1116	1.38	3.94892E-06	3.948923077			
6	1116	1.44	4.12062E-06	4.120615385	Average	6.46230769	µohm-cm

To measure the adhesion of copper onto glass, uniform patches of copper inkjet ink were printed onto glass and a grid of 11 horizontal and 11 vertical lines spaced 1 mm apart was made according to the ASTM3359 tape pull test. Both Intrinsiq and NREL purchased a Gardco tape test kit (PA-2000). We both used the PA-280630 tape supplied with the kit for the test. However, the scribing tool supplied with the kit was not used at Intrinsiq, as we found that good straight cuts in which all 11 scribing blades penetrated the coating could not be obtained. Rather, we scribed the 11 line cross hatch pattern using a razor blade and a metal straight edge and removed any debris from the scoring with the brush supplied in the kit. This method of creating grids is actually outlined in the Standard for cases in which the tool supplied in the kit does not give good results. Six separate patches were tested. In five of the patterns, no difference was seen in the scribed pattern before or after tape testing, so these were judged 5B. A typical pattern is shown (magnified) in Figure 1c. One of the samples had two squares removed, so was judged 4B. On average, these samples scored well above the 4B required for D0.

NREL attempted to use the scribing tool supplied with the kit and found, as Intrinsiq did, that it was difficult to make good cuts with all 11 blades of the tool all at once. The initial NREL data showed some samples, particularly in areas outside the grid and in places where the grid fell in a non-uniform area, that scored 3B. After some discussion with NREL we all agreed that confining assessment to areas which were well-gridded and which fell in uniform areas of the deposit were reasonable. Doing this, NREL judged their samples to be 4B, and the adhesion *milestone was passed*.

In the future, we agreed that NREL could use the scribing tool to make initial cuts and that places in the grid in which the coating was not fully penetrated would be further scribed with a razor blade and a straight edge.

D0.2 Results

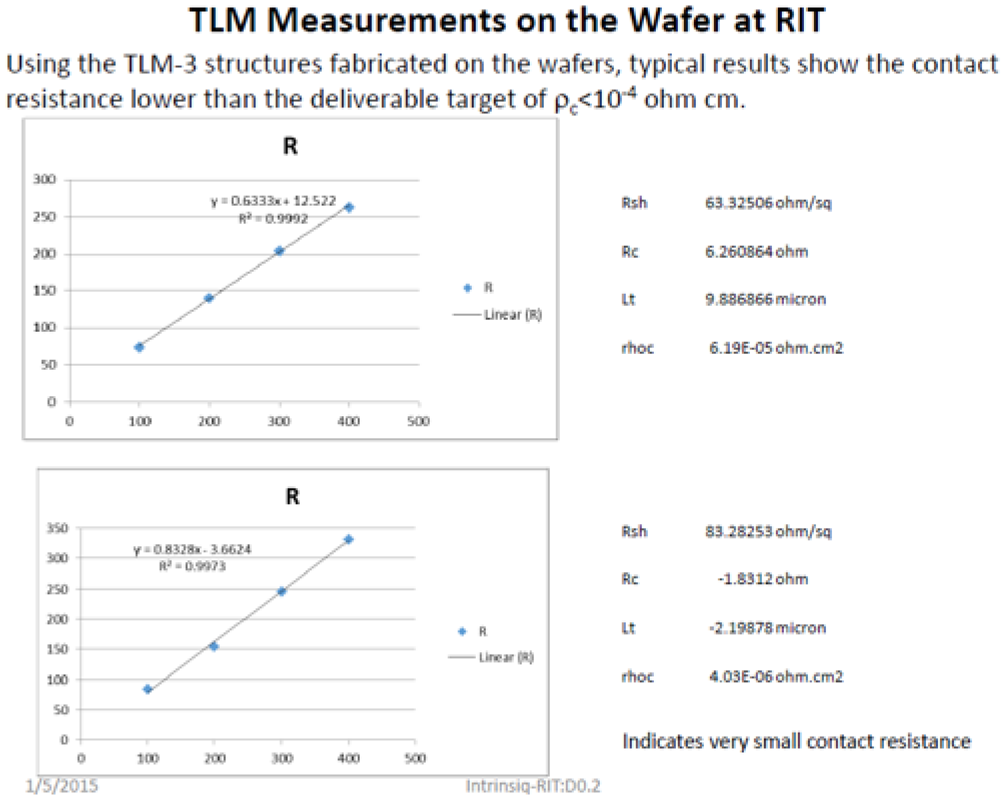
Measuring and comparing the volume resistivity of the Ti-Pd-Ag contacts on the baseline cells prepared at RIT proved to be very straightforward. NREL used the two point probe method on three different samples to generate the average resistivity in Table 2. The average for the 5 samples

Table 2. Cell Volume Resistivities	NREL Average	RIT Average
Volume Resitivity (µΩ-cm)	4.87	1.0

Measured at RIT is also shown. While the RIT number is somewhat better than that measure at NREL both average resistivities are below the target value of 10 µΩ-cm (10^-5 Ω-cm). This *milestone is passed*.

Measuring the specific contact resistance of those gridlines via the TLM method proved more problematic. RIT used the 4 point probe method to generate data like that exemplified in Figure 3. The values for four samples are shown in Table 3. NREL had to use a two point probe method because of limitations in their equipment. NREL has concluded that their methodology overestimates the contact resistance, and that they would not be able to reproduce the RIT numbers without a significant upgrade to their equipment or a change in the size of the pads of the TLM pattern on the cells generated at RIT. Because both options are time-consuming and expensive, NREL recommended that we all agree that the RIT numbers are valid and that we deem this *milestone passed*.

Figure 3.



TLM Measurements on the Wafer at RIT

Using the TLM-3 structures fabricated on the wafers, typical results show the contact resistance lower than the deliverable target of $\rho_c < 10^{-4}$ ohm cm.

Rsh	63.32506 ohm/sq
Rc	6.260864 ohm
Lt	9.886866 micron
rhoc	6.19E-05 ohm.cm2

Rsh	83.28253 ohm/sq
Rc	-1.8312 ohm
Lt	-2.19878 micron
rhoc	4.03E-06 ohm.cm2

Indicates very small contact resistance

1/5/2015 Intrinsiq-RIT:D0.2

Table 3. TLM Measurements of Specific Contact Resistance

TLM Sample Number	RIT Measured (Ω-cm^2)	NREL Measured (Ω-cm^2)
1	6.19E-05	1.3E-03
2	4.03E-06	4.8E-04
3	2.65E-06	1.3E-04
4	2.92E-05	

Addressing Deliverable Milestone D1 - Demonstrate Contact Resistivity of Printed NiSi

Deliverable: Contact resistivity by TLM of 1-100 mΩ-cm^2

This letter is written in response to contact resistance measurements taken at NREL for samples prepared by Intrinsiq Materials and SUNY Poly CNSE PVMDF. The samples were prepared as follows:

1. Multicrystalline Si (mc-Si) wafers with acid-textured surface, phosphorus emitter (~60 Ω/sq), and silicon nitride ARC were scribed using a green laser to produce multiple lines of 0.25 cm separation. The laser scribing was optimized such that silicon nitride was ablated with minimal damage to the underlying silicon crystal.
2. Scribed mc-Si wafers were treated with 5% HF for 30 seconds, rinsed and dried.

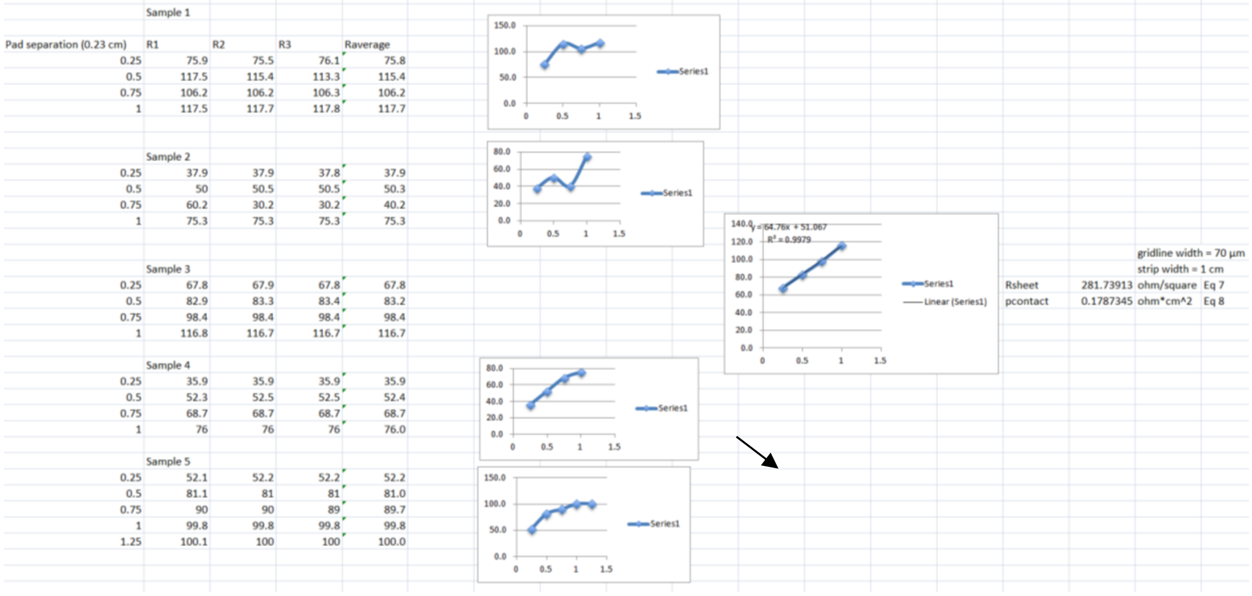
3. NiSi material was jetted over the scribed lines on the mc-Si wafers and annealed.
4. Cu was plated over the annealed NiSi lines.
5. One centimeter wide TLM strips were prepared by mechanical cleaving of wafers along laser-scribed lines on the rear side followed by contact resistance measurement.

We used the method of Meier, *et al.*,[8] in preparing samples and measuring contact resistance. Meier, *et al.*, cite the following equation for calculating contact resistivity (ρ_c) using measured line-to-line resistance versus line separation distance:

$$\rho_c = \frac{2R_C}{2} \cdot L_C \cdot W$$

where L_C is the line length (0.007 cm in our case) and *W* is the line width (1 cm in our case). From Reeves and Harrison[9], it can be seen that the *y-intercept* in a plot of line-to-line resistance versus line separation is equal to $2R_C$, where R_C is the contact resistance. Contact resistivity (ρ_c) is found by factoring the contact area (L_CW) into R_C, resulting in values with units of Ω-cm^2.

David Young at NREL returned a document titled "intrinsiq TLM data 10-27-15 – Ag Control samples.xlsx" via email on Tuesday, 10/28/15. In this spreadsheet can be found line-to-line resistance versus line separation data for the five NiSi/Cu samples sent for testing as well as similar measurements for screen-printed Ag control samples. A screen shot of the NiSi/Cu data from this spreadsheet is found on the below.



	Sample 1			
Pad separation (0.23 cm)	R1	R2	R3	Raverage
0.25	75.9	75.5	76.1	75.8
0.5	117.5	115.4	113.3	115.4
0.75	106.2	106.2	106.3	106.2
1	117.5	117.7	117.8	117.7
	Sample 2			
0.25	37.9	37.9	37.8	37.9
0.5	50	50.5	50.5	50.3
0.75	60.2	30.2	30.2	40.2
1	75.3	75.3	75.3	75.3
	Sample 3			
0.25	67.8	67.9	67.8	67.8
0.5	82.9	83.3	83.4	83.2
0.75	98.4	98.4	98.4	98.4
1	116.8	116.7	116.7	116.7
	Sample 4			
0.25	35.9	35.9	35.9	35.9
0.5	52.3	52.5	52.5	52.4
0.75	68.7	68.7	68.7	68.7
1	76	76	76	76.0
	Sample 5			
0.25	52.1	52.2	52.2	52.2
0.5	81.1	81	81	81.0
0.75	90	90	89	89.7
1	99.8	99.8	99.8	99.8
1.25	100.1	100	100	100.0

		gridline width = 70 µm	
		strip width = 1 cm	
Rsheet	281.73913	ohm/square	Eq 7
pcontact	0.1787345	ohm*cm^2	Eq 8

We question the accuracy of the data provided by David Young, which shows contact resistivity for one sample at 0.178 Ω-cm^2. In rebuttal to this data we submit contact resistivity measurements

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[8] Meier, D. L., *et al.* (2006) "Determining components of series resistance from measurements on a finished cell," 4th WCPEC, vol. 2, pp. 1315 – 1318.

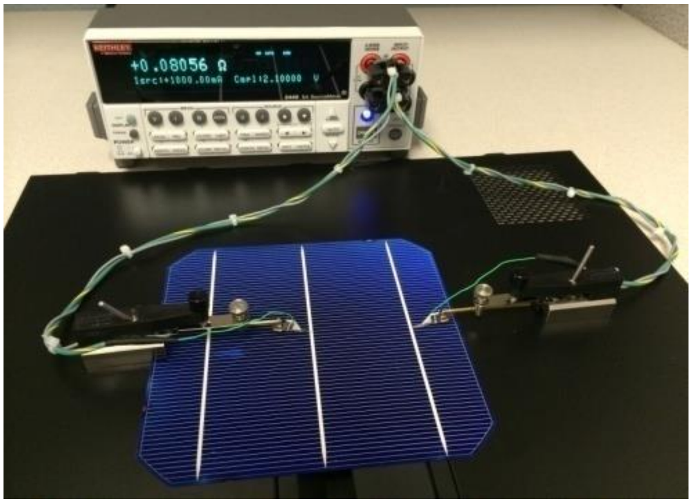
[9] Reeves, G. K., and Harrison, H. B. (1982) "Obtaining the specific contact resistance from transmission line model measurements," IEEE Electron Device Letters, vol. EDL-3, pp. 111 – 113.

for 3 NiSi/Cu samples and 1 screen-printed Ag control prepared by Intrinsiq Materials and SUNY Poly CNSE PVMDF measured independently at SUNY Poly CNSE PVMDF and RIT. See the Measurement section below for details of TLM sample preparation and measurement at SUNY Poly CNSE PVMDF. See Measurement Section for details of TLM sample measurement at RIT. Table 4 below summarizes the results of the independent measurements. For each NiSi/Cu sample selected the contact resistivity falls below 0.100 Ω-cm^2. **<u>These values for contact resistivity satisfy the deliverable for milestone D1.</u>** Data for each sample from both SUNY Poly and RIT are given in the Measurement Section. In that Section, raw data taken at SUNY Poly CNSE PVMDF and RIT matches quite well for each sample. We believe this agreement of data taken using two independent measurement apparatuses indicates that the contact resistivity data of Table 4 is accurate and correct.

Sample ID	**Contact Resistivity (ρ_c) in Ω-cm^2**	
	SUNY Poly CNSE PVMDF	**RIT**
1	0.010 (R^2 = 0.9981)	0.017 (R^2 = 0.9835)
2	0.070 (R^2 = 0.9992)	0.061 (R^2 = 0.9814)
3	0.064 (R^2 = 0.9947)	0.011 (R^2 = 0.9948)
Ag Control	0.002 (R^2 = 0.9999)	0.005 (R^2 = 1.0000)

Table 4. Contact resistivity summary

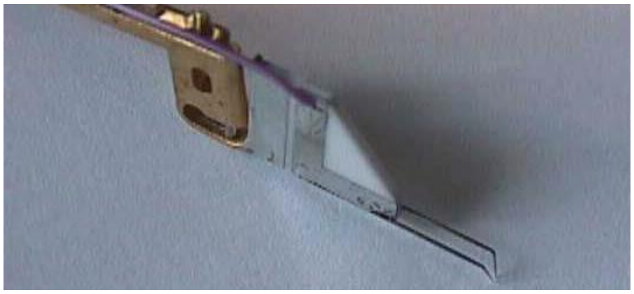
Measurement Section: SUNY Poly CNSE PVMDF Contact Resistivity Measurement Method



Built by Ian Cooper, Director of Silicon Solar Technology, SUNY Polytechnic Institute, Colleges of Nanoscale Science and Engineering, Photovoltaic Manufacturing and Technology Development Facility (SUNY Poly CNSE PVMDF)

Apparatus

1. Keithley Model 2440 5A SourceMeter
2. Tungsten Kelvin Probes from Accuprobe

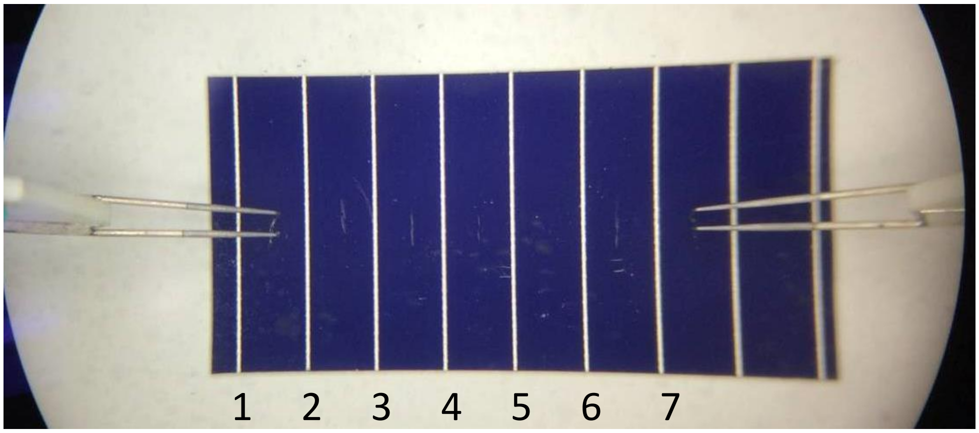


3. Signatone S-750 probe holders

4. Banana Plugs and large gauge wire

Sample preparation

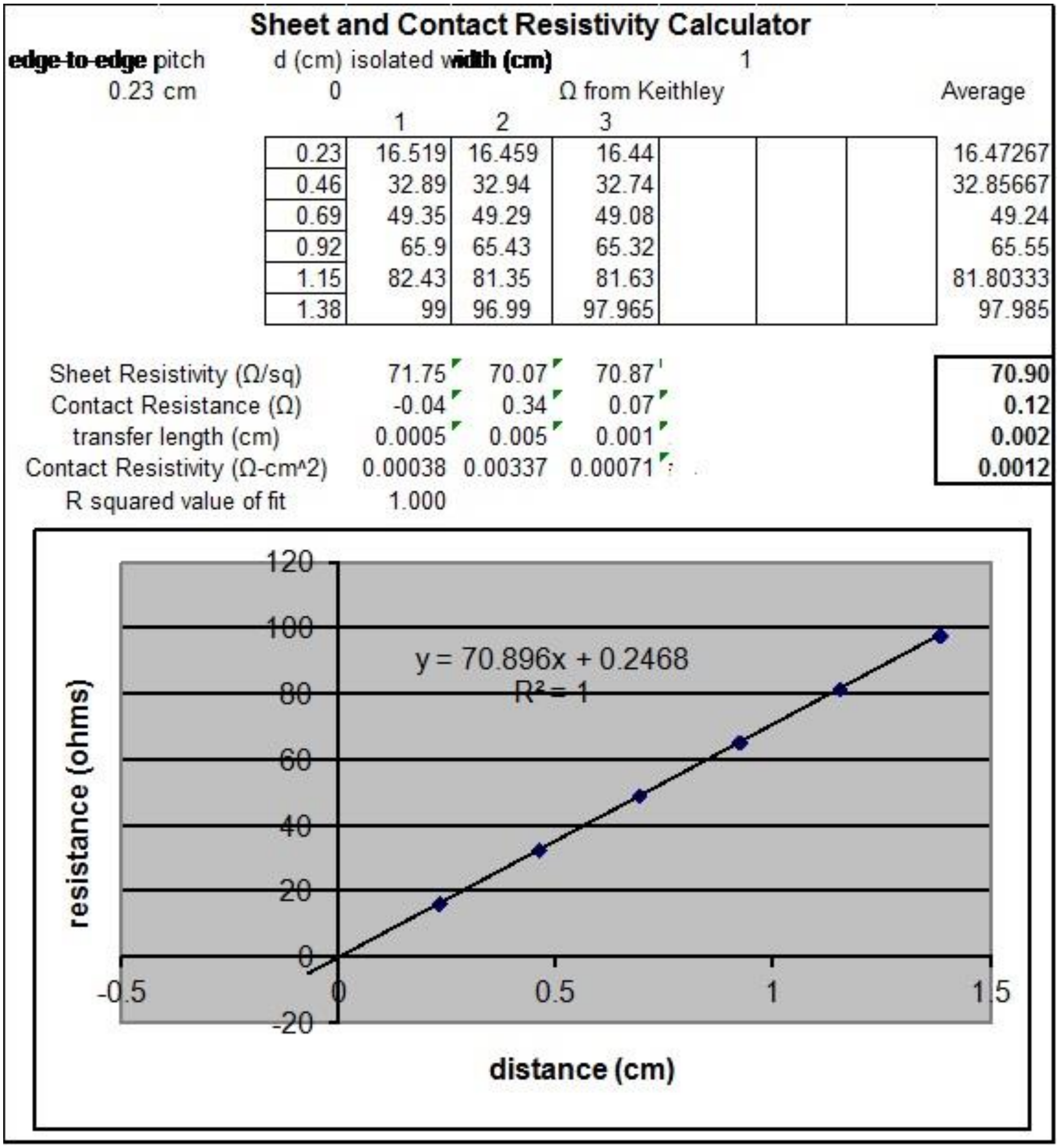
1. Contact resistance is calculated from data collected using the Transmission Line Model (TLM). The method used at the SUNY Poly CNSE PVMDF follows methods published by Meier, *et al.* (D. L. Meier, E. A. Good, A. Garcia, B. L. Bingham, S. Yamanaka, V. Chandrasekaran, and C. Bucher, "Determining components of series resistance from measurements on a finished cell," 4th WCPEC, 2006, vol. 2, pp. 1315 – 1318.) and Reeves and Harrison (Reeves, G. K., and Harrison, H. B. (1982) "Obtaining the specific contact resistance from transmission line model measurements," IEEE Electron Device Letters, vol. EDL-3, pp. 111 – 113.).
2. Using samples with pre-deposited metallization lines (ie – a finished silicon solar cell), a strip is extracted from an area containing only gridline conductors (no busbars). This is done by multi-pass laser scribed lines on the rear side of the sample. At least two scribed lines are made, separated by 1 centimeter. The scribed lines are such that slight pressure applied along the scribe will result in wafer cleavage. This cleavage along the scribed line electrically isolates the metallization lines for TLM measurement. It is important to note that laser scribing is NOT performed on the metallization line side of the sample. Preparation of samples from the metallization line side will lead to artifact in the TLM data due possibly to diffusion or alloying of pre-deposited metallization with silicon. Below is an image of a typical TLM sample.



Measurement Method

1. The Keithley Model 2440 5A SourceMeter is configured for 4-point sense mode and set to measure resistance (Ω). Engaging the source control, typical current/voltage combination for resistance measurement is 100 mA and 2 V.
2. One Kelvin Probe I/V pair is kept stationary on a metallization line. The second Kelvin probe I/V pair is placed on sequential metallization lines. Resistance is measured between point 1 and 2, 1 and 3, 1 and 4, etc., with numbering indicated in the image above. All measurements are performed in darkness.
3. Resistance measurements are plotted against probe distance as shown below. The slope of this line is the emitter sheet resistance (R_{SHEET}; average 70.9 Ω/sq in this case).The

contact resistance is taken as half the resistance value at the y-intercept of this line (R_C; average 0.12 Ω in this case). The contact resistivity (ρ_C) is calculated as $\rho_C = R_C \cdot d \cdot w$ (average 0.0012 Ω-cm^2 in this case), where d is the line width (0.01 cm in this case) and w is the line length (1 cm in this case).



Sheet and Contact Resistivity Calculator

edge-to-edge pitch 0.23 cm

d (cm) isolated **width (cm)** 1

0

	1	2	3				Average
0.23	16.519	16.459	16.44				16.47267
0.46	32.89	32.94	32.74				32.85667
0.69	49.35	49.29	49.08				49.24
0.92	65.9	65.43	65.32				65.55
1.15	82.43	81.35	81.63				81.80333
1.38	99	96.99	97.965				97.985

Ω from Keithley

	1	2	3	Average
Sheet Resistivity (Ω/sq)	71.75	70.07	70.87	**70.90**
Contact Resistance (Ω)	-0.04	0.34	0.07	**0.12**
transfer length (cm)	0.0005	0.005	0.001	**0.002**
Contact Resistivity (Ω-cm^2)	0.00038	0.00337	0.00071	**0.0012**
R squared value of fit	1.000			

Measurement Section: RIT Contact Resistivity Measurement Method

TLM Measurement at RIT

TOOLS USED

1. 4145A Semiconductor parameter analyzer
2. Probe station
3. Probe - Diameter (5 um – From Signatone)
4. ICE software
5. Microscope and light source
6. Switch Matrix –Text Fixture (HP)

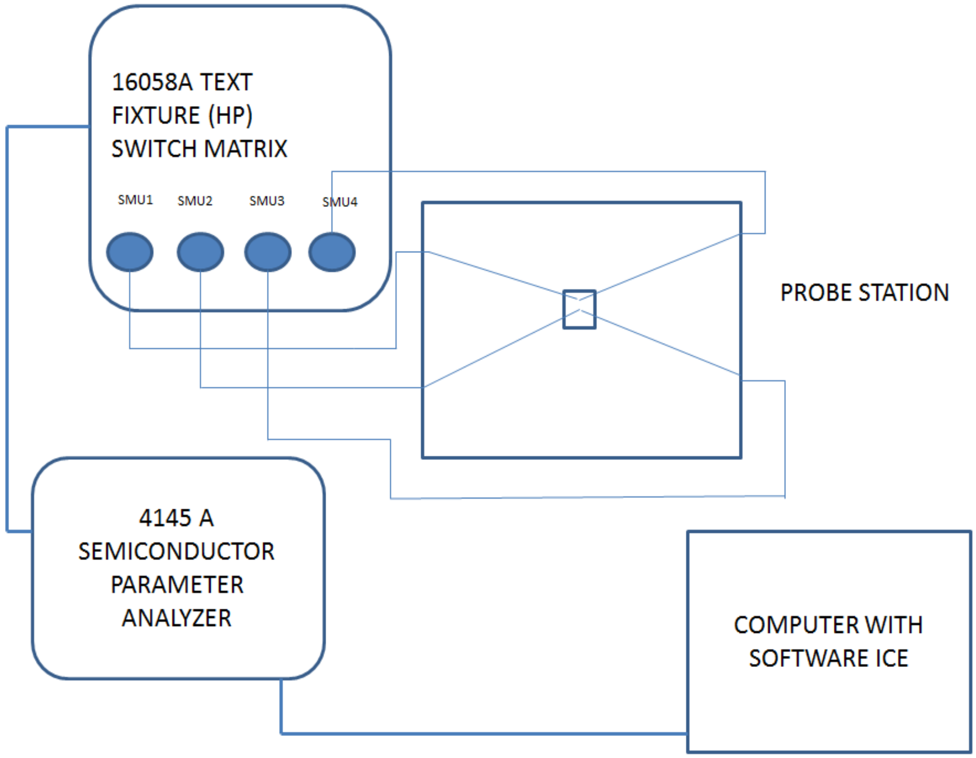


Figure 1: Setup of TLM measurement apparatus

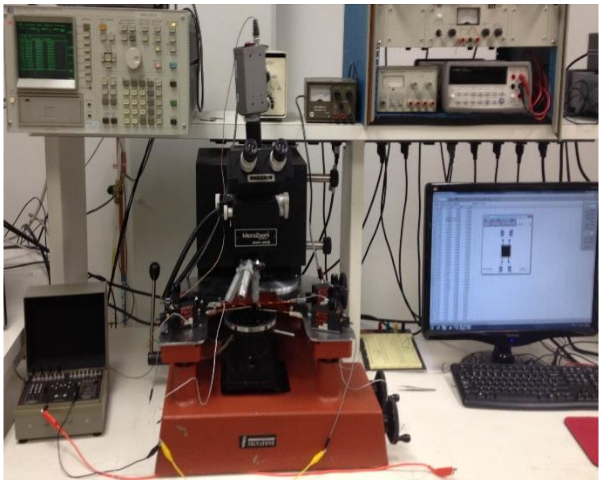


Figure 2: 4145 A semiconductor parameter analyzer, manual probe station, microscope and IC software.

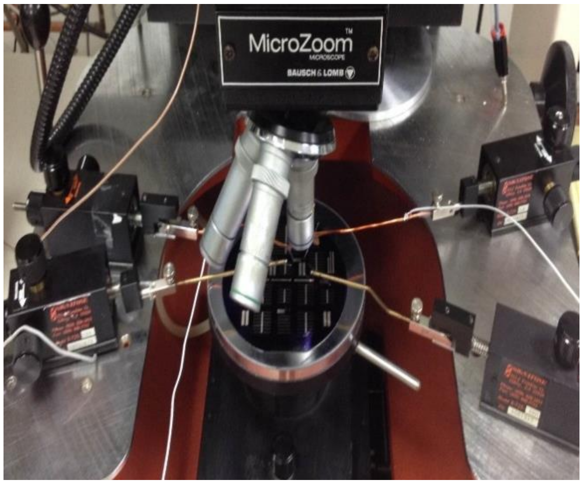


Figure 3: Zoomed in view of probes and sample

Procedure

1. 4145A semiconductor parameter analyzer and the computer are connected.

2. The wafer is placed on stage on the stage as shown in figure 3, this stage is connected to the light source.

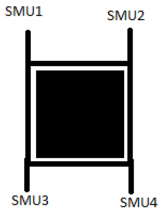
3. Probes from the probe station are connected to the power source (SMU1/SMU2/SMU3/SMU4)

4. A 4 probe measurement is done, two probes (SMU1, SMU2) are placed on the top square and two (SMU3, SMU4) on the bottom square of the particular TLM to be measured.

6. IC's software is used and set according to the specifications, source units are connected and appropriate stimulus and measure conditions are provided.

SMU1: Stimulus-Current
Measure-Current
Compliance-10
Mode-Sweep (50uA-500uA); 51 points

SMU2: Stimulus-Current
Measure-Voltage
0Amps



SMU3: 0V

SMU4: Measure-Voltage; 0Amps

7. The software plots I-V characteristics, excel is used to analyze the data and find resistance from I-V slope. From R at each spacing, we extract $\square_c$ as described below:

$$R_C = \frac{\sqrt{R_{Sh}\cdot\rho_C}}{W}\coth\left(\frac{L_C}{L_T}\right) \qquad L_T = \sqrt{\frac{\rho_C}{R_{Sh}}} \text{ Transfer Length}$$

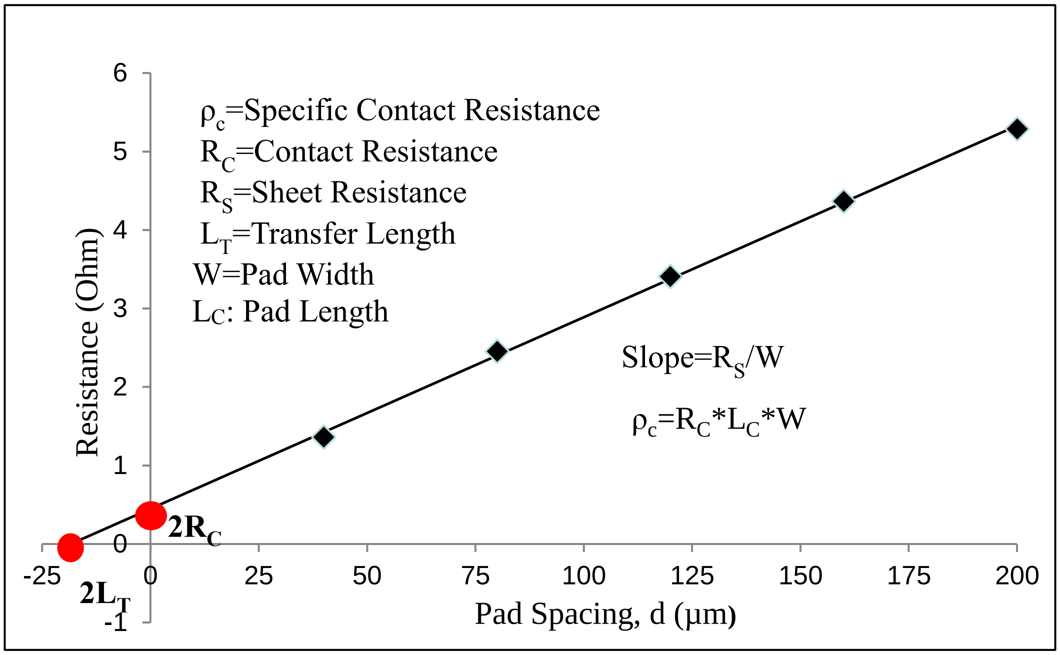
Two limiting cases:

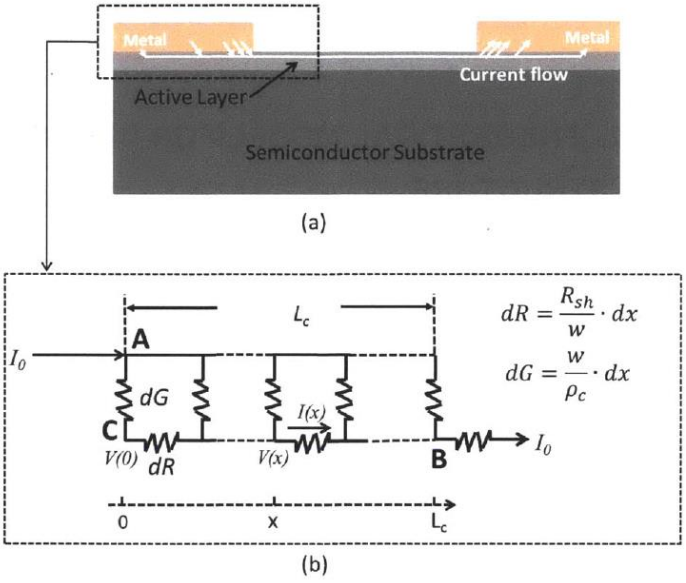
1. $L_C < 0.5L_T$ $\quad \coth\left(\frac{L_C}{L_T}\right) \approx \frac{L_T}{L_C} \qquad R_C = \frac{\sqrt{R_{Sh}\cdot\rho_C}}{W}\frac{L_C}{L_T} = \frac{\rho_C}{WL_C}$

This is the limit of a short contact in which, essentially, the current flows downwards over the entire contact length

2. For $L_C \geq 1.5L_T$ $\quad \coth\left(\frac{L_C}{L_T}\right) \approx 1 \qquad R_C = \frac{\rho_C}{WL_T}$

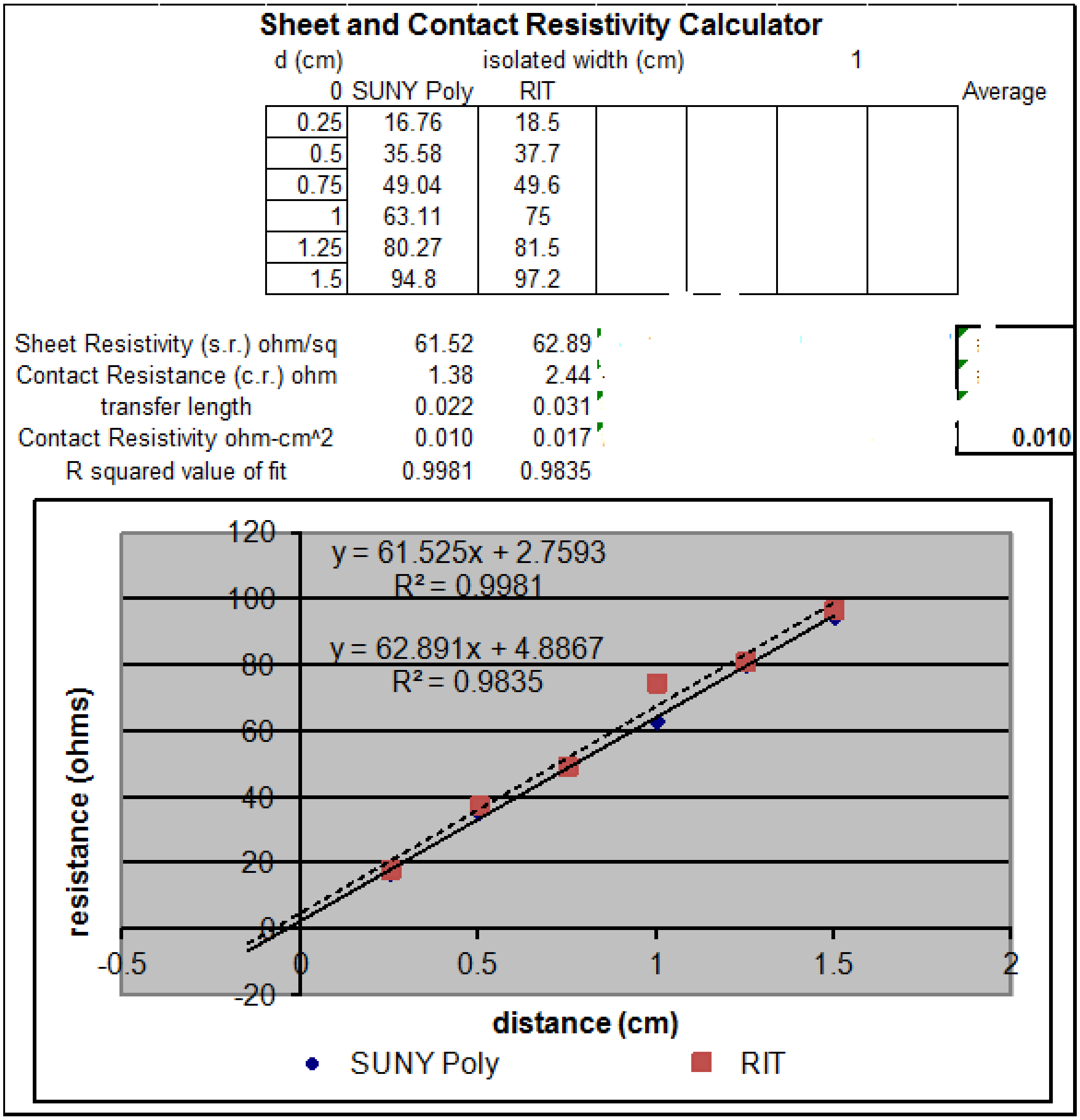
This is the limit of a long contact in which the current flows downwards on the scale of the transfer length.





Measurement Section: TLM data for NiSi/Cu samples 1 – 3 taken at SUNY Poly CNSE PVMDF and RIT

Sample 1



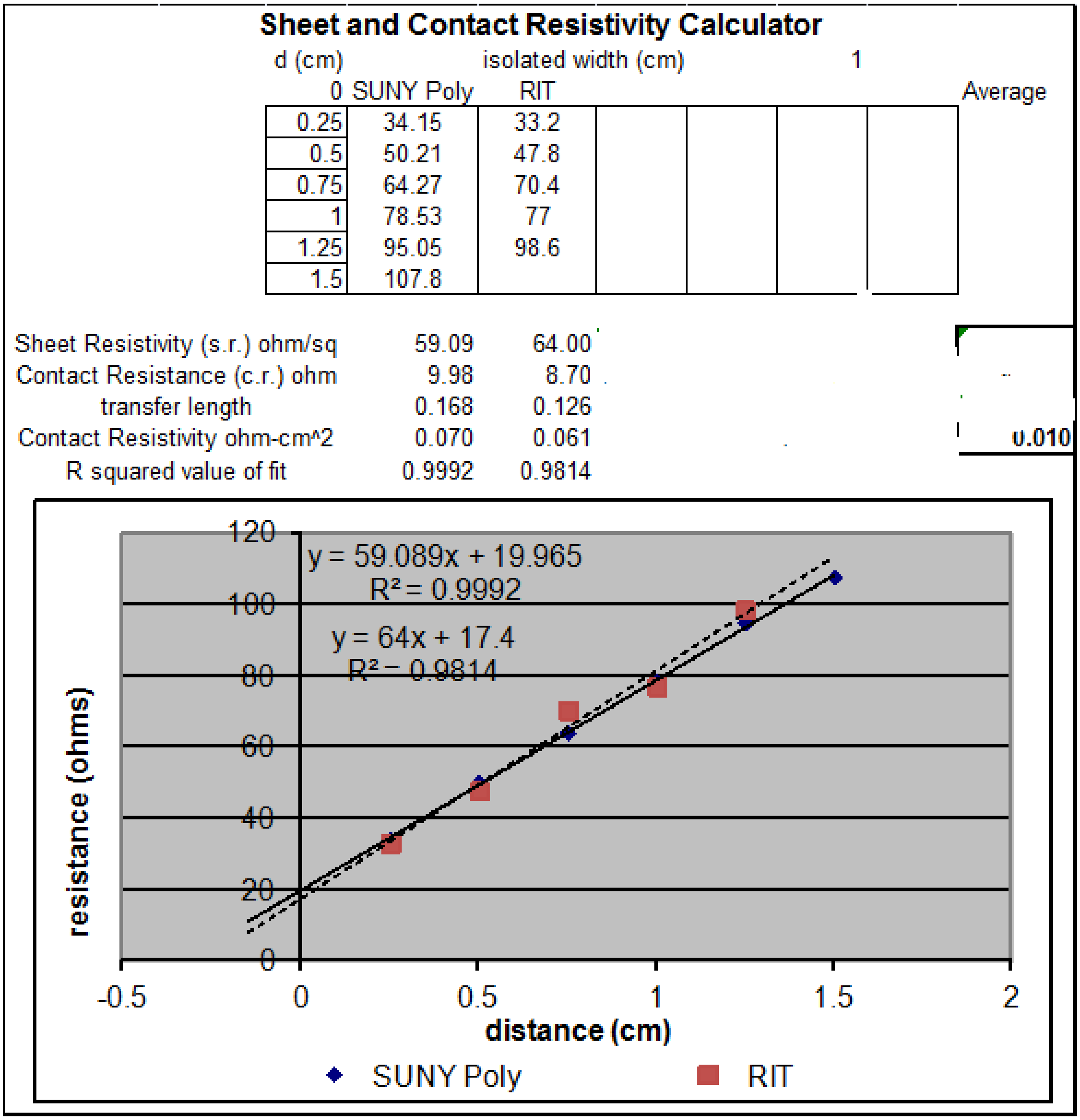
Sheet and Contact Resistivity Calculator

d (cm) isolated width (cm) 1

d (cm)	SUNY Poly	RIT					Average
0							
0.25	16.76	18.5					
0.5	35.58	37.7					
0.75	49.04	49.6					
1	63.11	75					
1.25	80.27	81.5					
1.5	94.8	97.2					

	SUNY Poly	RIT	Average
Sheet Resistivity (s.r.) ohm/sq	61.52	62.89	
Contact Resistance (c.r.) ohm	1.38	2.44	
transfer length	0.022	0.031	
Contact Resistivity ohm-cm^2	0.010	0.017	0.010
R squared value of fit	0.9981	0.9835	

Sample 2



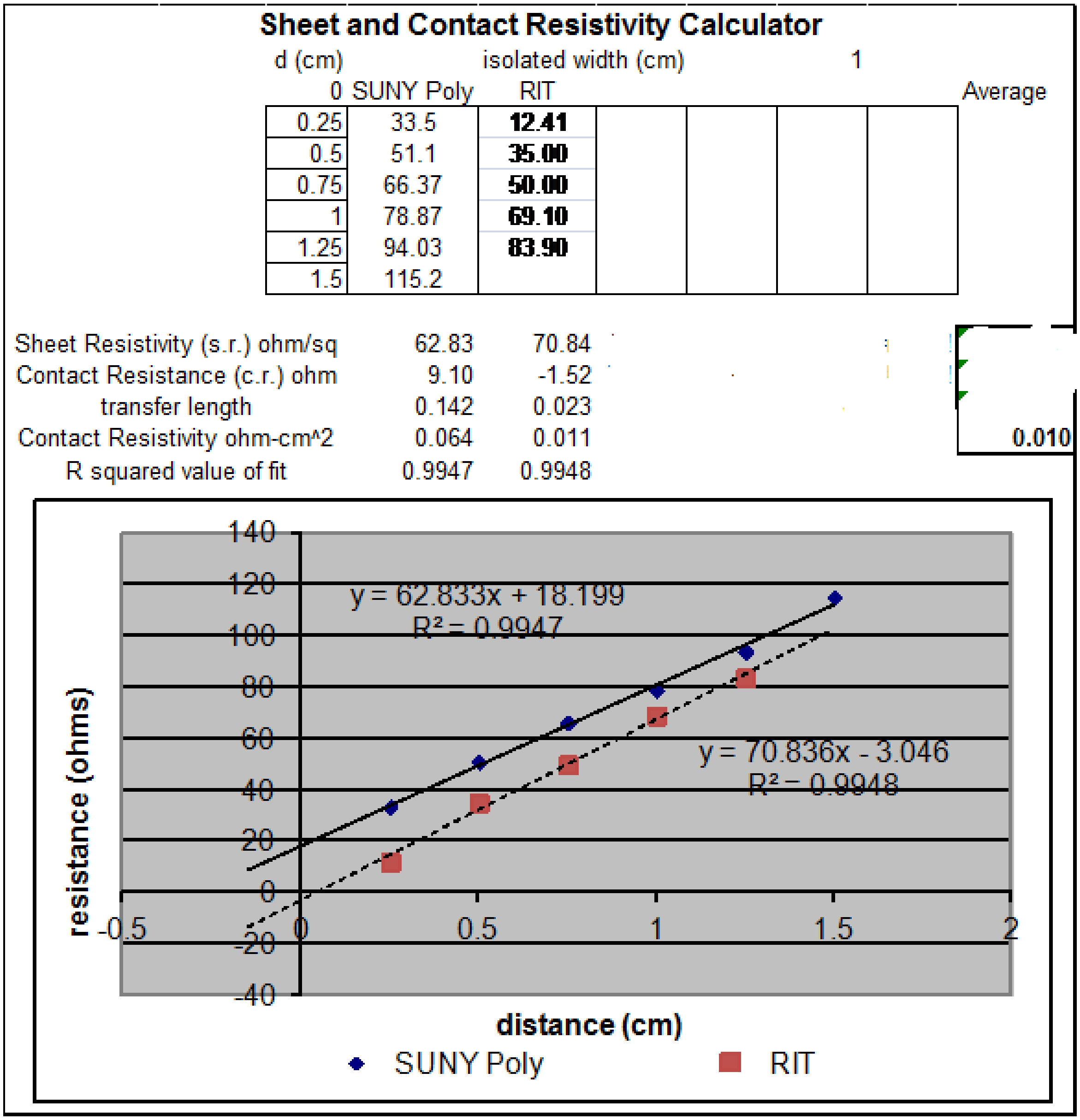
Sheet and Contact Resistivity Calculator

d (cm) isolated width (cm) 1

d (cm)	SUNY Poly	RIT					Average
0							
0.25	34.15	33.2					
0.5	50.21	47.8					
0.75	64.27	70.4					
1	78.53	77					
1.25	95.05	98.6					
1.5	107.8						

	SUNY Poly	RIT	Average
Sheet Resistivity (s.r.) ohm/sq	59.09	64.00	
Contact Resistance (c.r.) ohm	9.98	8.70	
transfer length	0.168	0.126	
Contact Resistivity ohm-cm^2	0.070	0.061	0.010
R squared value of fit	0.9992	0.9814	

Sample 3



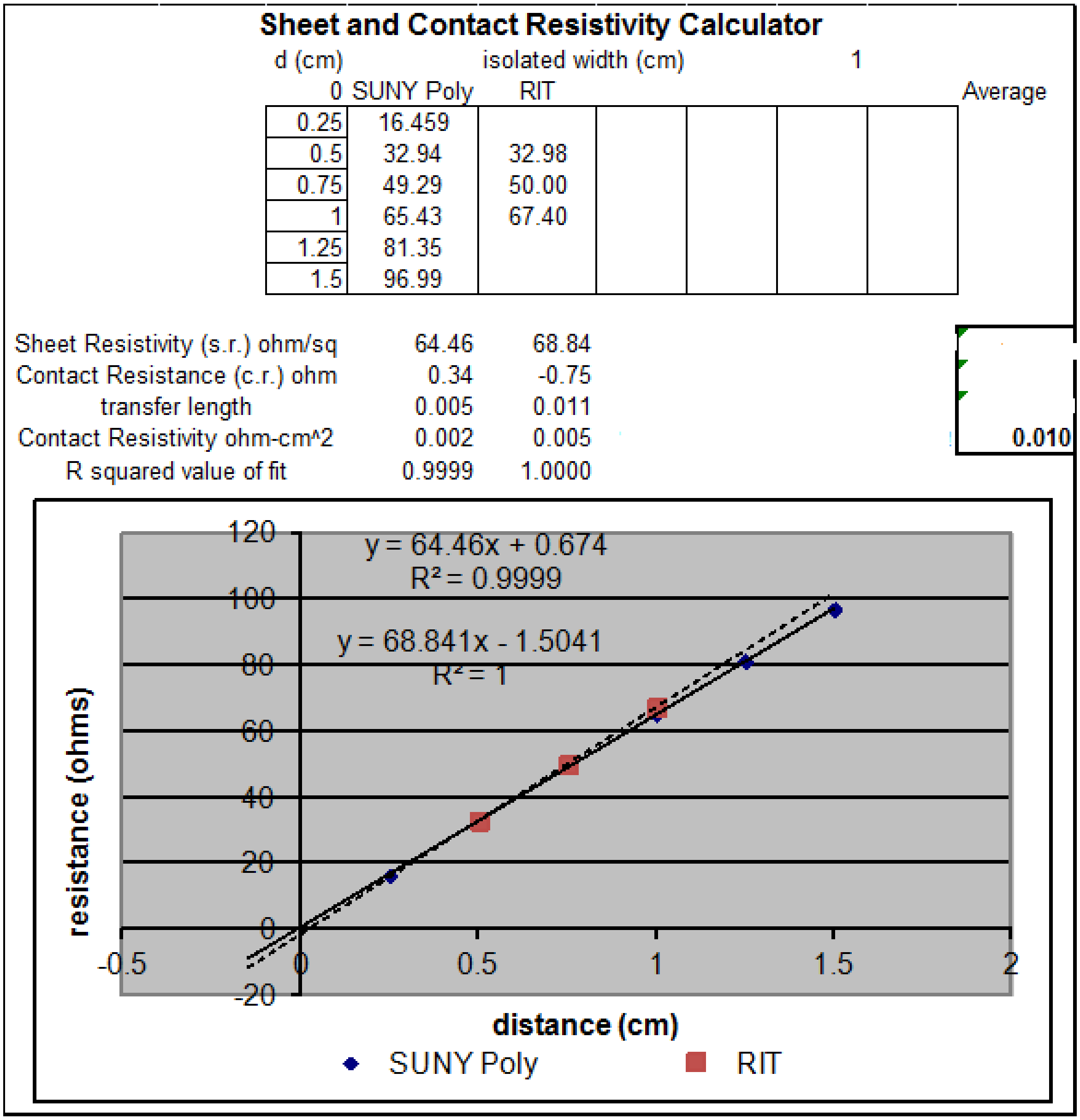
Sheet and Contact Resistivity Calculator

d (cm) isolated width (cm) 1

d (cm)	SUNY Poly	RIT				Average
0						
0.25	33.5	12.41				
0.5	51.1	35.00				
0.75	66.37	50.00				
1	78.87	69.10				
1.25	94.03	83.90				
1.5	115.2					

	SUNY Poly	RIT	Average
Sheet Resistivity (s.r.) ohm/sq	62.83	70.84	
Contact Resistance (c.r.) ohm	9.10	-1.52	
transfer length	0.142	0.023	
Contact Resistivity ohm-cm^2	0.064	0.011	0.010
R squared value of fit	0.9947	0.9948	

Ag Control



Sheet and Contact Resistivity Calculator

d (cm) isolated width (cm) 1

d (cm)	SUNY Poly	RIT					Average
0							
0.25	16.459						
0.5	32.94	32.98					
0.75	49.29	50.00					
1	65.43	67.40					
1.25	81.35						
1.5	96.99						

	SUNY Poly	RIT	Average
Sheet Resistivity (s.r.) ohm/sq	64.46	68.84	
Contact Resistance (c.r.) ohm	0.34	-0.75	
transfer length	0.005	0.011	
Contact Resistivity ohm-cm^2	0.002	0.005	0.010
R squared value of fit	0.9999	1.0000	

Addressing Deliverable Milestone D2 - Demonstrate Electrodes of NiSi and Cu on Silicon Solar Cells

Commercial multicrystalline silicon solar cells were obtained from Calisolar. These had silver top metallization prepared by screen printing silver paste and firing through the SiN ARC layer to make ohmic contact with the underlying n-doped silicon. No back electrode had been coated. The same cells but with no top metallization were used for the creation of the NiSi / Cu electrodes.

The silver controls were used as is, while the cells for copper metallization were obtained by laser dicing the 6X6 inch cells into 9 2X2 inch squares. Each cell had gridlines and/or busbar patterns created by using a green laser to etch through the ARC such that minimal damage was done to the underlying silicon.

For the silver controls, we had to measure the following:

1. Measure the bulk resistivity of the gridlines by the two point probe method, and
2. Show solderability by soldering solder tape to the busbar and measuring its adhesion with a pull strength test.

For the NiSi/Cu electrodes we needed to measure the following and compare to the silver controls:

1. Show bulk resistivities within 15% of the silver controls
2. Show contact resistances of 1-100 mΩ-cm^2 by the TLM method described in the D0 deliverables report, and
3. Show solderabilitiy by soldering solder tape to the busbars and measuring adhesion with a pull strength test.

Preparation of Copper Cells For Resitivity and Contact Resistance

An ink containing 14% NiSi nanoparticles in solvent was inkjet printed into the etched areas of the cells. For the contact resistance and bulk resistivity measurements, only the gridlines had been etched into the ARC layer. In order to remove any silicon dioxide, the etched cells were treated with 5% aqueous HF, washed with deionized water, dried, and immediately printed. It was found that 4 passes of ink were needed to prepare good NiSi layers and the platen of the printer needed to be heated to 60°C to avoid excessive spreading of the ink onto the ARC. The NiSi was annealed in a tube furnace by ramping the temperature to 400°C under argon. SEM images indicating that annealing had occurred are shown below in Figure 4. Note that it was the voids in these pictures that led us to make 4 pass coatings of the ink.

Annealed cells were placed in an electroless copper plating bath for 40 minutes, washed with DI water, and dried. An example of a cell before and after plating is shown in Figure 5.

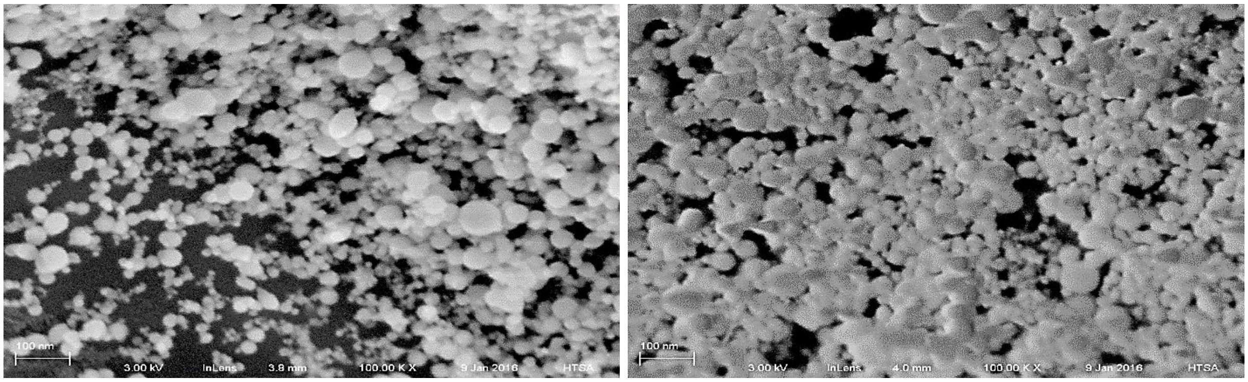


Figure 4. NiSi ink over Si before annealing (l) and after annealing at 400°C (rt)

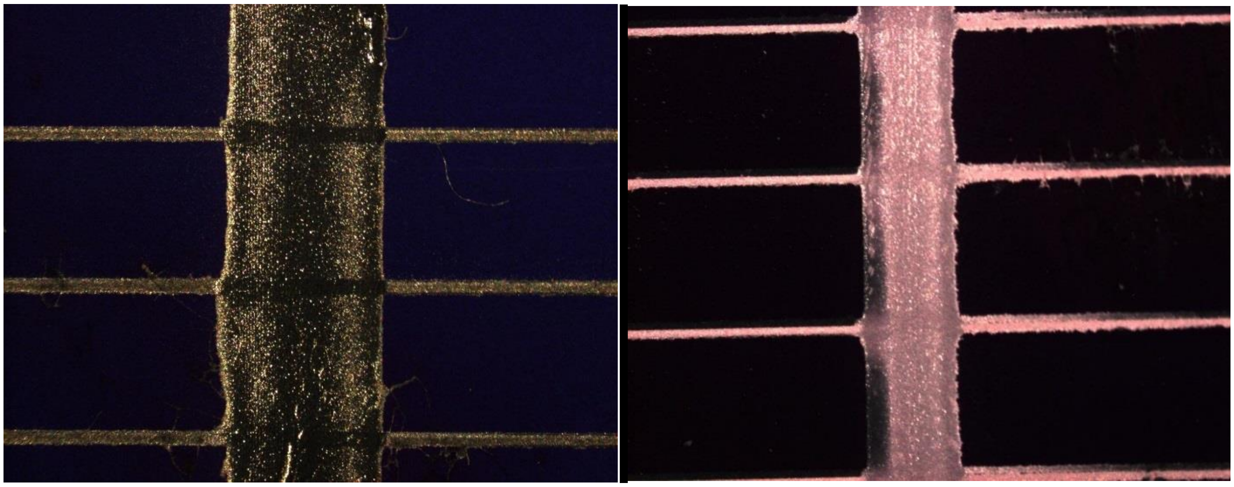


Figure 5. Printed and annealed NiSi ink before (l) and after (rt) electroless copper plating.

Measurement of bulk resistivities D2.1

Bulk resistivities were calculated by measuring the resistance along a known length of the gridline. The cross-sectional area of the line was determined by profilometry, and the resistivity (ρ) was calculated according to the formula:

P(rho) = (Measured Resistance (Ω) * Area (mm^2) * 1 cm /10 mm) / (Length (mm)

The values obtained are shown in Table 5 below. The average value of the silver control gridlines was 3.77 μΩ-cm which was close to a value we found in the literature. At Intrinsiq, we found that the resistivities of our three measurements of nickel silicide / copper electrodes was 4.01 μΩ-cm (6% higher than the control) and Solar Rochester measured 3.86 μΩ-cm (2.4% higher than the control). The line resistances measured at Solar Rochester are shown in Table 8 and in a separate attachment is a letter from Dr. Ian Cooper at Solar Rochester sending along those values. He used those resistance values and line lengths of 1.0 cm and cross sectional areas of 212, 281, and 253 μm>2 to calculate the rho values in Table 5.

The values measured at Intrinsiq therefore meet the deliverable and are verified by Solar Rochester, a second source.

Resistivity Measured at Intrinsiq (µΩ-cm)	**Resistivity Measured at Solar Rochester (µΩ-cm)**	**Resistivity of Ag Controls (µΩ-cm)**	**Resistivity from the Literature*(µΩ-cm)**
3.52	3.06	3.82	
4.12	5.91	4.12	
<u>4.4</u>	<u>2.61</u>	<u>3.36</u>	
Average 4.01	Average 3.86	Average 3.77	4.7

*D.L.Meier, IEEE J. of Photovoltaics Volume 3, Issue 1

Table 5. Bulk resistivity measurements of NiSi/Cu electrodes and Ag controls

<u>Measurement of Contact Resistances D2.3</u>

The contact resistances were measure on these samples exactly as those done for the previously reported D0. As before, the Rochester Institute of Technology served as the second source verifier. Values are shown in Table 6 below.

	RIT Measurements			SUNY Poly CNSE PVMDF Measurements		
Sample	Sheet Resistance (ohm/sq)	Contact Resistance (ohm)	Resistivity (ohm-cm2)	Sheet Resistance (ohm/sq)	Contact Resistance (ohm)	Resistivity (ohm-cm2)
AR2S1	46.89	10.04	0.070	53.66	11.12	0.078
AR1S2	54.06	7.31	0.051	60.55	6.71	0.047
AIR2S1	49.37	11.59	0.081	58.88	11.53	0.081

Table 6. Contact resistivity measurements for NiSi / Cu electrodes.

All values measured at SUNY CNSE (Solar Rochester) and RIT are < 0.1 ohms-cm^2 (or < 100 mΩ-cm^2) and therefore meet the deliverable.   The attached email message from Dr. Cooper mentioned above also documents receipt fo the RIT and Solar Rochester Contact Resistance data.

<u>Measurements of Solderability D2.3</u>

Solderability of the silver controls was measured by using a soldering iron to attach a commercial copper ribbon dipped in solder to the busbars of the cell and measuring the adhesion with a pull tester. The pull test methodology is described in IPC-TM-650 and we use a 90° manual peel tester purchased from Wenzhou Tripod Instrument Manufacturing Company in China. The tape is from Bruker-Spaleck USA and is a copper ribbon dipped with SnPbAg solder in the ratio of 62/36/2. The thickness of the ribbon and its width are 0.15 mm X 2.0 mm respectively.

Multiple samples of the silver controls were tested and data is shown in Table 3 below.

Peak Peel Strength (N/mm)	1.2	1.2	1.6	1.2	1.2	2.5	1.8	2.6	2.4	2.4	Average 1.8
Test ID	1	2	3	4	5	6	7	8	9	10	

Table 7a. Peel strength data for soldered silver control samples.

For copper solderability, busbars were created on the SiN ARC layers which had been cleaned with 5% aqueous HF and dried. We found that the HF treatment was necessary for good adhesion. Commercial paste Intrinsiq Materials CP-007 was screen printed on the cells, and the samples were sintered under a formic acid-argon atmosphere at 200°C for 1 hour. Busbars were 37 mm long, 1 mm wide, and 10 microns thick. Conductivity and adhesion were very good at this point. Cells were sent to Elmgrove Technologies (Rochester, NY) for treatment in a low temperature reflow oven.

A mild soldering procedure was developed at Elmgrove Technologies and begins with applying a low temperature solder paste to the copper busbars with a flat-bladed spatula. The paste is a tin:lead (63:37) alloy. To this was added a piece of the copper ribbon described above and the ribbon was imbedded in the solder paste with a spatula. The cells were placed in the solder reflow oven under the conditions documented in the attachment called “DOE Soldering Certification from Elmgrove.” Summary data for four samples are shown in Table 7b.

Peak Peel Strength (N/mm)	2.4	3.7	2.3	0.95	Average 2.3
Test ID	1	2	3	4	

Table 7b. Peel Strength data for soldered printed copper busbars.

Three of the four samples exceeded the average peel strength of the silver controls and were as good as the best silver values. The average of the four samples was better than that from the silver controls. Deliverable D2.3 requires that the copper values only need to be 85% (within 15%) of the silver controls, so the solderability criterion has been successfully demonstrated.

In conclusion, the data in Tables 1, 2, and 3 show that in the hands of outside testers, the bulk resistivity (Solar Rochester), contact resistance (Solar Rochester and RIT), and solderability of deposited copper (Elmgrove Technologies) meets or exceeds the criteria for passing the D2 technical deliverables.

Table 8. Line Resistances Measured at Solar Rochester, CNSE

AR2S1

Cu Line Resistance			
point 1	point 2	point 3	
1.4	1.423	1.37	ohm
1	1	1	cm
0.01	0.01	0.01	cm
0.001	0.001	0.001	cm
0.00001	0.00001	0.00001	
1.40E-05	1.42E-05	1.37E-05	ohm-cm

AR1S2

Cu Line Resistance			
Point1	Point2	Point3	
2.16	2.09	2.05	ohm
1	1	1	cm
0.01	0.01	0.01	cm
0.001	0.001	0.001	cm
0.00001	0.00001	0.00001	
2.16E-05	2.09E-05	2.05E-05	ohm-cm

AIR2S1

Cu Line Resistance			
Point1	Point2	Point3	
1.1	1.01	0.99	ohm
1	1	1	cm
0.01	0.01	0.01	cm
0.001	0.001	0.001	cm
0.00001	0.00001	0.00001	
1.10E-05	1.01E-05	9.90E-06	ohm-cm

Addressing Deliverable Milestone D3 – Demonstrate Barrier Properties of NiSi

In order to demonstrate the effective barrier properties of printed NiSi to copper migration into silicon, we committed to using the pseudo fill factor (pFF) test as described by Bartsch[10]. This test involves measuring a pseudo I-V curve on a fresh cell, calculating a pseudo fill factor (pFF) from that, and then monitoring the pFFs at intervals over time as the cell is heated on a hotplate. The reduction of the pseudo fill factor with time is taken as the measure of copper migration into the silicon.

The deliverables then are:

1. Control Samples
   a. Prepare 3 Control Samples by printing silver contacts on Silicon solar cells of commercial quality.
   b. Use light I-V measurements to determine cell efficiency and pseudo-fill factor measured by Suns-Voc.

2. Using Solar cells of same type and quality as control,
   a. Print NiSi, sinter NiSi, over-print/deposit copper, sinter copper, and protect with immersion tin, silver or similar material if necessary.

To pass the pFF test we need to show:

-Cu migration </= 5% degradation of pFF compared to no control cells after 100 hrs at 200°C
Use light I-V measurements to determine cell efficiency and pseudo-fill factor measured by Suns-Voc. Deviation must be less than or equal to 5% of control.
-3 Cells must pass these tests.

The control samples are actual commercial multicrystalline silicon cells with silver gridlines and busbars prepared by screen printing silver paste and firing it to allow glass frit in the paste to penetrate the silicon nitride (SiN) anti-reflection coating (ARC). These cells have no backside metallization.

The test cells are the same commercial cells complete through the ARC layer but with no top metallization. The cells were metallized by ablating a gridline and busbar pattern through the ARC in such a way as to not damage the underlying silicon. A nickel silicide (NiSi) ink was multipass inkjet printed into the etched channels while heating the cells at 60°C. The cells were then fired in a tube furnace ramped to 400°C and held one minute. Copper metal was electrolessly plated on the annealed NiSi. Similar cells were used to measure the gridline properties of D2. Cells prepared in this manner were then sent to Dr. Ian Cooper[11] from the Rochester Solar facility.

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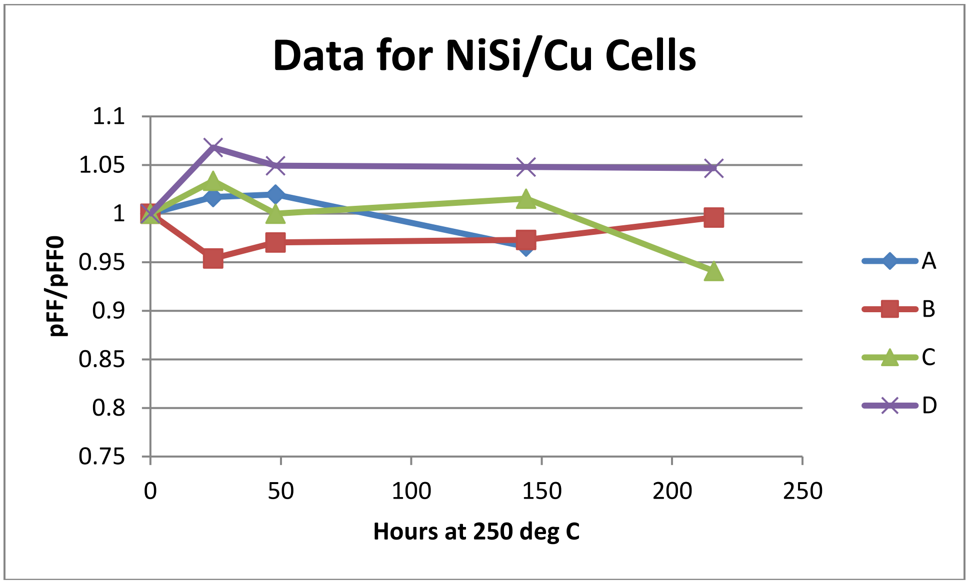
[10] J. Bartsch, et. al., J. of the Electrochemical Society, **157** (10) H942-H946 (2010)

[11] Ian B. Cooper, Director of Si Solar Technology, Photovoltaics Manufacturing and Technology Development Facility Colleges of Nanoscale Science + Engineering | SUNY Polytechnic Institute

The pseudo fill factors of the fresh cells were measured and the cells were heated at 250°C on a hot plate for over 200 hrs. Normalized data are shown in the Figure and Table below. The Solar Rochester software calculates pFF directly form the measured pseudo I-V curve. It can be readily seen that all four of the cells had pFF values greater than 95% (less than 5% degradation) of their original values out to 144 hours, thus meeting the Deliverables specification and showing that copper migration is inhibited by the printed, annealed NiSi layer no matter what the control cells do.



Raw pFF data
NiSi/Cu Cells

Sample	0	24	48	144	216
A	0.763	0.776	0.778	0.737	
B	0.78	0.744	0.757	0.759	0.777
C	0.712	0.736	0.712	0.723	0.67
D	0.75	0.801	0.787	0.786	0.785

pFF/pFF0 data

Sample	0	24	48	144	216
A	1	1.017038	1.019659	0.965924	Cell broken
B	1	0.953846	0.970513	0.973077	0.996154
C	1	1.033708	1	1.015449	0.941011
D	1	1.068	1.049333	1.048	1.046667

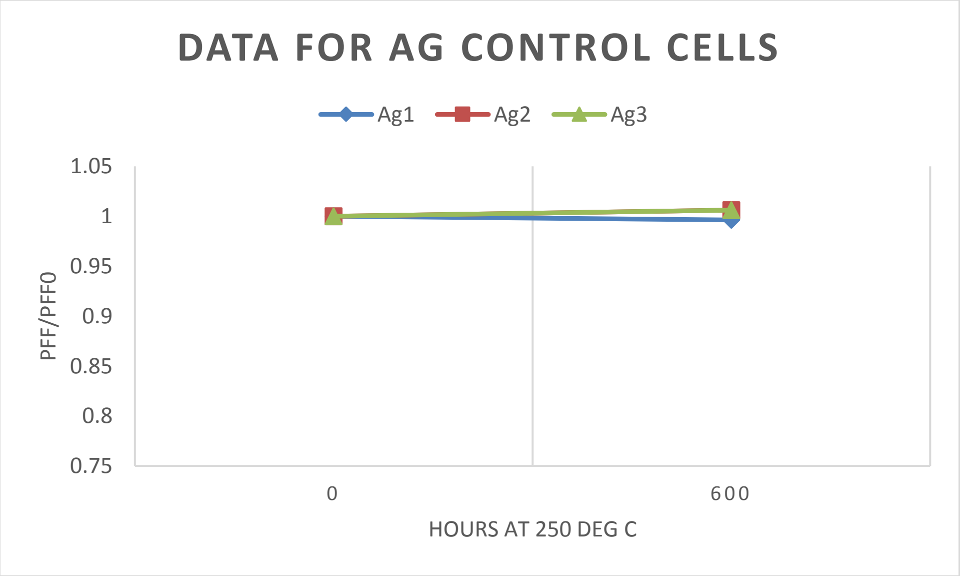
The data for the silver control cells is shown in the table and graph below.

Raw pFF data
Ag Cells

Sample	0	600
Ag1	0.813	0.810
Ag2	0.811	0.816
Ag3	0.815	0.820

pFF/pFF0 data

	0	600
Ag1	1	0.996
Ag2	1	1.006
Ag3	1	1.006



Due to an experimental error at Solar Rochester, the controls were allowed to bake at 250 deg C for 600 hours. Even so, these data show that the silver controls are NOT degrading, that is their % degradation is zero at 600 hours at 250 deg C. From the data for the NiSi/Cu cells, at 144 hrs at 250 deg C (the deliverable is for 100 hours at 200 deg C) the worst of the four cells tested had a 96% pFF, that is to say a 4% degradation. So overall degradation of the worst sample compared to the control is 4% - 0% = 4%. This value is within the 5% limit specified in D3, and all of the cells tested meet the D3 deliverable.

Significant Accomplishments and Conclusions

We were delighted to find that one of our *nano copper inks* could be printed onto glass and be sintered in a formic acid / argon reducing atmosphere. This ink gave between 30 and 40% of the conductivity of bulk copper, which was remarkable given that sintered nano inks are always porous (see Figure 1 to see the porosity of the annealed NiSi nano ink). Additionally, this ink gave outstanding adhesion according to the ASTM3359 tape test.

The *nickel silicide ink* prepared for the project jetted well, and we were able to print it within into the 75 micron wide fingers in the grid laser ablated into the ARC. This ink could be thermally annealed to make it conductive. Unfortunately, when we printed and sintered our copper nano ink over it, and sintered the copper to make it conductive, we were not able to measure the contact resistance into the siiicon. We had to resort to electrolessly plating copper on the NiSi to get contact resistivity. This was a change of approach and a change which made the overall process less desirable. This resistivity was good enough to meet the intermediate goals of the project, but still five to ten times more resistive than silver grids made by the “fire through” method. This was a real shortfall, and is something that would require significant work should this method be retried at a later date.

However, we were able to show that the printed and annealed NiSi part of the electrode was an *effective barrier to copper migration*. Heating at 250˚C for several weeks gave very little degradation in the cell. These are conditions under which less effective barriers fail (see reference 10). This was a very significant finding because it showed that a printed barrier could perform as well as a sputtered or plated one, and as we said earlier neither sputtering or plating are desirable for cost or environmental reasons.

The biggest technical shortfall which caused delays in the program and which factored into the decision to eventually stop the program, was the inability to get contact resistances into the silicon low enough to compete with those of silver electrodes created by the fire through process. Even if the resistivities had been optimal, we found out from our potential customers that the overall process was *not economically feasible* because there were simply too many steps involved. Each step adds manufacturing cost, and our customers felt that there were too many costly steps. This cost eroded any cost advantage accrued by using copper in place of silver. This effect was compounded by the fact that the cost of silver electrode creation fell throughout the duration of the project as cell manufacturers learned to use less and less of the silver paste, and silver paste manufacturers learned to use less costly silver ingredients.

As of now, it appears that the simplicity of the silver fire through process makes it a very difficult process to replace.

Inventions, Patents, and Publications

No patents or publications have resulted from this work.

Commercialization Plans

As we stated in the Accomplishments and Conclusions statement above, the complexity of the process makes it too expensive in the minds of the potential customers we polled, so there are no plans to commercialize.