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Final Technical Report (FTR)

a. Federal Agency	Department of Energy	
b. Award Number	DE-EE0008166	
c. Project Title	Direct Metallization with Reactive Inks – Assessment of Reliability and Process Sensitivities	
d. Recipient Organization	Colorado School of Mines	
e. Project Period	Start: 10/01/2017	End: 12/31/2023
f. Principal Investigator (PI)	Owen Hildreth Associate Professor ohildreth@mines.edu (303) 384-2457	
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Signature of Certifying Official

07/10/2024

Date

By signing this report, I certify to the best of my knowledge and belief that the report is true, complete, and accurate. I am aware that any false, fictitious, or fraudulent information, misrepresentations, half-truths, or the omission of any material fact, may subject me to criminal, civil or administrative penalties for fraud, false statements, false claims or otherwise. (U.S. Code Title 18, Section 1001, Section 287 and Title 31, Sections 3729-3730). I further understand and agree that the information contained in this report are material to Federal agency's funding decisions and I have any ongoing responsibility to promptly update the report within the time frames stated in the terms and conditions of the above referenced Award, to ensure that my responses remain accurate and complete.

1. Acknowledgement

"This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) Solar Energy Technologies Office (SETO) under the Photovoltaics Research and Development (PVRD) 2: Modules and Systems Award Number: DE-EE0008166"

2. Disclaimer

3. Executive Summary

The goal of this project was to reduce the amount of silver needed to metallize a Silicon Heterojunction (SHJ) Photovoltaic (PV) cell by 90%, from 110 mg/cell down to 10 mg/cell. Recent heat waves across the world emphasize the importance of replacing carbon-based electricity generation with renewables. The 'Solar Futures' reports clearly showcases the need to increase photovoltaic deployment rates by 5× per year to decarbonize 95% of the grid by 2030.[1] Unfortunately, the considerable amount of silver required to metallize a PV cell with existing techniques would consume approximately 80% of the world's silver production to produce the 50-60 Gigawatts per year new PV production to meet climate change goals.[1,2]

In the end, this project managed to reduce the amount of silver by 82%, down to 16 mg/cell for M2 sized devices (156.75 × 156.75 mm) using a relatively new and innovative metallization technology called reactive inks. In this project, we developed the fundamental and applied knowledge necessary to print high quality silver with good electrical properties, adhesion, contact resistance, and line widths using an ethylamine-based silver reactive ink. To achieve these results, an extensive set of experiments were conducted to fundamentally understand how heat transport, mass transport, evaporation, and reaction kinetics combine to determine key metallization outputs, including morphology, resistivity, contact resistance, and adhesion. The resulting SHJ cells showed increase cell efficiencies relative to the screen-printed counterparts while using significantly less silver. Additionally, this project lowered the metallization temperature for SHJ from the 180 ˚C used to sinter low temperature silver pastes down to 65 ˚C.

This project demonstrated that cell metallization times on the order of 1.5 min/cell are industrially accessible (typical processing time as the start of the project was on the order of 2 min/cell) and provides clear justification for future commercialization efforts. The largest two barriers to commercialization are line width and switching metallization equipment from the current screen-printing industrial standard to a dispensing printing approach. This project demonstrated that the line width of dispense-printed reactive inks are largely determined by the outer diameter (OD) of the printer nozzle (~3× OD). While the Team only had access to 60 μm OD, smaller OD nozzles are possible when purchased at industrial levels. Additionally, screen-printable mixtures of reactive silver inks with silver particles commercially exist and the knowledge generated through this project would translate to optimizing these commercial screen-printable reactive ink/particle mixtures for photovoltaic applications.

Overall, this project reduced the amount of silver needed to metallize a SHJ by 82% while lowering metallization times and temperatures. These results will lower the costs of PV electricity while ensuring that existing silver mining and refining capacity can meet the needs of the PV industry. By demonstrating high quality metallizations on 150 mm wafers while increasing efficiency, we have provided the necessary motivations for the PV community to pursue this new metallization strategy. In addition, the knowledge and innovations developed during this project provide the necessary insights to use reactive silver inks at a commercial scale.

4. Table of Contents:

5. Background

The Team recently published a paper in Energy & Environmental Science on the potential impact of reactive silver ink metallization to reduce silver consumption by 82%. This Introduction in this manuscript provides an excellent summary on the state-of-the-art for SHJ metallization, including meeting the technical discussions required by this Final Report.

From the paper titled*: Reactive silver inks: a path to solar cells with 82% less silver*, by Martinez-Swewczky, DiGregorio, Hildreth, and Bertoni:

Metallization for SHJ's has made several advances in recent years, namely the reduction of the finger width to sizes below 30 mm as proposed by ITRPV.[2] Figure 1a shows a comparative graph of the ITRPV silver usage projections for M2 size devices (156.75 × 156.75 mm) versus reactive silver inks and an advanced screen-printing technology. It is worthwhile to note that Pingel et al. reported finger widths below the ITRPV predictions for screen printed LT-SP.[3] This study was able to achieve finger widths down to 13 μm and consume 22 mg of silver through the use of high-end screens. While this study and many more have been evaluating screen printing as the primary mode of contact deposition, innovative technologies other than screen printing have been under development to reduce silver consumption and a summary is shown in Fig. 1b. One of these technologies is the FlexTrail technology developed by Fraunhofer ISE which utilizes a thin and flexible glass capillary filled with printing medium that achieved a finger width and height of 16 μm and 0.2 μm respectively.[4] The low height resulted in resistive losses, and subsequent optimization of the finger cross-sectional area yielded a finger width of 29.2 μm, finger height of 6.4 μm, efficiency of 22.87%, and silver consumption of 9.4 mg for an M2 sized device, which is a reduction of 68%.[5] Pospischil et al. of Highline technology GmbH demonstrated that the use of dispense printing silver paste can yield remarkable finger widths down to 17 mm for PERC cells, but due to spreading of the LT-SP resulted in finger widths of 45 mm and a silver consumption of 65 mg for SHJ cells.[6] Finally, Gensowski et al. utilized dispense printing to achieve a finger width of 41 mm and an aspect ratio of 0.4.[7] This device's silver consumption was 52 mg per cell with a power conversion efficiency of 21.5%, corresponding to an efficiency increase of 0.48% absolute (abs.) compared to traditional screen printing. Note that all of these technologies showcased in Figure 1b correspond to a busbarless design, thus the comparison with reactive inks should be made following the same busbarless design – see 16.4 mg per cell bar. All of these advanced demonstrate the efficacy of alternative printing methods to reduce silver consumption for SHJ solar cells while maintaining high performance.

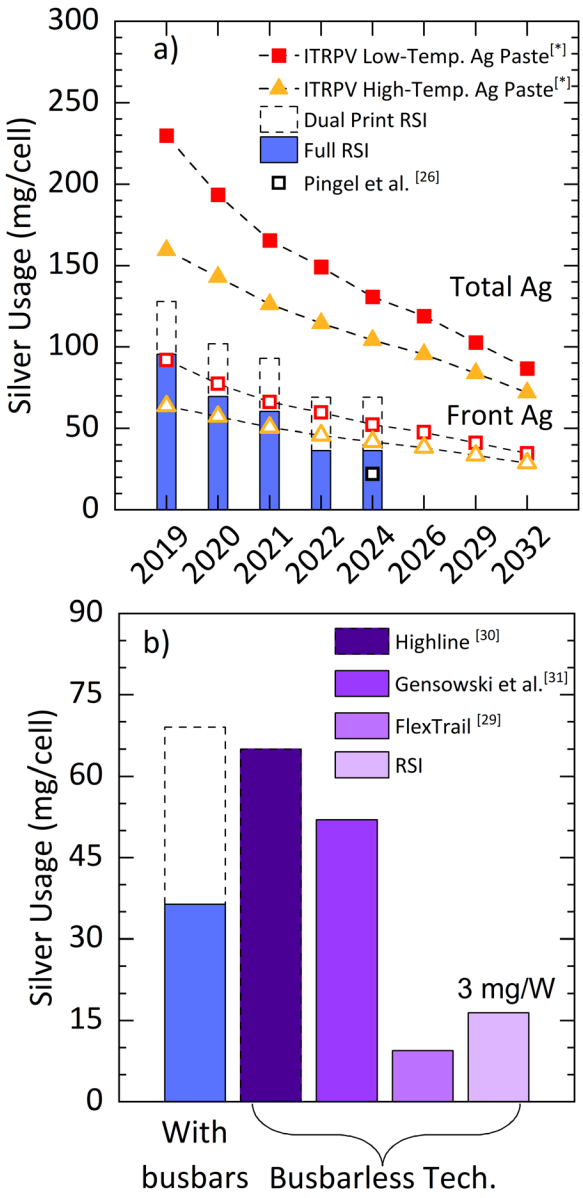


Figure 1. (a) Total silver usage for the low-temperature silver paste (LT-SP) and high-temperature silver paste (HT-SP) from ITRPV. Reactive silver ink (RSI) front silver usage compared to the calculated front silver usage of LT-SP and HT-SP from ITRPV assuming a partition of 40% front Ag. RSI front silver usage as compared to other novel metallization schemes. (b) Inset of RSI silver usage as compared to FlexTrail other novel metallization schemes. It is important to note that the reported literature values for silver usage are from busbarless cells. Performing a similar comparison with the RSI results in a very comparable front silver consumption of 16.4 mg per M2 sized cell.

Our previous work has demonstrated that RSI deposited by way of dispense printing can significantly reduce the silver consumption from the resulting metallization as compared to the LT-SP.[8–10] This ink, modified from the original formulation of Walker et al.[11] relies on ethylamine as the complexing agent and was printed at 78 ˚C giving comparable power conversion efficiency (PCE) using an identical grid design as the LT-SP paste (18.4% and 19.5% respectively). Additionally, Mamidanna et al. studied the adhesion of RSI on indium tin oxide

(ITO) and achieved improved adhesion by varying parameters such as the number of printed layers, ink dilution ratios, and droplet diameter.[12] Jeffries et al. also studied silver adhesion to the transparent conducting oxide (TCO)[8,9,13] as well as the corrosion mechanisms of reactive ink metallization and performed damp-heat reliability studies with promising results.[14] Recently, DiGregorio et al. investigated the impact of RSI formula and printing parameters on SHJ metallization.[15] The authors found that inks formulated with lower vapor-pressure complexing agents resulted in bottom-up silver growth, leading to more dense films and better electrical properties. This RSI, consisting of ethylamine, silver acetate, and formic acid was used to metallize an SHJ cell with an 84% improvement in electrical properties and 80% less silver consumption, compared to LT-SP.[10,16]

6. Project Objectives

This project will reduce silver consumption in photovoltaic cells by a factor of almost ten – from 95 mg/cell (the median across technologies) to 10 mg/cell. To achieve this goal, we will replace screen-printed silver pastes with contact dispensed reactive inks that produce lower resistivity metallizations at lower temperatures and with thinner films. This project will generate the understanding necessary to scale this reactive ink technology from the bench-scale to commercial throughputs. Specifically, it will combine fundamental understanding on physics and chemistries involved in contact printing of reactive inks with detailed performance and reliability studies to quantify how tightly processing parameters need to be controlled in order to reliably metallize high efficiency solar cells at commercial throughputs of 36,000 cells/hour.

The objective in Budget Period 1 (Y1-Y2) is to metalize heterojunction photovoltaic cells using reactive inks while meeting performance characteristics (device performance and reliability) that are within 15% or better of reference photovoltaics cells metallized using low-temperature screen-printed silver pastes at a rate of 2 wafers/day.

The objective in Budget Period 2 (Y3-Y4) is to metalize both heterojunction (HJT) and PREC silicon (c-Si) photovoltaic cells using reactive inks while meeting performance characteristics that are within 1% or better of reference photovoltaic cells metallized using either low temperature screen-printed silver pastes (for HJT cells) or high temperature silver pastes.

6.1 SOPO: Summary of Tasks

Dissemination of results from this project will be conducted through publications, and travel to present conferences, workshops, or collaborator meetings.

6.1.1 Budget Period 1: Ink and Metallization Optimization

Table 1 lists the quarterly milestones for Budget Period 1. These quarterly milestones were selected from the three tasks being conducted for this period.

6.1.2 Task 1: Ink Optimization (Q0 – Q8)

Task 1 Summary: The objective of this task was to understand how processing parameters during printing impact the porosity and resistivity of reactive ink metallizations printed using a contact dispenser printer. This understanding combined with experimental results was be used as inputs for global sensitivity analysis for ink and process optimization.

Reactive ink characterization, refinement, and printing was conducted by Mines. ASU supplied the photovoltaic cells for Mines to test their reactive ink printing parameters on.

6.1.3 Task 2: Photovoltaic Metallization (Q3 – Q8)

Task 2 Summary: The objective of this task was to continue improving the performance and reliability of c-Si and HJT photovoltaic cells metalized using reactive inks. Particular attention was paid to increasing wafer throughput and reducing silver consumption. Throughput increased from one 100 mm wafer/day to a 200 mm wafer in 1.5 minutes (current state of the art). The metallization adhesion strength, contact resistance, power loss, shading, media resistivity, and porosity will be measured. This data will be used as inputs into the sensitivity analysis and to down select the best in class processing parameters for silicon diffused junction and HJT photovoltaic cells.

ASU fabricated the photovoltaic cells, characterized cell performance, and identified failure mechanisms. Mines metallized the photovoltaic cells supplied by ASU and characterized metallization morphology to help understand failure mechanisms.

6.1.4 Task 3: Reliability of Reactive Inks at High Production Throughputs (Q9-Q16)

Task Summary: The objective of this task was to continue to quantify and improve the reliability of photovoltaic cells metallized using contact dispensed reactive inks.

ASU fabricated the photovoltaic cells, characterized cell performance, measured reliability, and identified failure mechanisms. Mines metallized the photovoltaic cells supplied by ASU and characterized metallization morphology to help understand failure mechanisms.

6.2 SOPO: Milestones and Go/No

Budget Period 1: Milestones

Table 1. Quarterly Milestones for Budget Period 1 (Y1 – Y2)

Q1	Metallize a solar cell using silver reactive ink and contact dispensing printer
Q2	Media resistivity of printed reactive ink ≤ 20 μΩ-cm
Q3	Shape (contact angle, contact area, droplet volume) of multiphysics model of evaporating reactive ink droplet from T_{start} (just as droplet has settled after printing) to T_{end} (the time where 80% of the fluid has evaporated) matches experimentally measured printed ink to within 10%.
Q4	Submit Paper on reaction kinetics of Ag, Cu, and Ni reactive inks to peer reviewed journal
Q5	Print speed ≥ 10 mm/second with continuous lines, line width < 120 μm
Q6	Media resistivity ≤ 10 μΩ-cm; Contact resistivity ≤ 10 × 10-3 Ω-cm2, area metallization loss during 180˚ scotch-tape peel test less than 3%
Q7	FF > 75%
Q8	Meet Go/No Go decision points.

Budget Period 1: Go/No Go (Q8)

- Media Resistivity ≤ 6 μΩ-cm
- Contact Resistivity ≤ 5×10^{-3} Ω-cm^2
- Deposition speed ≥ 10 mm/min
- Line width ≤ 100 μm ± 20%
- Fill Factor of an HJT or Al BSF cell with reactive ink front metallization ≥ 75%
- $\eta \geq +0.1\%$ abs. above current baseline for both cells metallized using reactive inks or screen-printing
- η of an encapsulated cell does not decrease by more than 5% of initial η after 1,000 hours of damp heat exposure at 85 ˚C with 85% relative humidity
- Submit a paper on reactive ink metallized photovoltaic cells to a peer reviewed journal

Budget Period 2: Milestones

Table 1. Quarterly Milestones for Budget Period 2 (Y3 – Y4)

Q9	Metallization consumption down to 40 mg/cell for a fabricated cell

Q10	In lab wafer metallization throughput equivalent to 5 minutes/wafer
Q11	Media resistivity ≤ 4 μΩ-cm; Contact resistivity ≤ 3 × 10-3 Ω-cm^2, adhesion between media/solder ribbon and wafer ≥ 3 Nmm-2 in 90˚ peel test
Q12	Δη < 1% of initial η after DH test; Submit paper on initial reliability studies
Q13	Wafer throughput equivalent to 1.5 minutes/wafer
Q14	Improve J_{sc} by more 3% and FF by more than 2% over the cell achieved with reactive ink metallization at end of budget period 1.
Q15	η < 0.25% of initial η after DH test; silver/metal consumption down to 10 mg/cell
Q16	Submit paper on reliability and reactive ink metallization sensitivity

6.3 End of Project Goal

The End of Project goals are to show on Al BSF and HJT cells the following:

- reduce silver consumption for top-side electrodes to 10 mg/cm^2 or less
- reliability metrics of less than 0.25% reduction in efficiency after 1,000 hours of damp heat testing at 85 ˚C with 85% relative humidity
- η ≥ +0.2% abs. above current baseline for cells metallized using reactive inks for samples sent to NREL for efficiency measurements
- media resistivity ≤ 3 μΩ-cm
- contact resistivity ≤ 2 × 10^{-3} Ω-cm^2 of reactive ink to full pre-metallization cell with passivation and antireflection coatings
- effective production throughput of at least 1 wafer in 1.5 minutes
- fill factor of cells with reactive ink metallization front contacts ≥ 75%
- provide a set of qualified response surfaces, sensitivity curves, and confidence curves on how processing parameters impact metallization, device performance and reliability

7. Project Results and Discussion

7.1 End of Project Goals

Goal	Met [Yes/No]	Result
Reduce silver consumption for top-side electrodes to 10 mg/cell or less	No	16 mg/cell
Reliability metrics of less than 0.25% reduction in efficiency after 1,000 hours of damp heat testing at 85 ˚C with 85% relative humidity	Yes	0.28%
Media resistivity ≤ 3 μΩ-cm	Yes	2.6 μΩ-cm
Contact resistivity ≤ 2 mΩ-cm^2 of reactive ink to full pre-metallization cell with passivation and antireflection coatings	Yes	2.1 mΩ-cm^2
Effective production throughput of at least 1 wafer in 1.5 minutes	Yes	< 1.5 min/cell
Fill factor of cells with reactive ink metallization front contacts ≥ 75%	Yes	80.4%

7.2 Progress Over Time

The graphs in Figure 2 show our progress in key milestones and metrics over the course of this project. The end goals (for those metrics that have them) are denoted in dashed green lines along with the target numerical value listed above the line. Notice that all key milestones and metrics were either met or were extremely close and that progress was a mix of steady improvement with occasional jumps in improvement when new insights lead to sudden improvements in process. The final silver consumption for a 15 cm × 15 cm cell was 16 mg, which translates to 0.067 mg/cm^2 (67 μg/cm^2) while achieving area-corrected efficiencies of 21.3% for our best cell. In contrast, the final screen-printed silver 89.2 mg/cell, which translates to 0.396 mg/cm^2 (396 μg/cm^2) with area corrected efficiencies 20.2%.[17] While 16 mg/cell doesn't hit our target goal of 10 mg/cell, we actually did print cells with 10 mg of silver; however, the low amount of silver was too hard to make good contact with the existing tabbing wire and 16 mg/cell to 20 mg/cell was often used towards the end of this project.

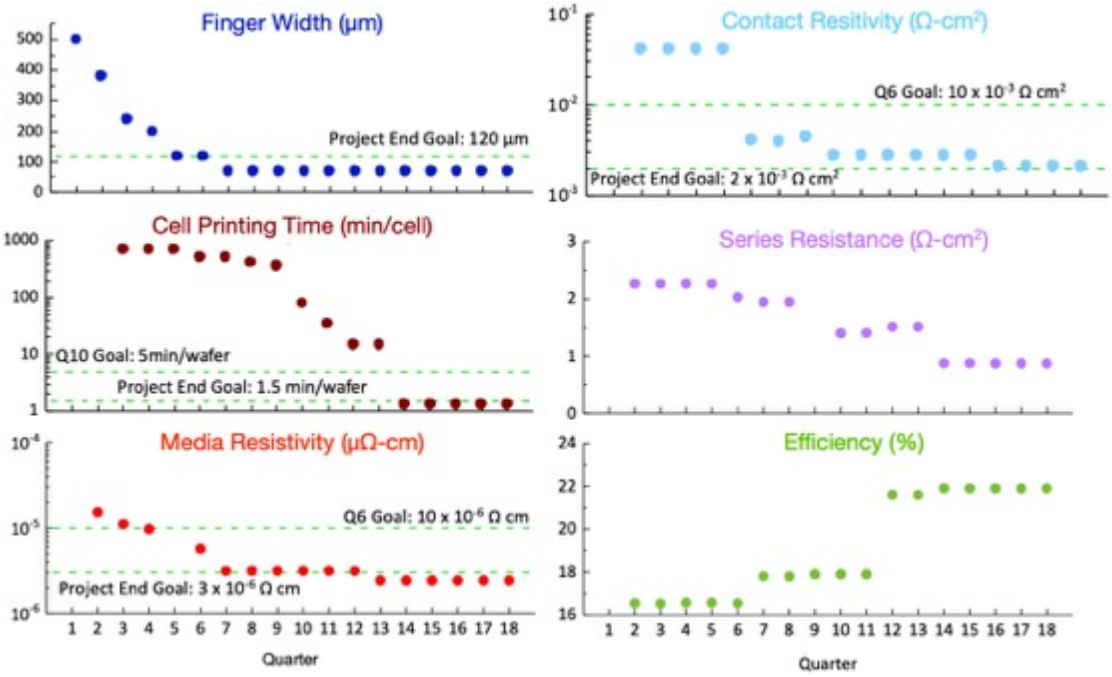


Figure 2. Graphs showing goal progress over the duration of the project. The end goals (for those metrics that have them) are denoted in dashed green lines along with the target numerical value listed above the line.

7.2.1 BP1 – Task 1 Milestones Progress: Ink Optimization

The objective of this task was to understand how processing parameters during printing impact the porosity and resistivity of reactive ink metallizations printed using a contact dispenser printer.

The following milestones were associated with this task:

- Q2: Media resistivity of printed reactive ink ≤ 20 μΩ-cm
- Q3: Shape (contact angle, contact area, droplet volume) of multiphysics model of evaporating reactive ink droplet from T_{start} (just as droplet has settled after printing) to T_{end} (the time where 80% of the fluid has evaporated) matches experimentally measured printed ink to within 10%.
- Q4: Submit Paper on reaction kinetics of Ag, Cu, and Ni reactive inks to peer reviewed journal
- Q5: Print speed ≥ 10 mm/second with continuous lines, line width < 120 μm

Q2: Media resistivity of printed reactive ink ≤ 20 μΩ-cm

This milestone focuses on demonstrating that we can improve the resistivity of silver printed using reactive silver inks. Figure 3 plots the resistivity data we presented at the end of Q2. It shows that we decreased the resistivity by two orders of magnitude to produce a Q2 resistivity of 15.2 μΩ·cm by changing from the ammonia-based complexing agent to ethylamine.

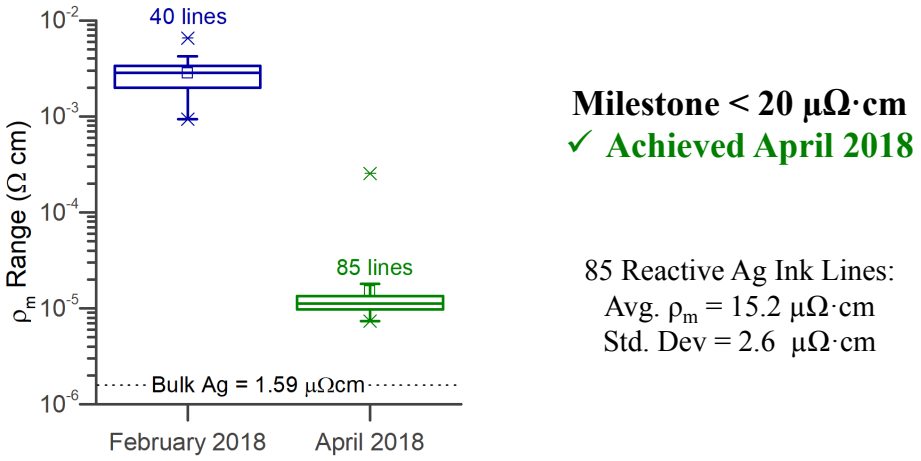


Figure 3. Plot of Resistivity at the end of Q1 (Feb. 2018) and by the end of Q2 (April 2018) showing that the resistivity of the printed silver using the ethylamine complexing agent was 15.2 μΩ·cm. This is below the 20 μΩ·cm goal for Q2.

Q3: Shape (contact angle, contact area, droplet volume) of multiphysics model of evaporating reactive ink droplet from T_{start} (just as droplet has settled after printing) to T_{end} (the time where 80% of the fluid has evaporated) matches experimentally measured printed ink to within 10%.

This milestone focuses on demonstrating a Comsol Multiphysics model of the evaporation of printed reactive silver inks. For this quarter, we compared our multiphysics evaporation model to high-speed videos of evaporating droplets of ethanol, water, and reactive ink. The change in diameter as a function of time for the model (Figure 4) and video data (Figure 5) was compared to show that we can accurately model reactive ink droplets.

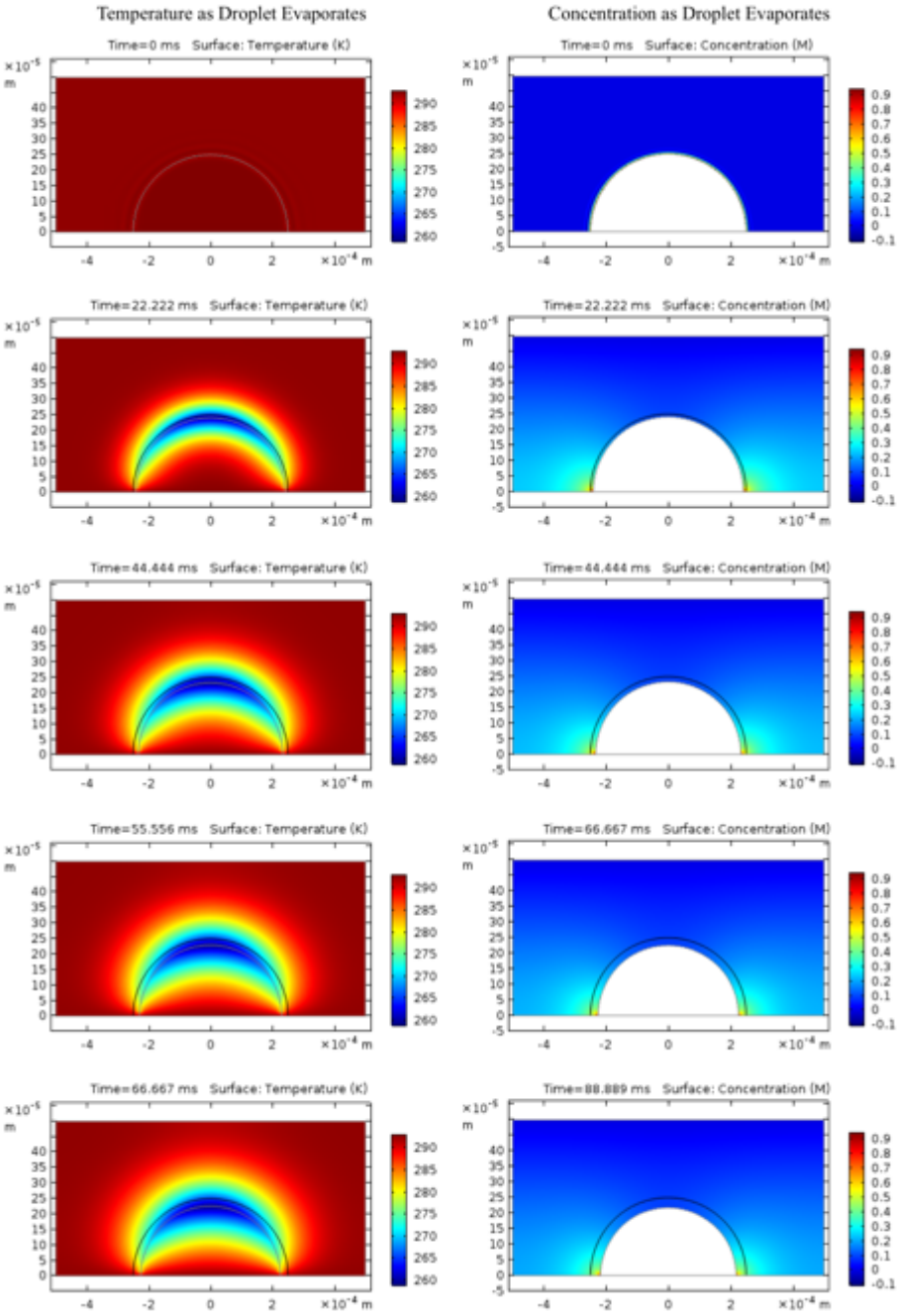


Figure 4. Temperature and Concentration over 66 milliseconds of a 200 µm diameter water droplet on a substrate held at 293 K. The original diameter is shown in black while the dynamic diameter is outlined in grey.

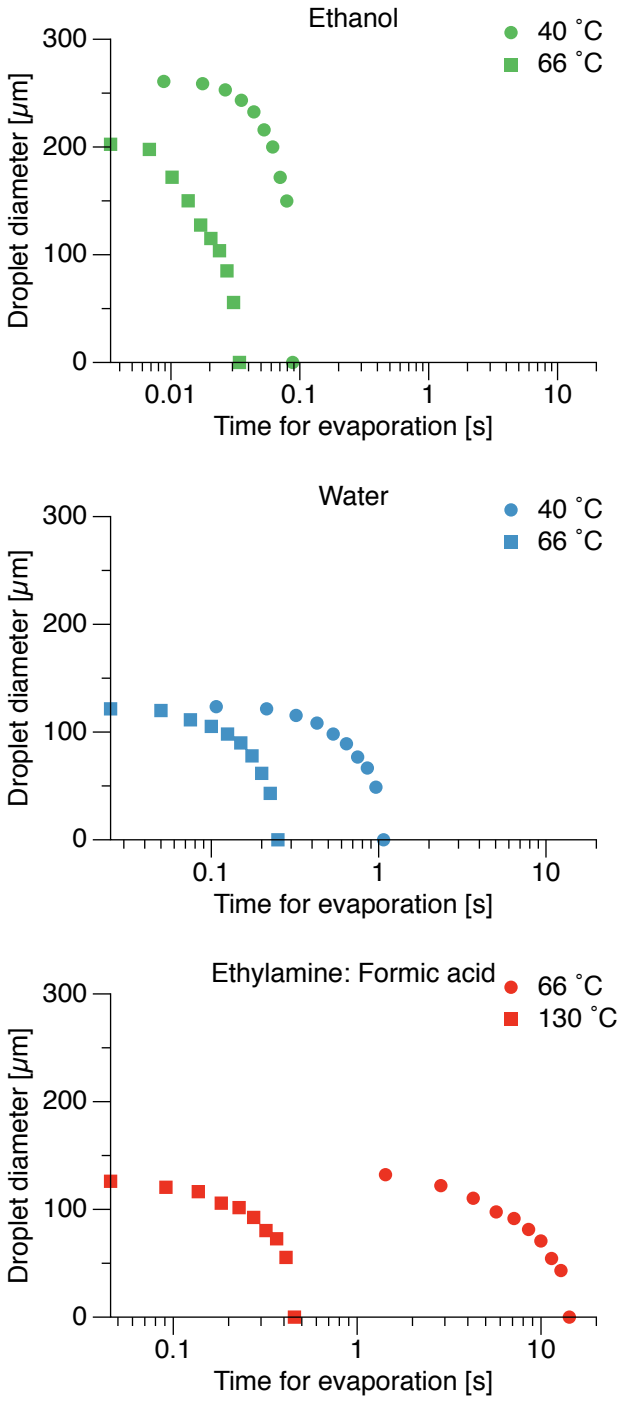


Figure 5. Plot for Time for evaporation vs. Droplet diameter of a) Ethanol – When printed at 66 ˚C which is close to the boiling point of ethanol, the droplet evaporates faster than when printed at 40 ˚C as expected b) Water – Similar trend can be seen with the water droplet with the droplets printed at 66 ˚C evaporating faster than when printed at 40 ˚C and c) Ethylamine: Formic acid – This solvent mixture evaporates the slowest compared to Ethanol and Water droplets. At 66 ˚C, the droplets take about 15 s which is 2 orders of magnitude slower than the water droplet and about 3 orders of magnitude slower than the Ethanol droplet at the same temperature; at 130 ˚C, the total evaporation time is about an order of magnitude faster

Q4: Submit Paper on reaction kinetics of Ag, Cu, and Ni reactive inks to peer reviewed journal

This milestone wasn't fully completed. The first problem was that the copper and nickel reactive inks tested and developed in this project were not stable enough to produce high quality metal films. The second problem was that, while the data necessary to write the paper was nearly complete, the student that developed the multiphysics model graduated and we did not have bandwidth to retrain a new student to finish the model and still make necessary progress on the rest of the project.

Despite not getting the paper out, we did finish collecting the reaction kinetic data and integrate it into a rough multiphysics model. Example reaction kinetic data is shown in Figure 6 and Figure 7.

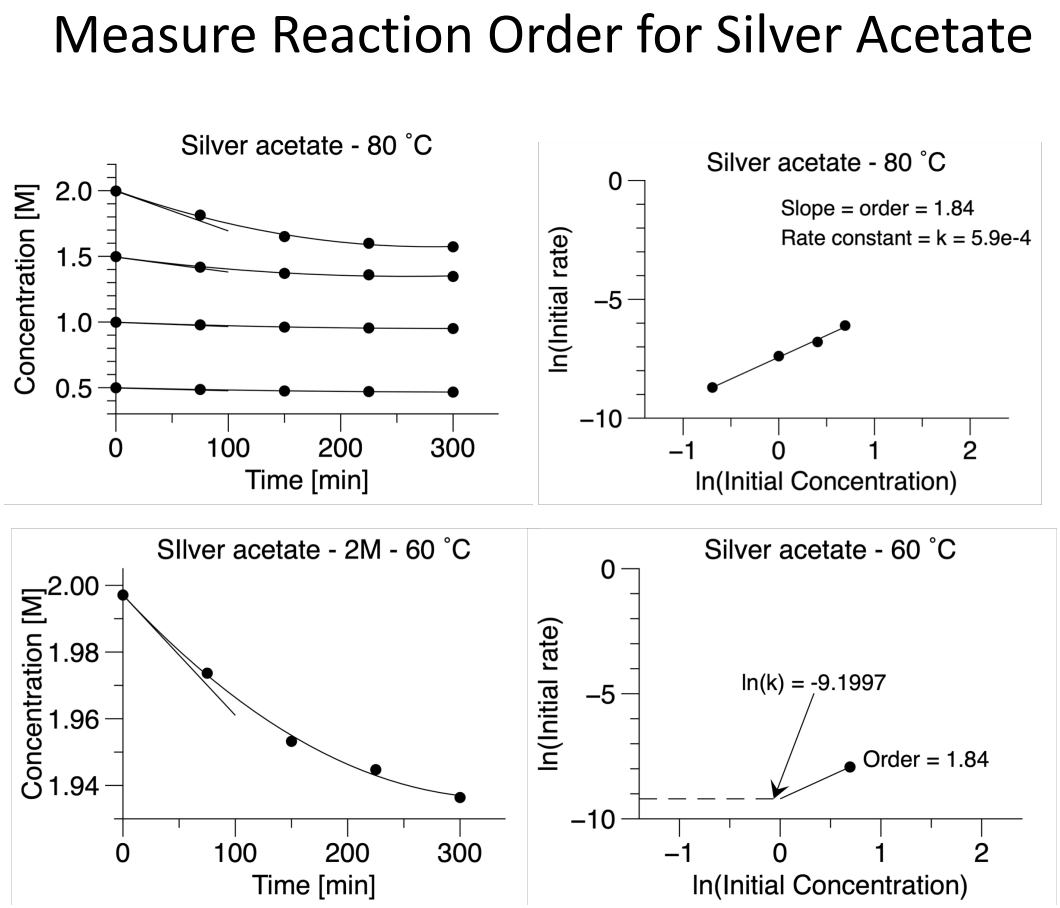


Figure 6. Data to calculate the silver acetate reaction order showing that the silver reduction rate scales with $[Ag^{+}]^{1.8}$.

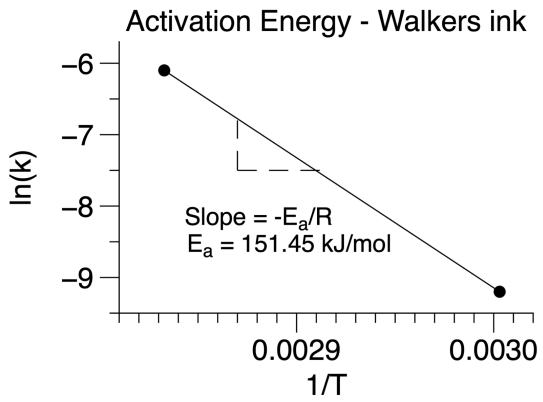


Figure 7. Shows data used to calculate the Activation Energy (E_a) for the Ammonia-based complexing agent (often called "Walkers Ink"). Notice that the activation energy for the Ammonia-based ink is only 151 kJ/mol, which lower than the 330-376 kJ/mol typically reported for the direct decomposition of silver acetate decomposition.

As shown in Figure 8, this data was integrated into a multiphysics model to connect reaction rate distribution with substrate temperature and ink composition. These plots show the log of the total silver reduction rate as a function of time for a silver reactive ink droplet deposited on a substrate held at 333 K. Notice that the ammonia-based RSI (Walker) suddenly "crashes out" after ~120 ms while the reduction reaction for the ethylamine-based RSI (Gaitan, developed in our lab as part of this project) is largely confined to the solid/liquid interface. This is consistent with what was observed in the high-speed video and is one the reasons why the ethylamine-based ink we developed produced higher quality silver films. This bottom-up growth reduces both porosity and solvent trapping.

Figure 9 shows the reaction rate distribution within the ammonia and ethylamine-based reactive inks. Notice that ethylamine-based reactive ink confines the reaction rate distribution to solid/liquid interface and produces a denser film. Note, this image came from our Q5 report.

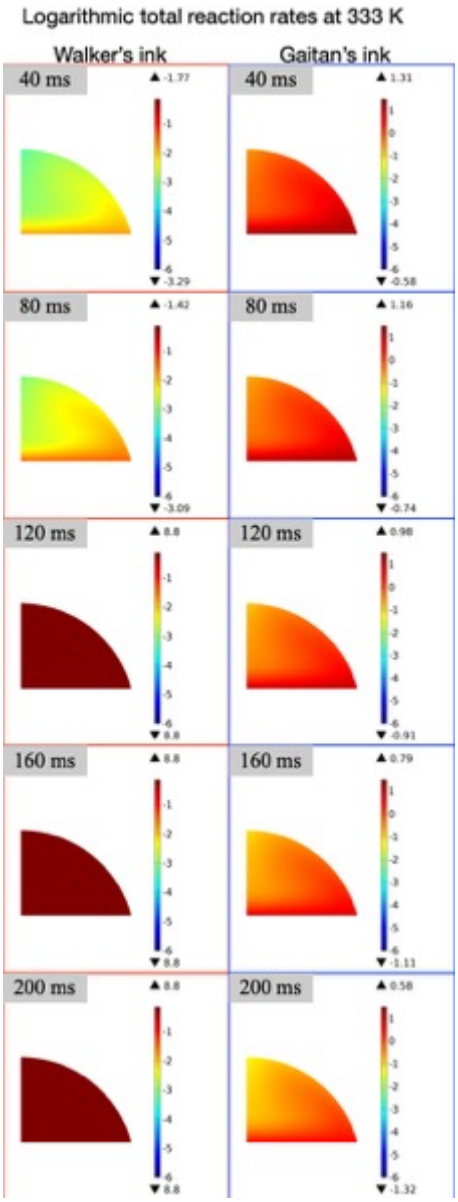


Figure 8. Plots from Comsol Multiphysics Model showing the Log of the Reaction Rate as a function of time at 333 K for the Ammonia-based (Walker) and Ethylamine-based (Gaitan) reactive silver inks. Notice that the Ammonia-based ink "crashes out" at 120 ms while the reduction reaction for the Ethylamine-based reactive silver ink is largely confined to the solid/liquid interface. This is one of the reasons why the ethylamine-based reactive silver ink produces a denser silver film.

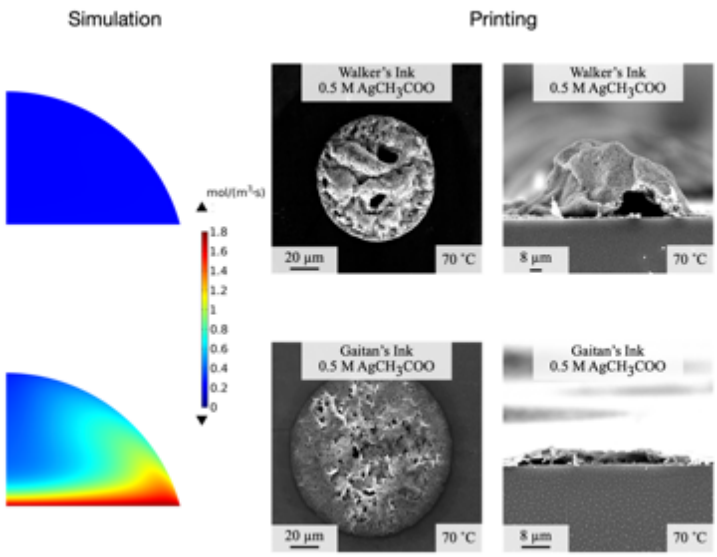


Figure 9. Multiphysics models of the Ammonia-based (Walker) and Ethylamine-based (Gaitan) reactive inks compared to printed morphology (data from Q5).

Q5: Print speed ≥ 10 mm/second with continuous lines, line width < 120 µm

This quarter's milestone focused on demonstrating high speeds to enable RSI-based metallization of RSI photovoltaic cells at large-volume manufacturing levels. As shown in Figure 10, print speeds of 150 mm/sec were achieved with good line widths. Notice the line width decreases with increasing print speed. Eventually, we settled on print speeds of 50 mm/sec to 70 mm/sec to metallize the cells to balance line width, nozzle stability, and silver deposition thickness.

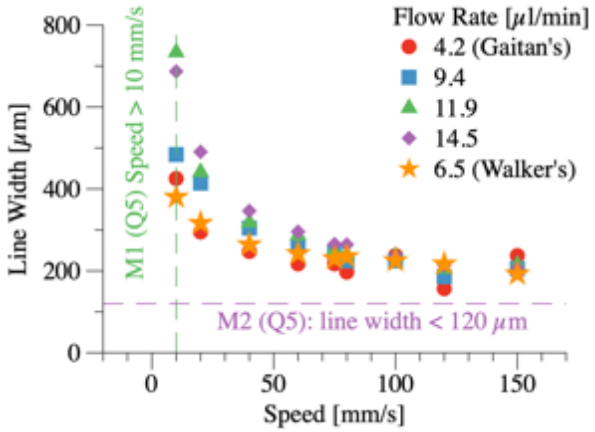


Figure 10. Plot of print speed vs. line width for the Ethylamine-based (Gaitan) and Ammonia-based (Walker) inks. Notice that print speeds upwards of 150 mm/sec were achieved.

7.2.2 BP1 – Task 2 Milestones Progress: Photovoltaic Metallization

The objective of this task is to determine the optimum finger width and number of layers for silicon diffused junction and HJT photovoltaic cells with and without adhesion promoting layers as throughput is increased from one 50 mm wafer/day up to three 100 mm wafers per day. The metallization adhesion strength, contact resistance, power loss, shading, media resistivity, and

porosity was measured. This data was used to down select the base in class processing parameters for silicon diffused junction and HJT photovoltaic cells.

The following milestones were associated with this task:

- Q1: Metallize a solar cell using silver reactive ink and contact dispensing printer
- Q6: Media resistivity ≤ 10 μΩ-cm; Contact resistivity ≤ 10 × 10-3 Ω-cm^2, area metallization loss during 180˚ scotch-tape peel test less than 3%
- Q7: FF > 75%

Q1: Metallize a solar cell using silver reactive ink and contact dispensing printer

The objective of this milestone was to demonstrate that we could metallize a silicon heterojunction (SHJ) photovoltaic cell. Figure 11 shows the first cell we metallized with a reactive silver ink (RSI). Notice that there are some print defects at the beginning and ending of the printed silver lines along with some defects along their lengths. These issues are eventually fully addressed through the duration of this project. The cell performance of the RSI metallized cell was compared to a low-temperature silver-pasted metallized SHJ cell. While the initial cell performance was below that of a screen-printed metallization, the end-performance of the RSI metallized cells eventually surpassed that of the screen-printed cells.

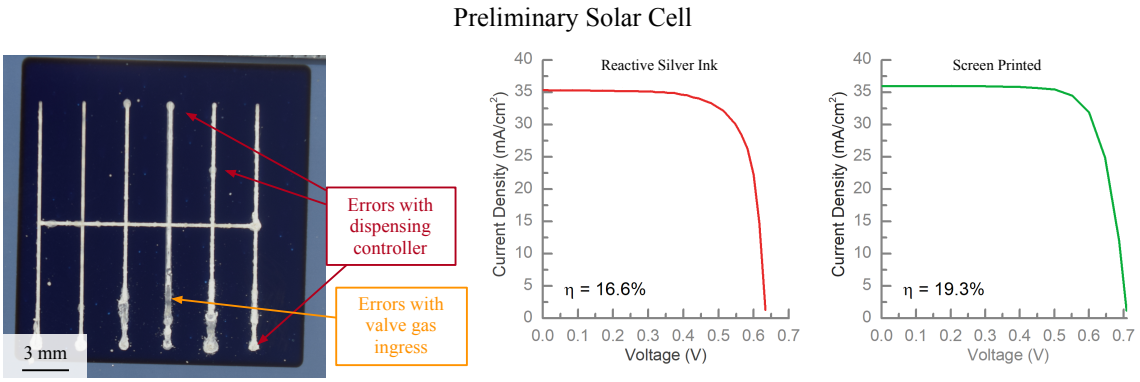


Figure 11. Optical image and performance results of first cell metallized using an ammonia-based reactive silver ink compared to a cell metallized using low-temperature screen-printed pastes.

Q6: Media resistivity ≤ 10 μΩ-cm; Contact resistivity ≤ 10 × 10-3 Ω-cm^2, area metallization loss during 180˚ scotch-tape peel test less than 3%

Figure 12 plots the resistivity of the Ammonia-based (Walker) and Ethylamine (Gaitan, in-house developed) inks as a function of during-print substrate temperature. Printing the ethylamine-based ink at 70 ˚C and 80 ˚C produced silver with resistivities on the order of 5-9 μΩ·cm, which is below the 10 μΩ·cm Q6 goal.

Figure 13 shows the Transfer Line Method (TLM) measurements used to determine the contact resistance. The Ammonia-based (Walker) and Ethylamine-based (Gaitan) reactive inks had contact resistances of $\rho_c = 6.1 \times 10^{-3}$ Ω-cm^2 and $\rho_c = 4.5 \times 10^{-3}$ Ω-cm^2 respectively. Notice that the RSI metallizations had contact resistances lower than the contact resistance of the screen-printed low-temperature silver pastes ($\rho_c = 10 \times 10^{-3}$ Ω-cm^2) and below the Q6 target contact resistance of $\rho_c = 10 \times 10^{-3}$ Ω-cm^2).

The optical images in Figure 14 shows that the optimized Ethylamine-based inks before and after tape-peel tests. The tape was on the left side of each sample. Notice that the printed RSI

adhesion is larger than the adhesion of the tape itself, with tape residue being left behind on the printed silver. The silver loss was less than 3%.

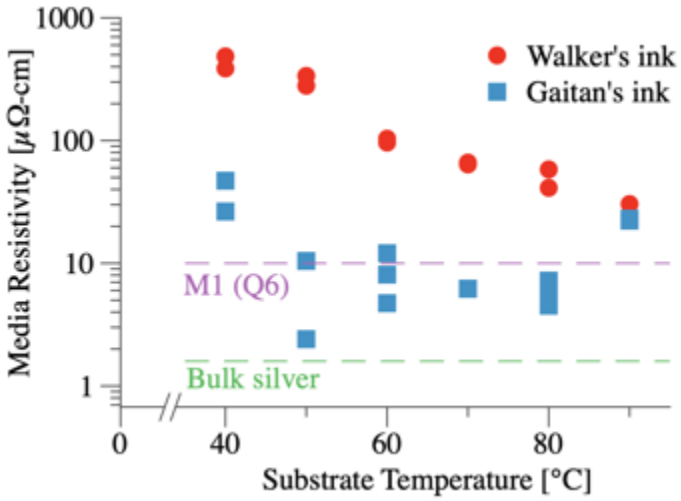


Figure 12. Graph of printed RSI silver resistivity vs. substrate temperature at Q6. The purple dashed line shows the Milestone 1 (Q6) goal of 10 μΩ·cm resistivity. This study showed that printed on substrates on held at 70 ˚C and 80 ˚C produce high quality silver.

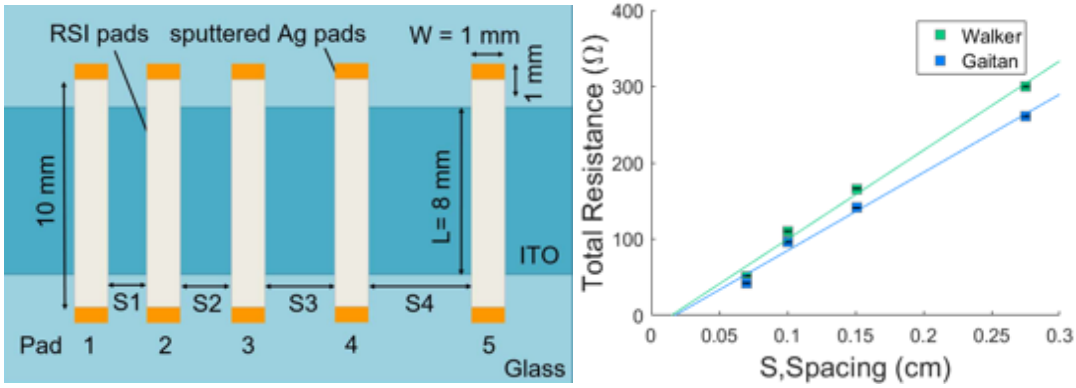


Figure 13. Setup for contact resistivity measurements and raw data for the Ammonia-based (Walker) and Ethylamine-based (Gaitan) reactive inks with contact resistances of $\rho_c = 6.1 \times 10^{-3}$ Ω-cm^2 and $\rho_c = 4.5 \times 10^{-3}$ Ω-cm^2 respectively. Notice that this is lower than the contact resistance of the screen-printed low-temperature silver pastes ($\rho_c = 10 \times 10^{-3}$ Ω-cm^2).

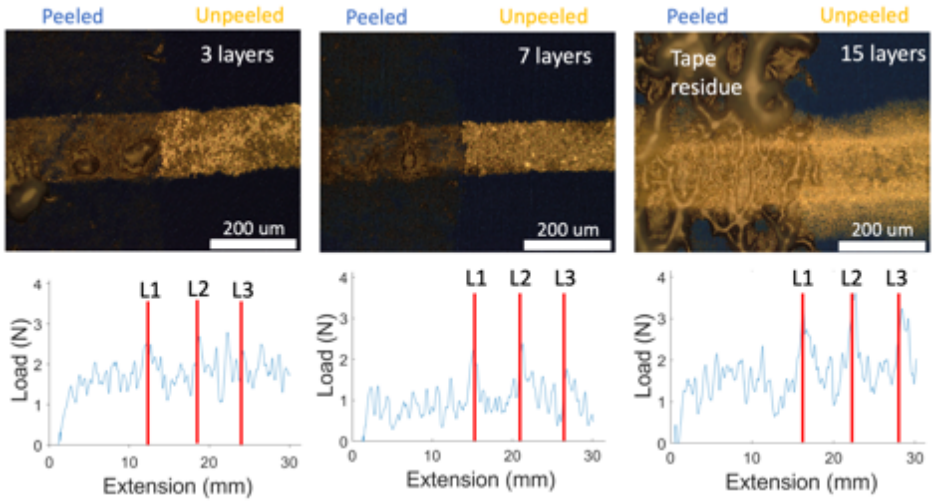
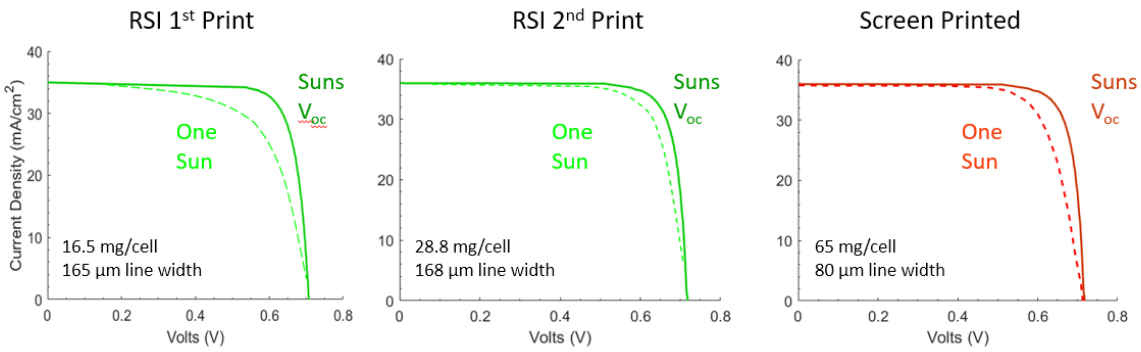


Figure 14. Optical images showing Ethylamine-based inks before and after tape-peel tests. The tape was on the left side of each sample. Notice that the printed RSI adhesion of the is larger than the adhesion of the tape itself, with tape residue being left behind on the printed silver.

Q7: FF > 75%

The Summary Results in Figure 15 show that the RSI metallized SHJ M2 sized (156.75 × 156.75 mm = 24570 mm^2 area) cells have Fill Factors ranging from 73.1% to 77.1%.



Suns-V_{oc}

	V_{oc} (V)	J_{sc} (mA/cm²)	Efficiency (%)	Fill Factor (%)	R_s (Ω-cm²)	V_{mp} (V)	J_{mp} (mA/cm²)
SP	0.718	36	**20.2**	**81.9**	0.72	0.671	31.56
RSI 1	0.709	34.6	**19.4**	**79.1**	0.86	0.606	32
RSI 2	0.717	35.7	**21.1**	**82.5**	0.69	0.652	32.4

IV

	V_{oc} (V)	J_{sc} (mA/cm²)	Efficiency (%)	Fill Factor (%)	R_s (Ω-cm²)	V_{mp} (V)	J_{mp} (mA/cm²)
SP	0.713	35.2	**19.2**	**76.5**	0.78	0.616	31.3
RSI 1	0.707	34.3	**17.8**	**73.1**	0.93	0.556	31.9
RSI 2	0.717	35.4	**19.7**	**77.4**	0.76	0.642	30.6

Figure 15. Data and results of RSI metallized cells showing the RSI metallized SHJ cells with Fill Factors ranging from 73.1% to 77.4%.

7.2.3 Q8: Meeting Go-No Go Decision Points

- Media Resistivity ≤ 6 µΩ-cm (~2.4 µΩ·cm)

- Contact Resistivity ≤ 5×10^{-3} Ω-cm^2 (4.5×10^{-3} Ω-cm^2)
- Deposition speed ≥ 10 mm/min (50 mm/sec to 70 mm/sec)
- Line width ≤ 100 µm ± 20% (116 µm for best resistance, < 50 µm for higher resistances)
- Fill Factor of an HJT or Al BSF cell with reactive ink front metallization ≥ 75% (77.1% achieved)

The Figures below supply the data for any Go/No-Go Decision Points not supplied in earlier Task/Milestone discussions.

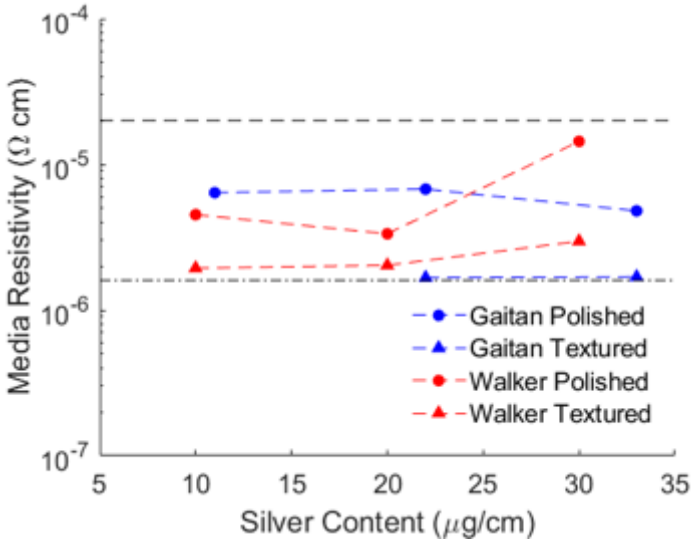


Figure 16. Graph of silver content vs. media resistivity showing that the printed Ethylamine-based (Gaitan) RSI printed on textured wafers almost matches that of bulk silver (~2.4 µΩ·cm).

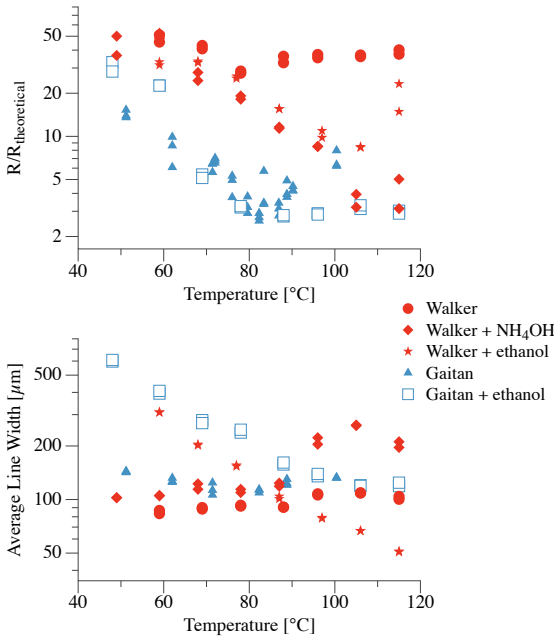


Figure 17. Graph showing resistances vs. theoretical resistance and line width (if 100% dense, pure silver was deposited) as a function of ink composition and substrate temperature (Walker – Ammonia-based, Gaitan = Ethylamine-based). notice that the line width at an optimized substrate temperature (~80 ˚C) is 116 µm wide. Lower line widths below 50 µm, were achieved, but resistance was higher.

7.2.4 BP1 – Task 3 Milestone Progress: Initial Reliability of Reactive Inks

The objective of this task was to quantify the reliability of photovoltaic cells metallized using the initial set of processing parameters for contact dispensed reactive inks. Exploratory tests were conducted in parallel with the reactive ink optimization process (Task 2) so that any potential issues with the ink composition and metal/substrate interface can be identified early and adjustments made to the processing parameters.

The damp-heat reliability studies were delayed due to issues connecting the tabbing wire to the RSI metallized SHJ cells. This is because so little silver is used that the solder used in the tabbing wire was dissolving the printed silver. Unfortunately, we didn't discover the mechanism until later in the project and considerable time was lost trying to connect the busbars. As a result, most of the reliability tests were delayed until BP2. Figure 18 shows some of the challenges making electrical connection to the RSI cells with traditional tabbing wires. Specifically, the shadowing in RSI EL images show that the RSI fingers have poor connection to soldered busbars. By Q10 we identified that the extremely low amount of silver combined with the high silver solubility in standard tabbing wire solders was root cause of the problem. As shown in Figure 24 (page 30), the small amount of silver in the fingers was being dissolved into the tabbing wire's solder. Traditional screen-printed silver fingers don't exhibit this problem because they use significantly more silver and can saturate the tabbing-wire's solder without consuming all of the screen-printed silver's fingers.

Figure 19 shows Raman spectra and summary data of silver printed with reactive silver inks when exposed to acetic acid environments. Notice that the intensity of the Ag-acetate peak decreases with time and acetic acid exposure. This is a unique feature of reactive silver inks.

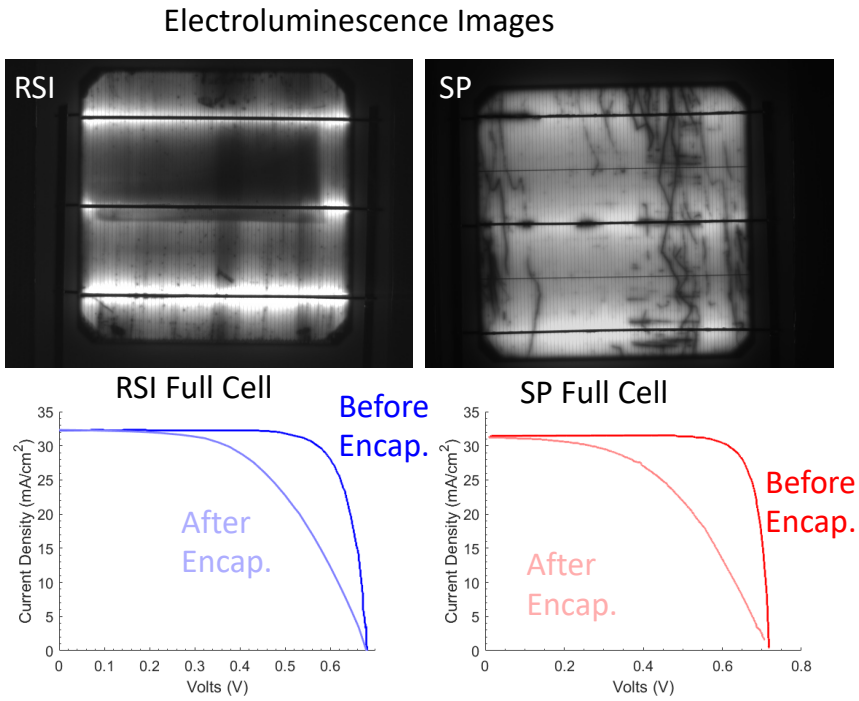


Figure 18. Electroluminescence images showing performance after encapsulations.

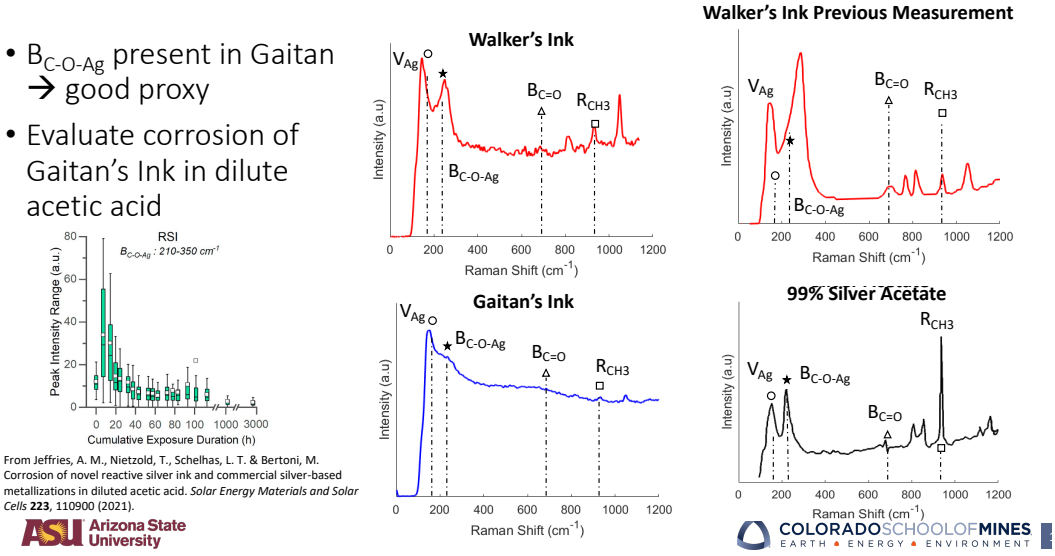


Figure 19. Raman data and spectra on the chemical state of the ink after exposure to acetic acid showing that the Ag-acetate bond decreases over time even when exposed to acetic acid.

7.2.5 BP2 – Task 1: Ink Optimization for High Production Throughputs

The objectives of this task were to increase the print speed and continually refine the reactive inks based upon the performance and reliability data collected in Budget Period 1 and throughout

Budget Period 2. Inks composition and processing parameters will be continually refined, printed, and electrical performance tested to both improve the inks and test/validate the global sensitivity analysis simulations.

- Q10: In lab wafer metallization throughput equivalent to 5 minutes/wafer
- Q13: Wafer throughput equivalent to 1.5 minutes/wafer

Q10: In lab wafer metallization throughput equivalent to 5 minutes/wafer

The objective of the Q10 Milestone was to demonstrate that the dispense-printing reactive silver inks can scale for large volume manufacturing. Dispense-printing was chosen because multiple nozzles can be used in parallel with minimal costs so that multiple lines and layers can be rapidly printed. For this Quarter we upgraded the Nordson Dispensing Robot to have 6 nozzles. Six was chosen because the number of fingers on the cell was 66 and using an integer divisor simplified the dispensing program. This improvement reduced our metallization time from 240 min/cell down to 40 minutes/cell. The metallization time would reduce to 3.6 min/cell when scaled to an industrially relevant 66 nozzles. Overall, dispensing printing is an easy and scalable process to pattern simple lines and metallize traditional PV cells. Note that the RSI we developed does not require any post-print annealing steps.

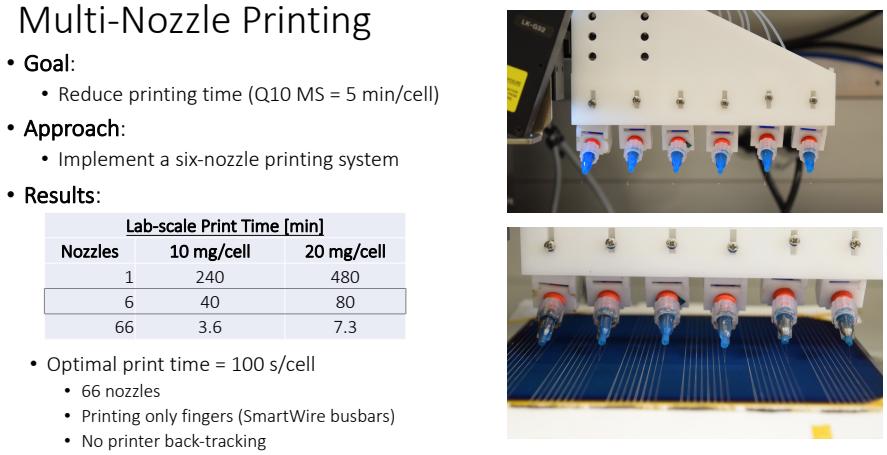


Figure 20. Summary slide showing our multi-nozzle printer setup demonstrating that fingers metallization lines can be printed in parallel.

Q13: Wafer throughput equivalent to 1.5 minutes/wafer

The objective of the Q13 Milestone was to further demonstrate that the dispense-printing reactive silver inks can scale for large volume manufacturing by decreasing the time to metallize a SHJ cell to less 1.5 min/cell. Building off the multi-nozzle printer setup developed for Q10, we demonstrated a conveyor belt printing approach that reduced printing time by 50%. The issue is that our lab printer can only move ~300 mm in any direction, so printing multiple layers requires that we dispense ink in one direction, lift the nozzle, return back to the starting point, and then print the next layer. An industrial system would have a dedicated array of nozzles, one for each layer, with the SHJ cell continuously moving in one direction. This allows the layers to be printed continuously with minimal wasted time. Overall, this quarter we demonstrated printing times of less than 1.5 wafers/cell in an industrial capacity.

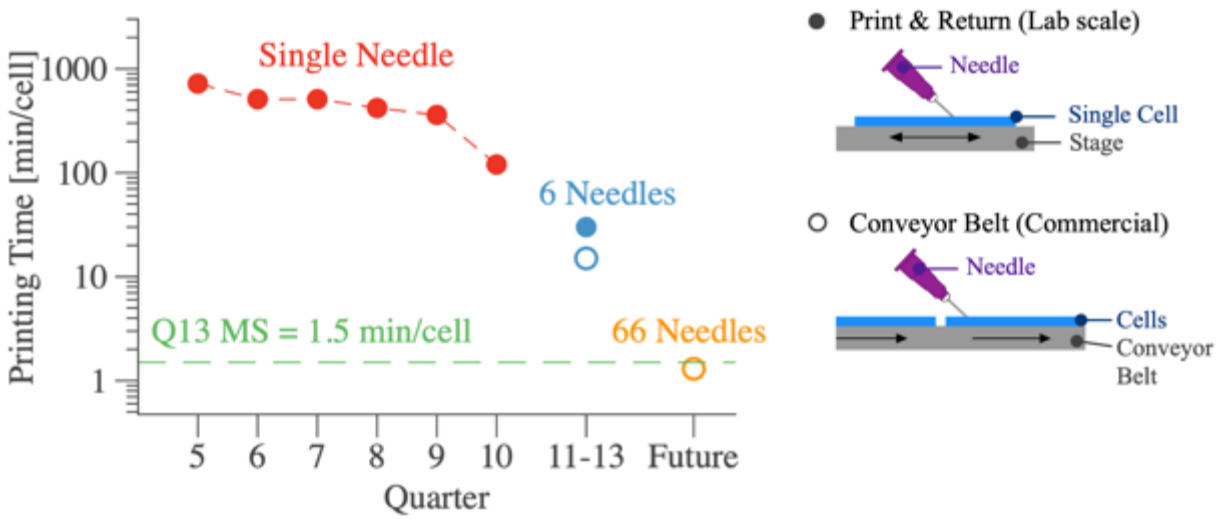


Figure 21. Chart of cell printing time from quarters 5 to 13. The dashed green line shows the quarter 13 milestone. The solid markers represent lab-scale printing time, where the stage returns to the starting position after each layer. The hollow markers represent the equivalent printing time in a commercial environment that eliminates wasted printer movements. The equivalent printing time for a 66-needle array and conveyor belt printing is 1.3 min/cell.

7.2.6 BP2 – Task 2: Photovoltaic Metallization at High Production Throughputs

The objective of this task was to continue improving the performance and reliability of c-Si and HJT photovoltaic cells metalized using reactive inks. Particular attention was paid to increasing wafer throughput and reducing silver consumption while meeting cell performance goals. Throughput was increased from one 100 mm wafer/day to one 150 mm wafer in 40 minutes in the lab using a 6-needle system. This translates to one 150 mm wafer in a 1.5 minutes assuming a commercial system with 66 needles (one for each finger) operating in a convoy belt setup.

- Q9: Metallization consumption down to 40 mg/cell for a fabricated cell
- Q11: Media resistivity ≤ 4 μΩ-cm; Contact resistivity ≤ 3×10^{-3} Ωcm^2, adhesion between media/solder ribbon and wafer ≥ 3 N·mm^{-2} in 90˚ peel test
- Q14: Improve J_{sc} by more 3% and FF by more than 2% over the cell achieved with reactive ink metallization at end of Budget Period 1

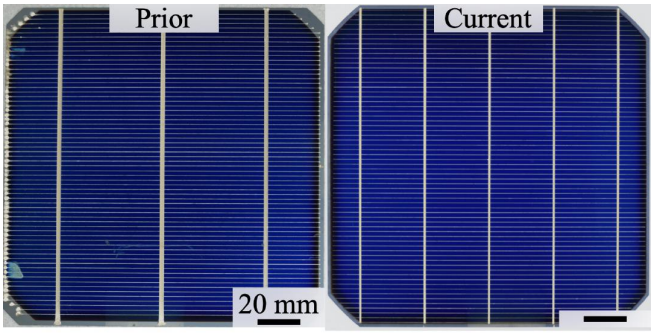
Q9: Metallization consumption down to 40 mg/cell for a fabricated cell

The objective of the Q13 Milestone was to demonstrate that we can reduce silver consumption to less than 40 mg/cell. Figure 22 is a summary slide from the Q9 Quarterly Meeting. This slide shows the improvements we made in print quality and that the amount of silver consumed to metalize the cell was 10 mg/cell. Figure 23 is a summary slide from Q9 Quarterly Meeting showing the challenges of RSI-based busbars. Specifically, even though the quality of our metallization was high, the amount of silver we were using was too little for the pogo-pins on the Suns V_{co}/IV measurement tool and it could not make good electrical contact to the silver. This measurement challenge reduced the measured efficiency of the cell. This was temporarily solved by increasing the amount of silver used to metallize the busbars while

keeping the amount of silver consumed to metallize a SHJ cell less than 40 mg/cell. Additionally, we found that soldering the tabbing wire to the busbars was also challenging because the solder on the tabbing wire was dissolving the ~ 3 µm thick RSI busbars. As shown in Figure 24 (from Q15 report), this problem was solved by changing the solder to one that has a lower, but non-zero, silver solubility. This will allow PV manufacturers to maintain a low silver metallization to 16 mg/cell.[17]

Improve Full Cell Metallization

- Goal:
  - Reduce line width
  - Increase throughput
- Approach:
  - Implement higher flow rate
  - Mask off heads and tail
  - Automated needle maintenance
- Results:
  - Line width = 117 µm ± 13 µm
  - Print time reduced by 3x
  - No heads or tails



Prior	Current
Line width = 170 µm	Line width = 117 µm
Print time = 6 h	Print time = 2 h
Silver consumed = 15 mg	Silver consumed = 10 mg

Figure 22. Summary slide from Q9 Quarterly Meeting showing the improvements in metallization qualities made by Q9. Additionally, the fingers on the cell consumed 10 mg of silver.

Cell Characterization

- 4 RSI Full Cells fabricated
- 2 SP Sister Cells
- Suns V_{oc} values comparable with **98% less silver** per length
  - Low IV due to poor pin contact
- Need to determine best interconnection method

Suns V_{oc} / IV Measurements

	Fill Factor (%)	Efficiency (%)	R_s (Ω cm²)
RSI	83.20/48.61*	17.89/10.45*	0.74/8.8*
SP	83.78/67.86	19.56/15.84	0.65/1.5

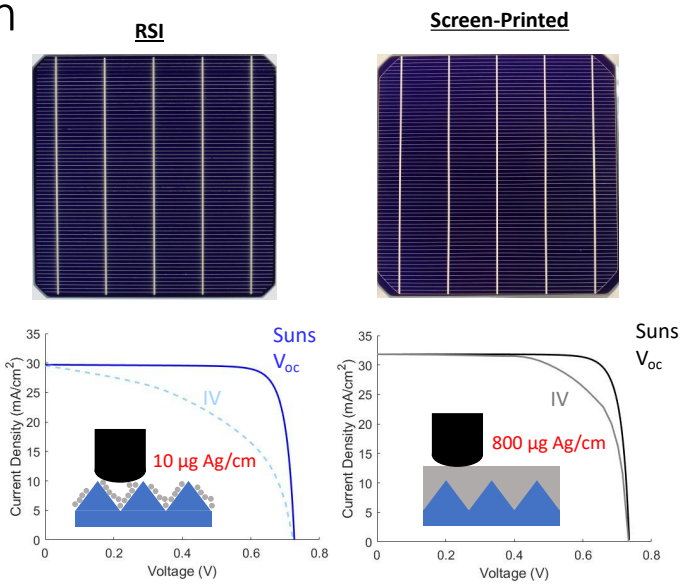


Figure 23. Summary slide from Q9 Quarterly Meeting shows the challenges of RSI-based busbars. Specifically, even though the quality of our metallization was high, the amount of silver we were using was too little for the pogo-pins on the Suns V_{co}/IV measurement tool could not make good electrical contact to the silver. This measurement challenge reduced the measured efficiency of the cell.

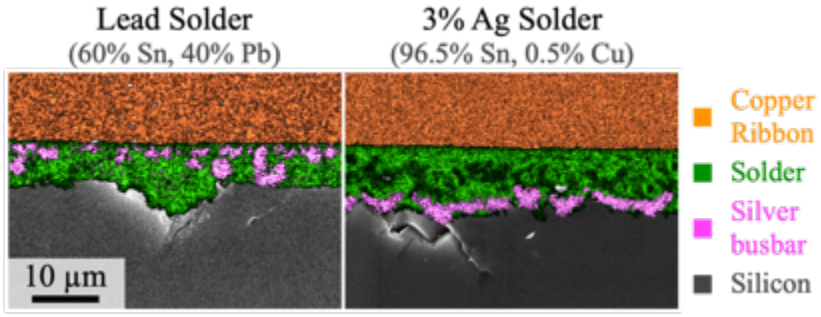


Figure 24. EDS data showing silver migration due to dissolution while soldering. The lead solder dissolves the silver at high temperature. The 3% Ag solder does not dissolve the busbars, and therefore the silver does not migrate.

Q11: Media resistivity ≤ 4 µΩ·cm; Contact resistivity ≤ 3 × 10^{-3} Ω·cm^2, adhesion between media/solder ribbon and wafer ≥ 3 N·mm^{-2} in 90° peel test

The objective of the Q11 Milestone was to demonstrate continued metallization progress, emphasizing low silver media resistivity, low contact resistivity, and good adhesion. Adhesion ≥ 3 N·mm^{-2} was previously demonstrated in Q6 (see Figure 14, page 13). The plots in Figure 25 show the progress to-date on the electrical properties of the printed Ethylamine and Ammonia reactive silver inks. notice that the ethylamine ink with 0.5 M silver loading has low porosity and good electrical properties when printed at low temperatures. The resistivity was measured at 2.0 µΩ·cm to 2.4 µΩ·cm. As shown in Figure 26, the contact resistance was measured at 2 mΩ·cm^2.

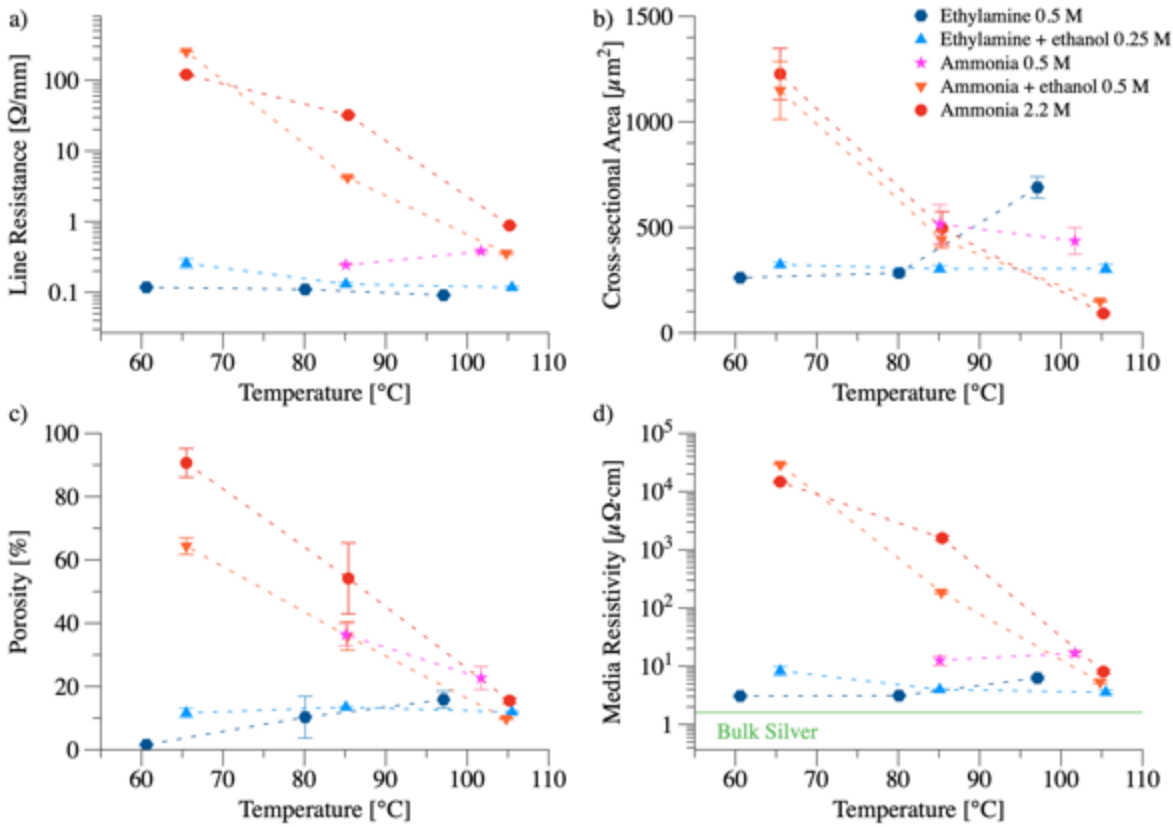


Figure 25. Cross-section characterization plots. a) Line resistance vs. temperature. b) Cross-sectional area vs. temperature. c) Porosity vs. temperature. Porosity ranges from 1.6% to 91%. d) Media resistivity vs. temperature. The solid green line indicates the resistivity of bulk silver. Error bars indicate the standard deviation. The dashed lines intend to guide the eye between data points.

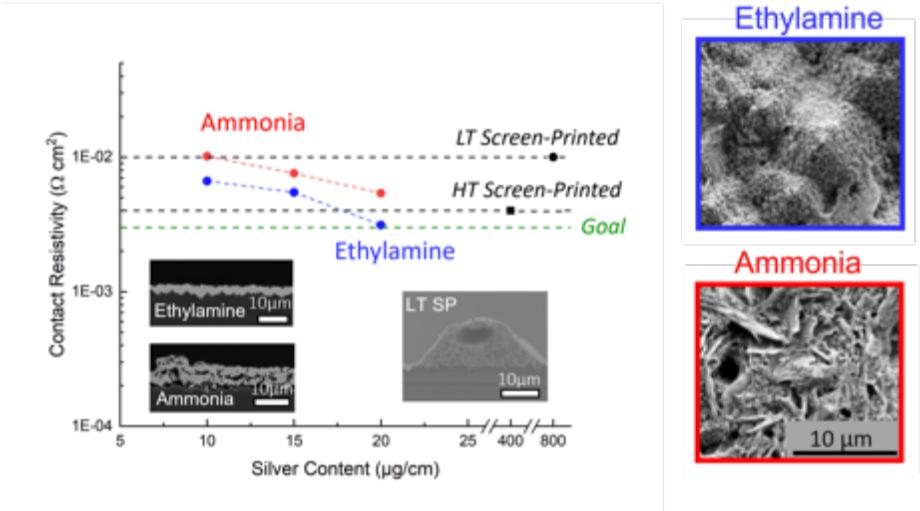


Figure 26. Contact resistivity vs silver content for the ethylamine and ammonia inks as compared to the high-temperature (HT) and low-temperature (LT) screen-printed silver paste. The SEM images depict the two inks in cross-section and top down compared to the LT SP paste.

Q14: Improve J_{sc} by more 3% and FF by more than 2% over the cell achieved with reactive ink metallization at end of Budget Period 1

The objective of the Q11 Milestone was to demonstrate continued improvement in cell performance. Figure 27 shows summary data from our Q14 report. This data shows that our J_{sc} has improved by more than 3% over BP1 RSI results and is 2.5% higher than the low-temperature screen-printed pastes. This data also shows that the Fill Factor (FF) improved from 73.1% in BP1 to 80.4% by Q14. Additionally, we see that the RSI metallized SHJ cells show a Fill Factor 1.7 abs.% above the low-temperature screen-printed paste cells (LT-SP).

Overall, the progress shows that the RSI metallization approach uses less silver (20 mg/cm^2 for these results) while improving cell performance.

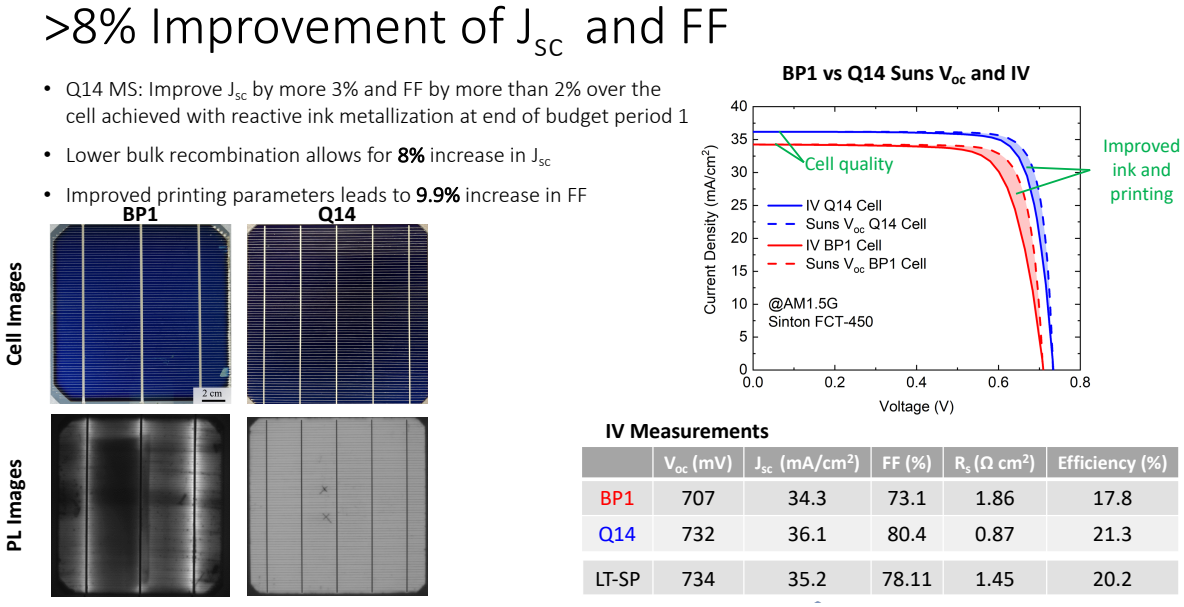


Figure 27. Summary Slide from Q14 Report showing Fill Factor (FF) improvement from 73.1% in BP1 to 80.4%. Additionally, we see that the RSI metallized SHJ cells show a Fill Factor 1.7 abs.% above the low-temperature screen-printed paste cells (LT-SP).

7.2.7 BP2 – Task 3: Reliability of Reactive Inks at High Production Throughputs

The objective of this task was to continue to quantify and improve the reliability of photovoltaic cells metallized using contact dispensed reactive inks.

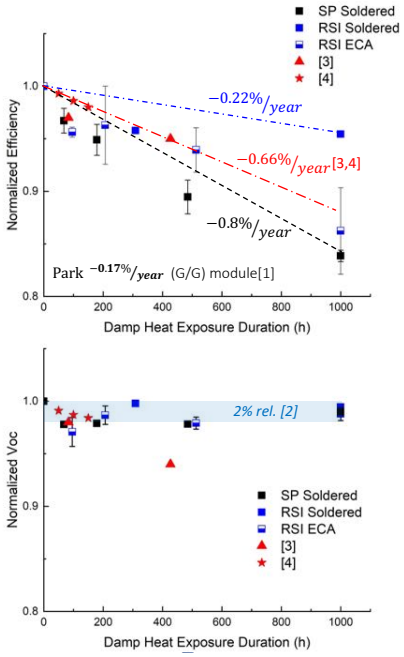
- Q12: $\Delta\eta < 1\%$ of initial η after DH test; Submit paper on initial reliability studies
- Q15: $\eta < 0.25\%$ of initial η after DH test; silver/metal consumption down to 10 mg/cell
- Q16: Submit paper on reliability and reactive ink metallization sensitivity

Q12: Δη < 1% of initial η after DH test; Submit paper on initial reliability studies

The objective of the Q12 Milestone was to demonstrate progress on both measuring the reliability of RSI-metallized SHJ cells and that this metallization scheme will meet the target reliability goal of less than 0.25% performance degradation in performance. As shown in Figure 28, the degradation rate of the RSI-metallized SHJ cells was 0.22% over 1,000 hours of damp heat testing at 80 ˚C and 80% Relative Humidity (RH). This is below both the $\Delta\eta < 1\%$ goal for Q12 and $\Delta\eta \leq 0.25\%$ goal for Q15. What is particularly interesting is that the bulk of the degradation for the RSI-metallized SHJ cells with soldered tabbing wire occurred within the first 100 hours with minimal change after that.

Damp Heat Exposure

- RSI cells demonstrate lower degradation rates than SP sisters interconnected with same technology
- Efficiency change is lower and approaches G/G module reliability performance [1]
- Voc change comparable to 23.6% best in class (IWO) cell [2]



[1] Park et al. "A Reliability study of silicon heterojunction photovoltaic modules exposed to damp heat testing", *Microelectronic Engineering*, vol. 216, (2019).
[2] Liu et al. "Damp-Heat-Stable, High-Efficiency, Industrial-Size Silicon Heterojunction Solar Cells", joule 4(4) (2020).
[3] Jordan et al. "Silicon Heterojunction System Field Performance. IEEE Journal of Photovoltaics" 8(1), 177–182, (2018).
[4] Ishii et al, "Annual degradation rates of recent crystalline silicon photovoltaic modules", Prog. Photovolt: Res. Appl;25:953–967 (2017).

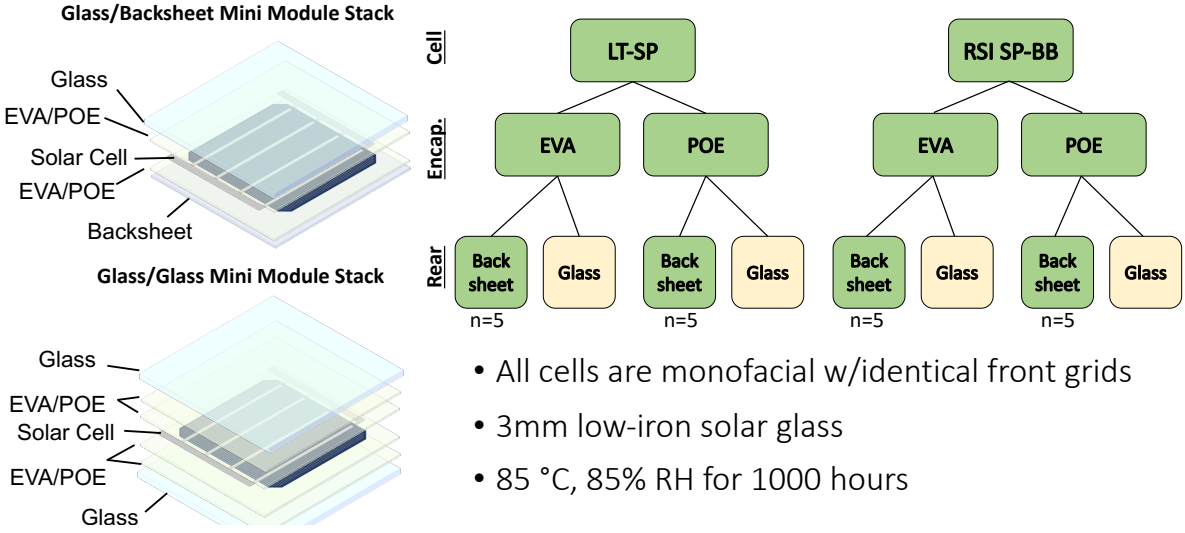
Figure 28. Summary slide from Q12 Presentation showing that the RSI-metallized SHJ cells showed less than 0.22% degradation in normalized efficiency after 1,000 hours of Damp Heat (DH) testing at 80 ˚C and 80% Relative Humidity (RH).

Q15: η < 0.25% of initial η after DH test; silver/metal consumption down to 10 mg/cell

The objective of the Q15 Milestone was to demonstrate progress on both measuring the reliability of RSI-metallized SHJ cells and that this metallization scheme meets the target reliability goal of less than 0.25% performance degradation in performance. Figure 29 shows the layup of the test cells. Two different metallization strategies were tested: Low-Temperature Screen Printed Pastes (LT-SP) and Reactive Silver ink with Screen-Printed Busbars (RSI SP-BB). Two different encapsulants were tested: EVA and POE. Two different rear backings were tested: Polymer back sheet and Glass. Five modules were tested at 85 ˚C and 85% HR for 1,000 hours for each of the 8 possible configurations with performance data collected approximately every 100 hours.

Figure 30 shows the cells efficiency during damp heat testing. Notice that the RSI metallized cells showed low degradation rates on the order of -0.28%/year when encapsulated with EVA, which is close to the -0.25%/year target. Additionally, this is lower than the screen-printed metallized cells, which were -0.36% for the EVA encapsulated samples. The PL images in Figure 31 shows that the RSI metallization is not responsible for the EVA degradation and, instead, the degradation is associated with degradation of the passivation layer within the cell itself.

Damp Heat Sample Set



- All cells are monofacial w/identical front grids
- 3mm low-iron solar glass
- 85 °C, 85% RH for 1000 hours

Figure 29. Schematic showing the two different layups tested. One with Glass on the top with an EVA or PEO backing sheet on the bottom and the second with glass on both sides. Including variations in the metallization approach and type of encapsulation, a total of 8 different layups were tested.

Damp Heat Update

- Q15: η < 0.25%/year of initial η after DH test
- LT-SP and RSI EVA degradation rates are similar
- V_{OC} and J_{SC} change within range of best in class IWO cell [1] for all cells

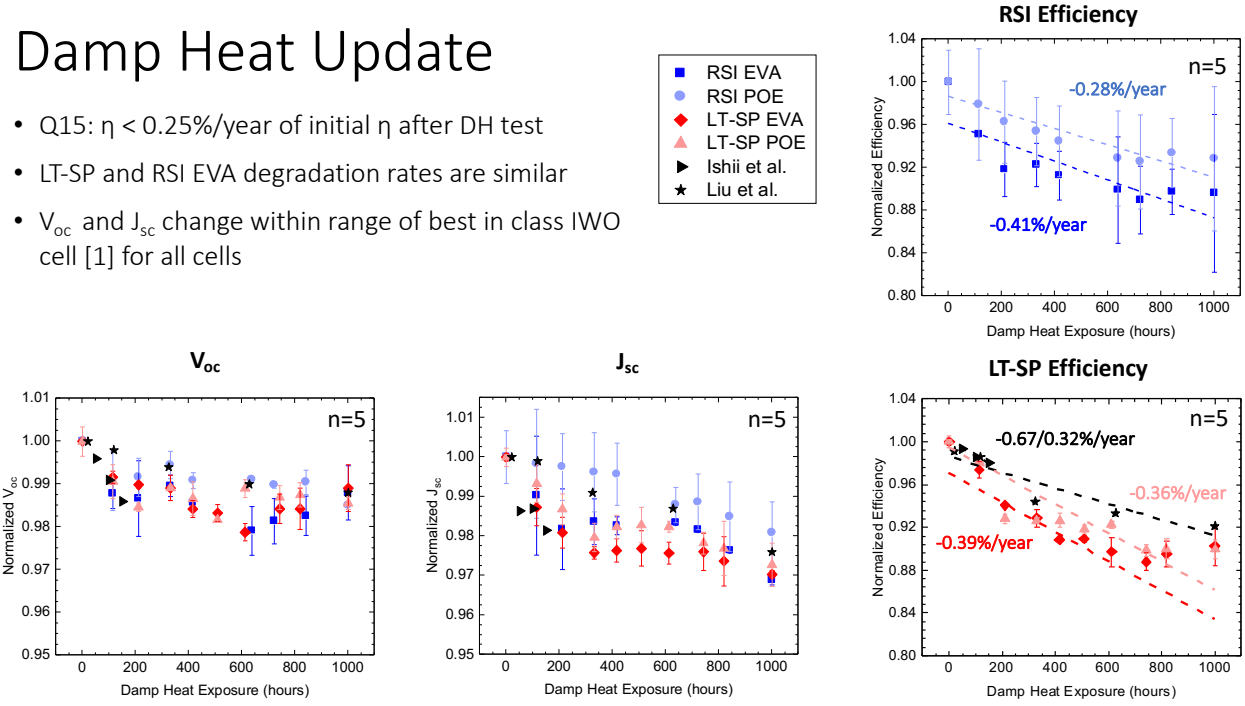


Figure 30. Summary slide from Q15 presentation showing the performance of the RSI and LT-SP metallization after 1,000 hours of damp heat testing. Notice that the RSI with POE encapsulation degradation was estimated at -0.28%/year.

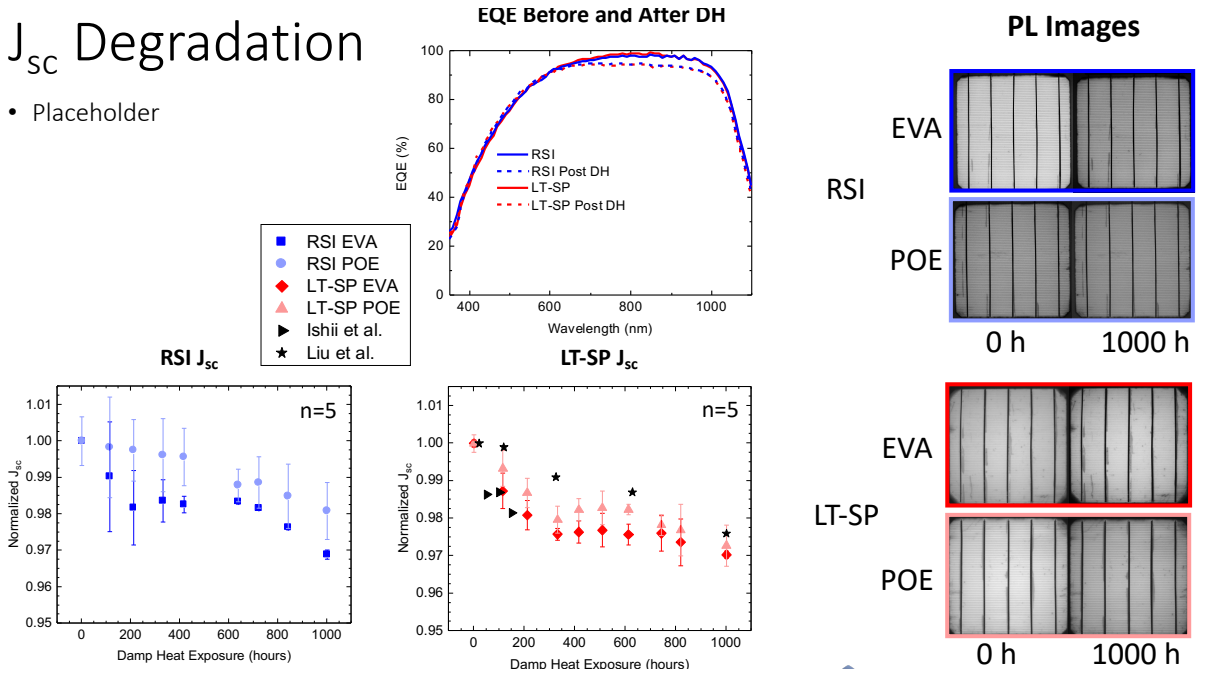


Figure 31. Summary slide from Q15 presentation showing the degradation mechanisms for the RSI was largely associated with degradation of the of the SHJ while the LT-SP samples show evidence of corrosion-induced delamination of the metal.

Q16: Submit paper on reliability and reactive ink metallization sensitivity

This paper is currently in progress, some of the reliability data is shown above.

8. Significant Accomplishments and Conclusions

The list below summarizes some our key accomplishments to date.

- Achieved contact resistivity ≤ 10 × 10^{-3} Ω-cm^2 with best at 2.1 × 10^{-3} Ω-cm^2
- Achieved media resistivity ≤ 10 μΩ-cm with some samples at 2.4 μΩ-cm
- Reduced silver consumption by 93% (16.4 mg/cell) 67 μg/cm^2
- Achieved cell efficiencies exceeding 21% with improvement to 22.29% modeled
- Modeled RSI metallized panels achieved 1.5% increase in yearly energy yield compared to LT-SP
- Demonstrated pathway to wafer throughput of < 1.5 min/wafer
- Supported 3 Ph.D. dissertations, 6 published manuscripts with 2 more under review or in progress
- Presented at 5 conferences

9. Path Forward

The PIs are currently working to secure NSF-PFI funding with Electron Inks to support commercialization of this technology. These proposed efforts focus on an innovation developed at the end of this project that could enable a 5× increase in silver ion loading without degrading metallization performance. This would reduce the number of printed layers from 50 layers down to 10 layers. This reduction is important because it decreases equipment costs by ~5×, reduces

manufacturing time from ~2 minutes/cell down to less than 24 seconds/cell, and increases yield by reducing the number of print-error opportunities.

Additionally, the team has received EERE-SIPS funding to develop silver and/or copper reactive inks to metallize temperature sensitive perovskite tandem cells. For this project, we have partnered with Beyond Silicon to supply the perovskite tandem cells and provide a perovskite PV manufacturer. This project is significant for two reasons. First, perovskite PV cells are very temperature sensitive and existing low-temperature metallization strategies require either significant amounts of low-temperature silver paste or a mix of photolithography and evaporated metal. Both approaches are expensive and limit the adoption of perovskite technologies. The second reason that this project is significant is because developing a new metallization strategy is both expensive and risky while large-volume PV manufacturers tend to be conservative. Expecting RSI metallization to immediately compete with screen-printed silver pastes would be challenging. Working in tandem with perovskite PV cells means that we can both solve a critical manufacturing challenge for perovskite adoption while developing the RSI metallization process in tandem.

10. Products

10.1 Publications

- Martinez-Szewczyk, M. W.; DiGregorio, S.; Hildreth, O.; Bertoni, M.* *Reactive Silver Inks: A Path to Solar Cells with 82% Less Silver*. Energy Environ. Sci. In Press 2024. https://doi.org/10.1039/d4ee00020j
- DiGregorio, S.; Raikar, S.; Hildreth, O.*, *Importance of the Heat Treatment Scheme on Self-Reducing Reactive Silver Inks.* ACS Appl. Electron. Mater., 2024, vol. 6, issue 1, pages 203-212; doi: 10.1021/acsaelm.3c0108
- DiGregorio, S; Martinez-Szewczyk, M; Raikar, S; Bertoni, M; Hildreth, O.* *Investigation of Reactive Silver Ink Formula for Reduced Silver Consumption in Silicon Heterojunction Metallization*. ACS Applied Energy Materials. 2023, vol. 6, issue 5, 2747-2757; doi: 10.1021/acsaem.2c03503
- Jeffries, A. M., Nietzold, T., Schelhas, L. T. & Bertoni, M.* *Corrosion of novel reactive silver ink and commercial silver-based metallizations in diluted acetic acid*. Solar Energy Materials and Solar Cells, 2021, vol. 223, 110900-8; 10.1016/j.solmat.2020.110900

10.2 Publications in Progress

- Martinez-Szewczyk, M. W.; DiGregorio, S.; Hildreth, O.; Bertoni, M.* Damp Heat Performance of Silicon Heterojunction Solar Cells with Reactive Silver Ink Metallization.
- DiGregorio, S; Martinez-Szewczyk, M; Raikar, S; Bertoni, M; Hildreth, O.* Importance of the Heat Treatment Scheme on Self-Reducing Reactive Silver Inks. Finalizing draft. To be submitted to Appl. Mat. and Inter. in 2024

10.3 Books or Other Non-periodical, One-time Publications

- DiGregorio, S. *Interfacial Reduction Phenomena in Self-Reducing Reactive Inks*. Ph.D. Dissertation. Presented to and Approved by Faculty at Colorado School of Mines on 07/28/2024.
- DiGregorio, S; Hildreth, O*; *Particle-less Reactive Inks*; Gupta, R; Nguyen, T; Eds: *Smart Multifunctional Nano-Inks: Fundamentals and Emerging Applications*; Elsevier; 2022, 125-158
- Mamidanna, A. *Morphology prediction of reactive silver ink systems.* Ph.D. Dissertation. Presented to and Approved by Faculty at Colorado School of Mines on 12/19/21
- Debruin, D. Formulating a Particle-Free and Low Temperature Nickel Reactive Ink for Inkjet Printing Conductive Features. *Masters Thesis* Presented to and Approved by Faculty at Arizona State University on 4/1/19

10.4 Patent Applications

- DiGregorio, S.; and Hildreth, O. Method and System for Controlling Morphology and Properties of Printed Reactive Inks. EIR# 0130501-23-0002, Filed 07/22/2024

11. Project Team and Roles

11.1 ***PI: Owen Hildreth*** *(CSM)*

Hildreth was the PI and oversaw both the overall project and primarily the reactive ink research. These efforts included: project management, graduate student mentoring, experiment development, data review, manuscript review, and presenting the results. Hildreth contributed to reactive ink development with intellectual contributions associated with: improving metallization adhesion, improving metallization density, integrating reactive inks into photovoltaic cells, improving metallization electrical properties, soldering to tabbing wire, reducing line width, measuring reaction kinetics, measuring metallization properties, understanding how of environment and processing parameters impact printed reactive silver inks, and developing reactive ink chemistries.

11.2 ***Co-PI: Mariana Bertoni*** *(ASU)*

Bertoni was the Co-PI and helped oversee the project and oversaw the photovoltaic cell fabrication, characterization, and optimization. These efforts included: project management, graduate student mentoring, experiment development, data review, manuscript review, and presenting the results Bertoni made intellectual contributions associated with: improving metallization performance, integrating reactive inks to photovoltaic cells, improving adhesion, improving interconnection between RSI and busbar technologies, interpreting corrosion studies, interpreting and improving damp-heat performance, and developing reactive ink processes.

11.3 ***Post-Doc: Maria Gaitan*** *(ASU)*

Gaitan tested and developed reactive ink chemistries tuned to the needs of photovoltaic metallization. This included investigating the performance of various reducing agents and complexing agents and the development of the ethylamine ink widely used in this project.

11.4 ***Ph.D. Student: Avinash Mamidanna*** *(CSM)*

Mamidanna developed initial printing processes to metallize SHJ cells using dispense printed reactive silver inks, measure the reaction kinetics of ammonia- and ethylamine-based reactive inks, and developed multiphysics models of evaporating reactive ink droplets. Mamidanna contributed to reactive ink development with intellectual contributions associated with: improving metallization density, integrating reactive inks into photovoltaic cells, improving metallization electrical properties, measuring reaction kinetics, measuring metallization properties, and developing reactive ink chemistries.

11.5 ***Ph.D. Student: April Jefferies*** *(ASU)*

Jefferies fabricated and measure the performance of early SHJ cells metallized using both reactive silver inks and low temperature silver pastes. Jefferies made intellectual contributions associated with: improving metallization performance, integrating reactive inks to photovoltaic cells, improving adhesion, interpreting corrosion studies, interpreting early damp-heat performance, and developing reactive ink processes.

11.6 ***Ph.D. Student: Steven DiGregorio*** *(CSM)*

DiGregorio developed reactive ink recipes, optimized reactive inks, optimized reactive ink printing processes, and studied the impact of processing parameters on silver printed with reactive silver inks. DiGregorio contributed to reactive ink development with intellectual contributions associated with: improving metallization adhesion, improving metallization density, integrating reactive inks into photovoltaic cells, improving metallization electrical

properties, soldering to tabbing wire, reducing line width, measuring reaction kinetics, measuring metallization properties, understanding how of environment and processing parameters impact printed reactive silver inks, and developing reactive ink chemistries.

11.7 ***Ph.D. Student: Michael Martinez-Szewczyk*** *(ASU)*

Martinez-Szewczyk fabricated and characterized SHJ cells metallized using both reactive silver inks and low temperature silver pastes. Martinez-Szewczyk made intellectual contributions associated with: improving metallization performance, integrating reactive inks to photovoltaic cells, improving adhesion, improving interconnection between RSI and busbar technologies, interpreting corrosion studies, interpreting and improving damp-heat performance, and developing reactive ink processes.

11.8 ***Ph.D. Student: May Pat Nicodemus*** *(CSM)*

Nicodemus fabricated and characterized SHJ cells metallized with reactive silver inks. Nicodemus joined at the end of the project and learned the metallization processing knowledge developed by DiGregorio to ensure that the knowledge was passed on to other members.

11.9 ***Ph.D. Student: Subbarao Raikar*** *(CSM)*

Raikar made contributions at the beginning of the project. Including printing initial cells and transitioning from the drop-on-demand printer to the dispense printer.

11.10 ***Masters Student: Dylan Debruin*** *(ASU)*

Debruin investigated nickel reactive ink chemistries. Intellectual contributions included insights into the instability of nickel reactive inks and the formation of polymerizing nickely hydroxides that impede full reduction of the nickel reactants.

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