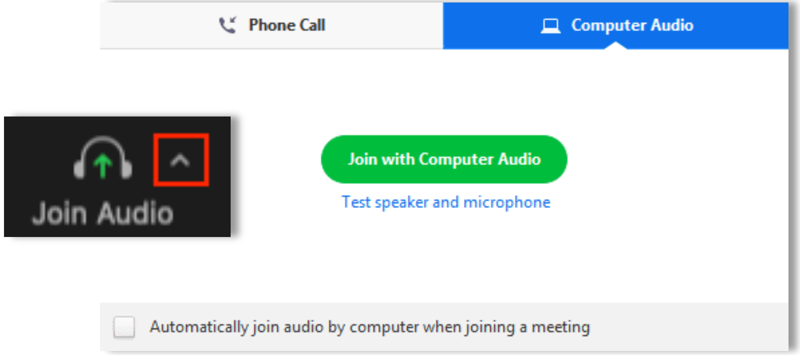
DuraMAT
Durable Module Materials Consortium

Copper Screen Printed Pastes Fired in Belt Furnace

Thad Druffel – Bert Thin Films
Paul Stradins – NREL
Ajeet Rohatgi – Georgia Tech

12th February 2024

Housekeeping - Audio

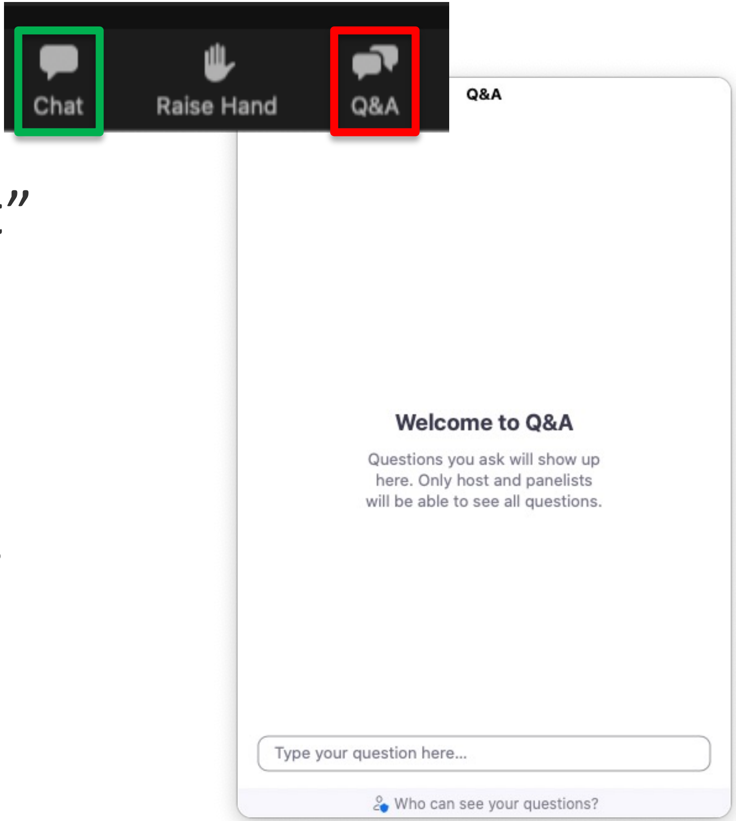


- Everyone is muted.
- Two Options for Audio:
  1. Listen through your computer:
     Click the ‘up arrow’ next to the “mute” button in the bottom left corner.
     Under “Select a Speaker,” click “Same as System.”
  2. Listen by telephone:
     Click the ‘up arrow’ next to the “mute” button in the bottom left corner.
     Click “Switch to Phone Audio.”

Housekeeping – Q&A

- Technical issues? Message the “Host” using the Chat panel.

- Have a question?
  - Please submit it using the “Q&A” panel.
  - We will answer as many questions as possible at the end of the webinar.



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Contents

Contents

The Team

Bert Thin Films – Thad Druffel (PI)

Dustin Williams, Kevin Elmer, Erin Yenney, Apolo Nambo, Ruvini Dharmadasa

Georgia Institute of Technology – Ajeet Rohatgi (co-PI)

Ajay Upadhyaya, Vijaykumar Upadhyaya

National Renewable Energy Laboratory – Paul Stradins (co-PI)

Suchsmita Mitra, Harvey Guthrie, Peter Hacke, Bill Nemeth, Steve Johnston

Bert Thin Films

- **2014** – Founded Based on Technology developed at the University of Louisville
- **2015** – Spin Out: NSF STTR
- **2019** – Investment, pivot to paste manufacturing
- **2023** – DuraMAT funding studying durability

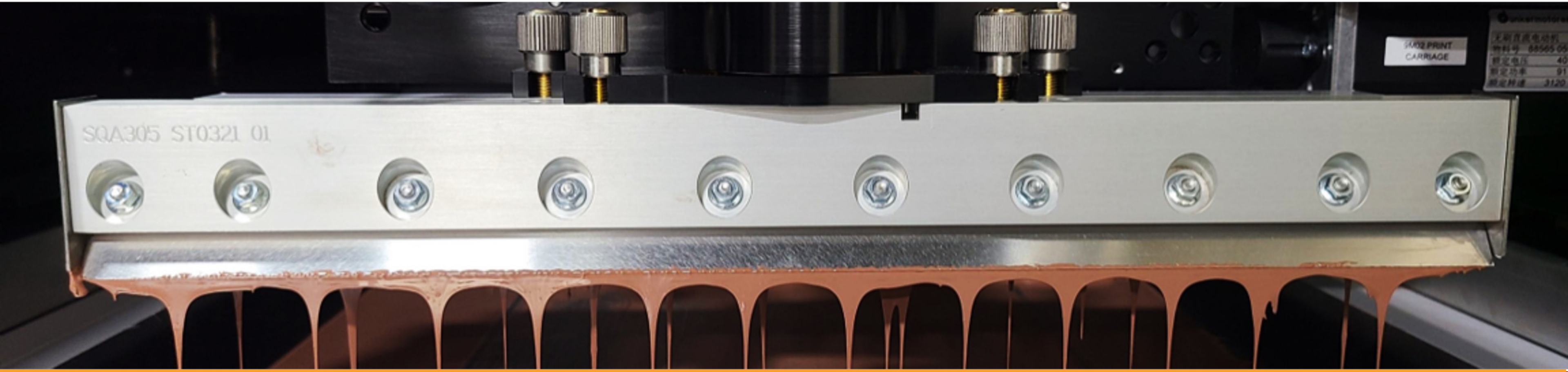
BERT THIN FILMS LLC

- 6 FTE, 2 PTE

Copper Pastes

CuBert™ Paste is a direct replacement for silver.

- Fits in with existing equipment.
- Copper is very abundant.
- 1/100th the cost of silver.
- Can be adapted to newer technologies.



Contents

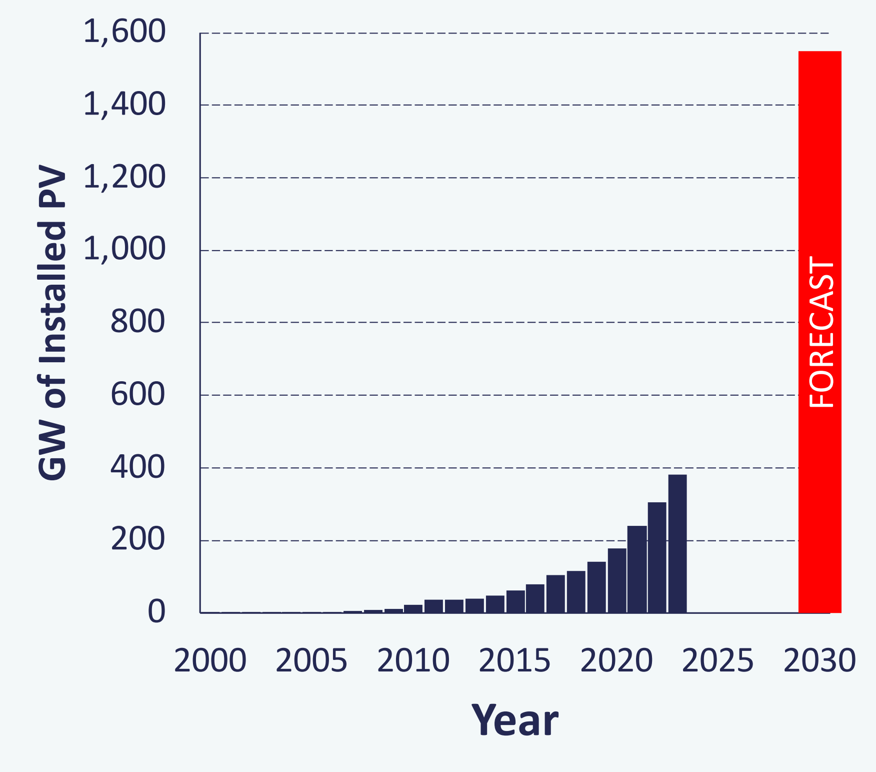
SOLAR MARKET

2022:

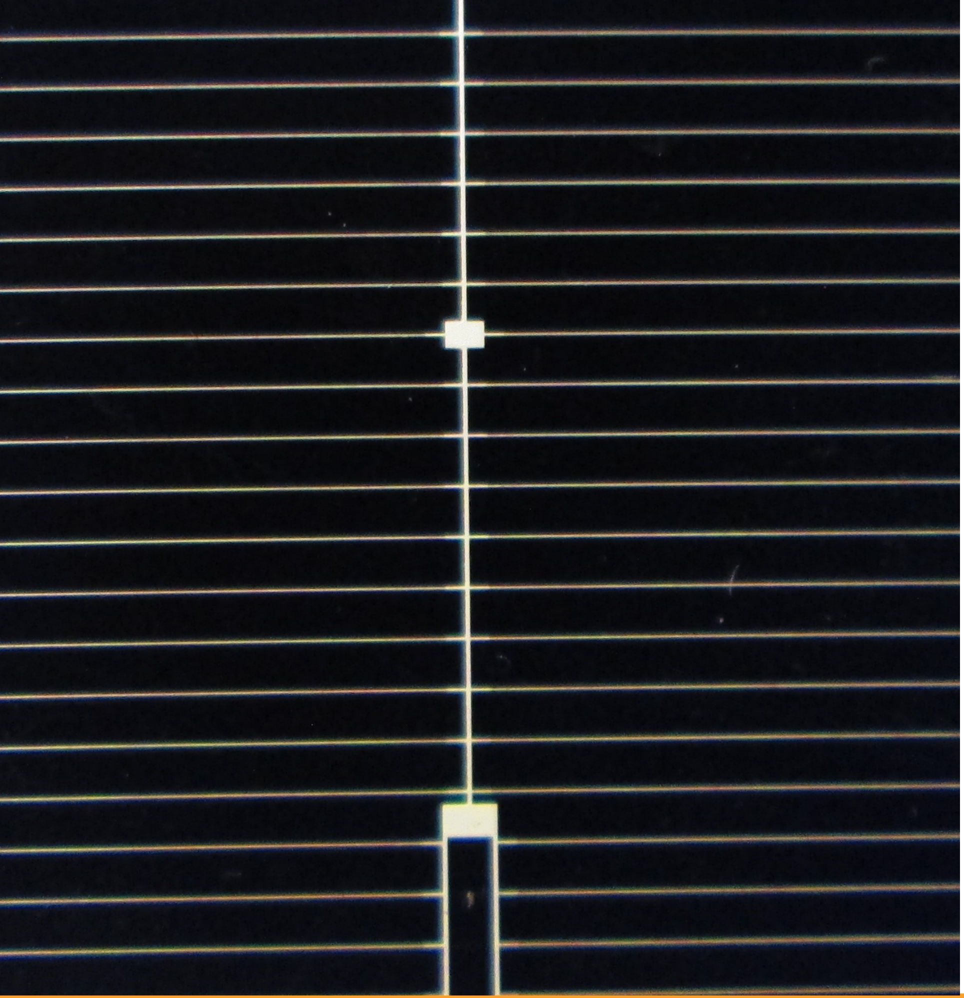
283 GW/$170B installed.

Growth:

15-20% CAGR yr/yr expected for next 5 years.



Solar manufacturing capacity since 2000.



Metallization

- Silver conducts electrons from front interface.
  - Fingers
  - Bus Bars
- Largest non-silicon cost in cell.

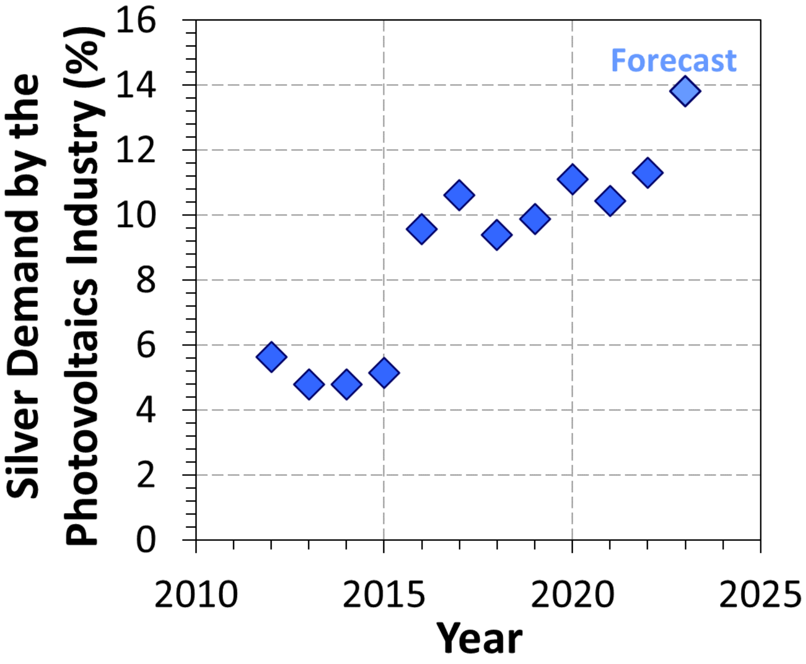
Silver DEMAND

2023: 14% of silver

Usage: TOPCon and SHJ use more silver than PERC

Technology: TOPCon is projected to take over from PERC.

2030: > 40% of total demand.

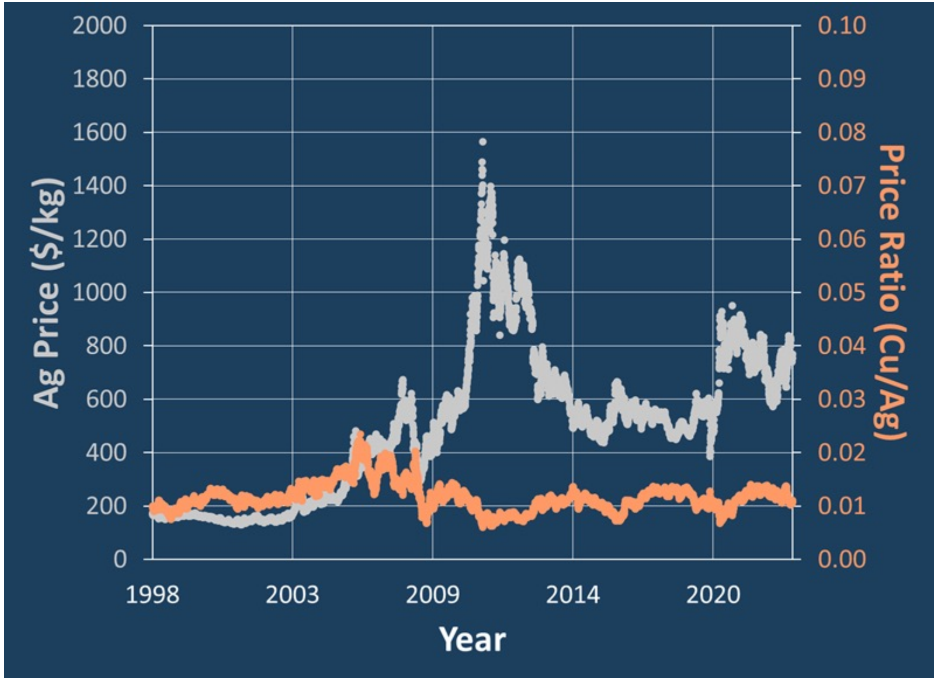


World Silver Survey 2023, The Silver Insitute

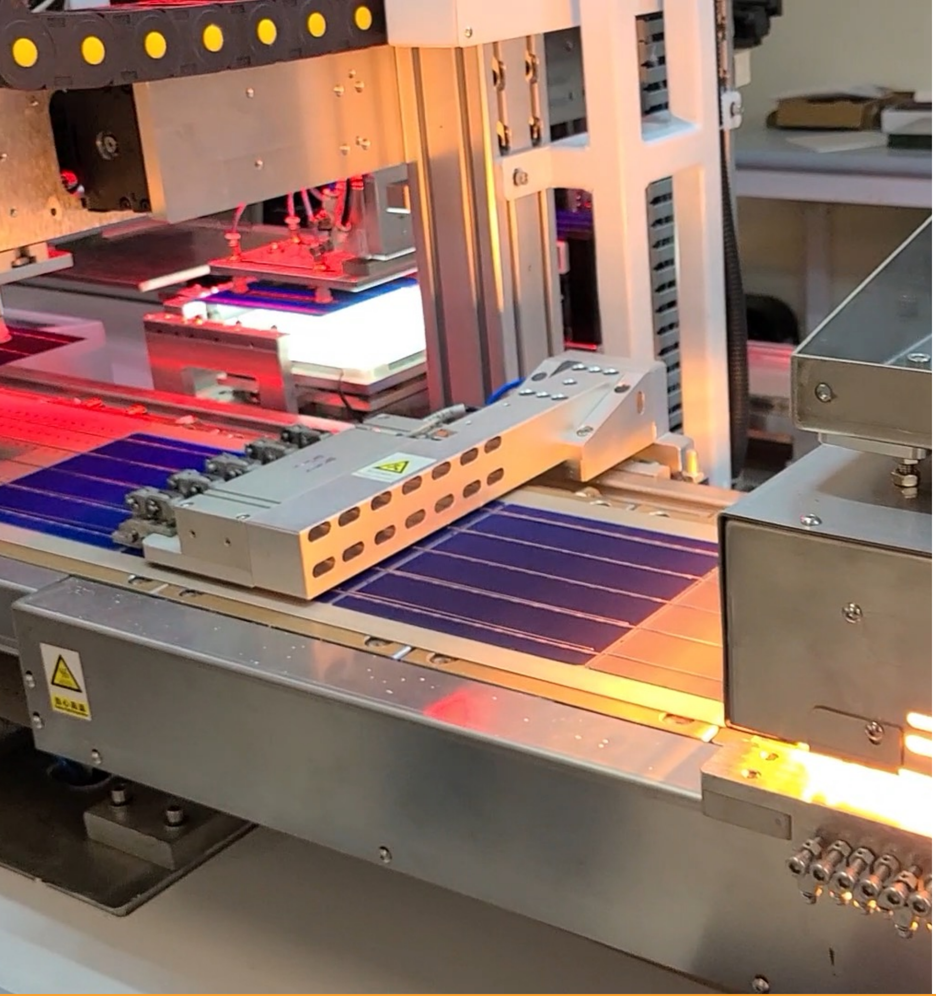
Solar's increasing demand for silver.

Silver VOLATILITY

- Price has varied from $180/kg to > $1,500/kg since 2000.
- Increase demand from solar is expected to push prices up to more than $1,000/kg .
- Copper is consistently 1/100th the cost of silver.



Price of silver (Ag) and price ratio of Copper Cu/Ag over the past 25 years.



Manufacturing

- 400 GW Global Manufacturing
- Expected > 1 Terawatt 2030
- 90% CAPEX not depreciated

Production today (and future)

  - Screen Printed
  - Fire

Need for Alternative Metallization Paste

PV and Ag

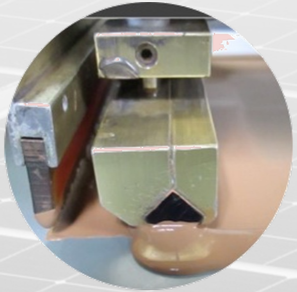
PV accounts for over 14% of global Ag

Global PV

PV production will see 10X growth

Copper

Cu is 1/100th cost of Ag and is sustainable



Screen Print

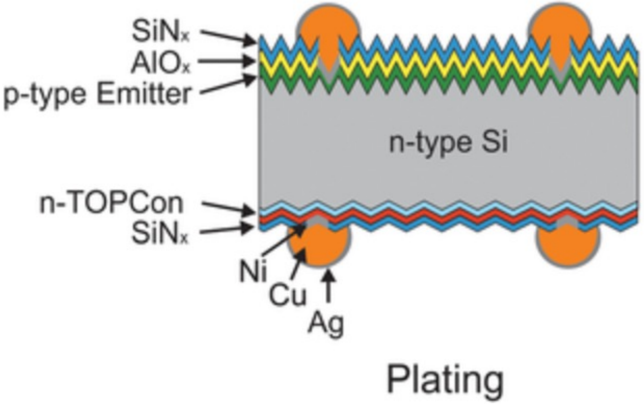
Screen printing is the default metallization

Challenges

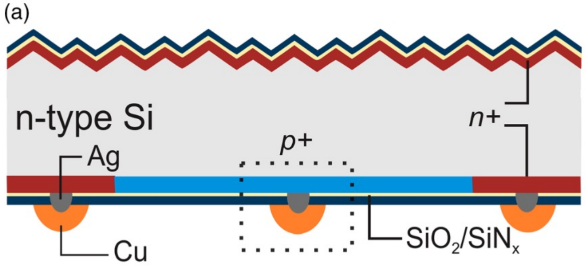
Oxidation and diffusion of Cu

Contents

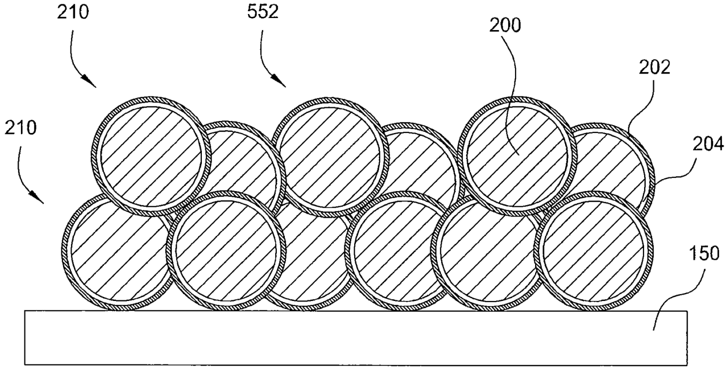
What’s been tried before



*Grübel B, Cimiotti G, Schmiga C, et al. Direct contact electroplating sequence without initial seed layer for bifacial TOPCon solar cell metallization. IEEE J Photovolt. 2021;**11**(3):1-7. doi:[10.1109/JPHOTOV.2021.3051636](https://doi.org/10.1109/JPHOTOV.2021.3051636)*



*Chen, N., D. Rudolph, C. Peter, M. Zeman, O. Isabella, Y. Rosen, M. Grouchko, O. Shochet, V. D. Mihailetchi (2023) “Thermal Stable High-Efficiency Copper Screen Printed Back Contact Solar Cells” , Solar RRL, **7**(2) DOI https://doi.org/10.1002/solr.202200874*



Gee, James, M (2011) Copper Paste Metallization for Silicon Solar Cells, European Patent EP 2 625 722 B1

Prior Work on COPPER PASTES

Cu paste

Low temperature (SHJ)

1. Dow Corning[1,2]
   - Polymer paste comprising Cu and SnBi/SnAg solder particles
   - To be used in combination with Ag fingers for printing busbars without a firing-through step

2. National Institute of Advanced Industrial and Scientific Technology (AIST)[3]
   - polymer paste containing low melting point alloy (LMPA)

3. Samsung Electro-Mechanics Co., Ltd
   - Average particle size~150 nm
   - Capping material~fatty acid or fatty amine

4. Institute of Nuclear Energy Research (INER), Taiwan[4]
   - Antioxidant copper nanoparticles are synthesized by a wet chemical reduction process , which is transferred to paste form

5. Toyota Technological Institute, NAMICS Corporation[5]
   - Ag coated Cu paste

6. Copprint Technologies Ltd. [6]
   - Busbars of ISC's Zebra™ solar cell

High temperature (PERC, TOPCON)

1. Bert Thin Films[7,8]

2. Applied Materials, Inc.[9]

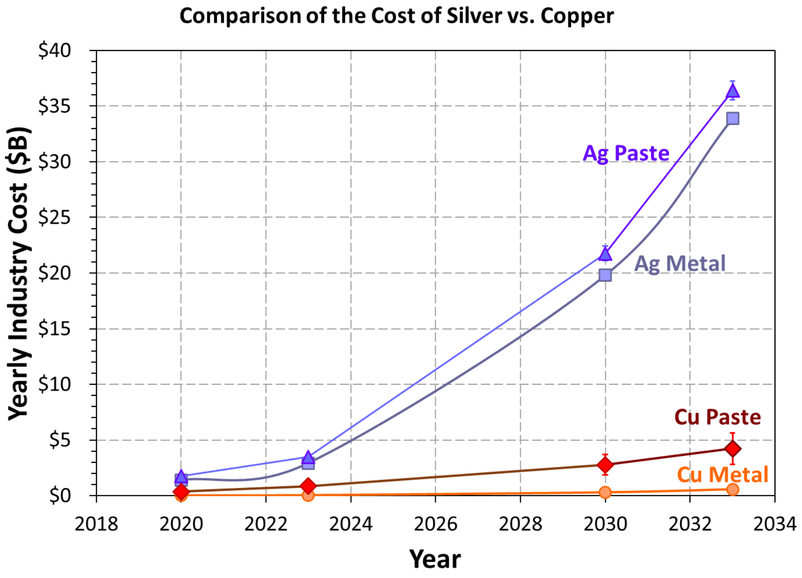
Review and Cost

Key Results

- Review of prior copper metallization including plating and low temperature firing.
- Information related to durability testing.
- Includes top-level cost analysis.

Core Objective & Teaming

- Brought team focus on copper diffusion.
- Effort lead by NREL.
- Input from BTF and GIT.
- Aggregated data on Teams site.



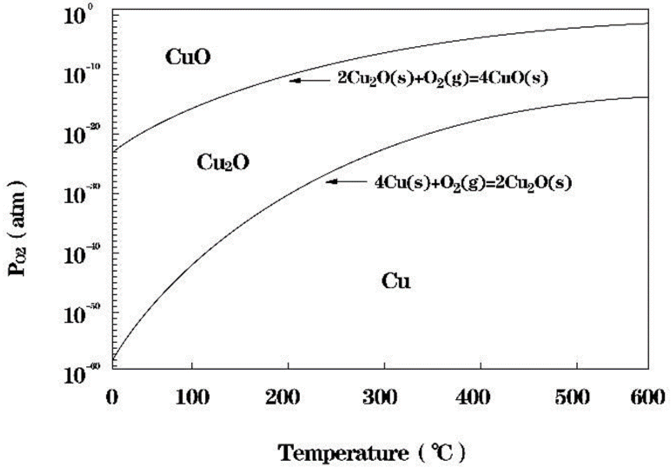
Cost projections of base metal (Ag and Cu) as well as copper pastes.

Contents

Why Not Copper Paste?

- **Oxidation:** Reduces conductivity.
- **Diffusion:** Can destroy the device.

Thermodynamic phase transition diagram of Cu to Cu_2O or CuO.



Shang, Shengyan & Kunwar, Anil & Wang, Yanfeng & Yao, Jinye & Ma, Haitao & Wang, Yunpeng. (2018). Influence of Cu nanoparticles on Cu 6 Sn 5 growth behavior at the interface of Sn/Cu solder joints. 10.1109/ICEPT.2018.8480619.

Diffusion of metals into silicon.

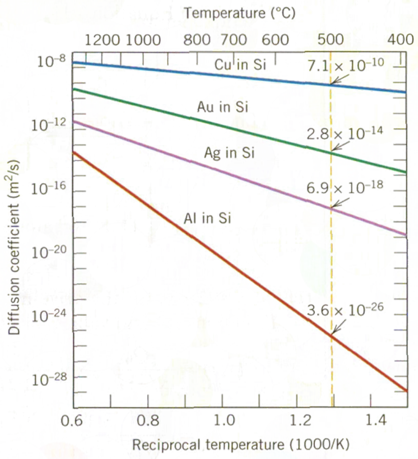
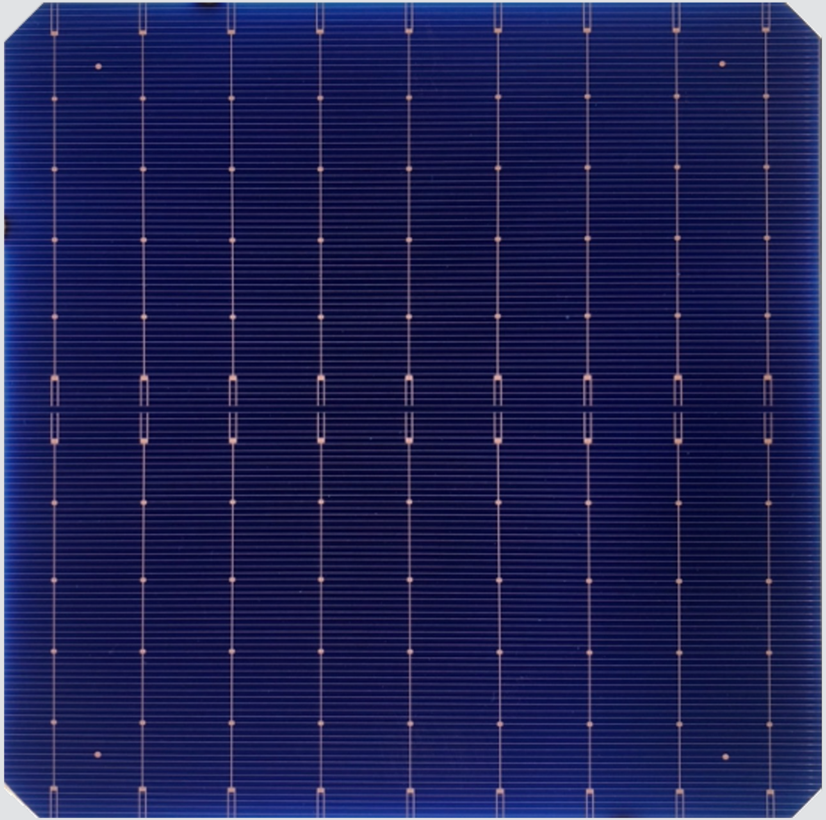


Figure 7.12 Logarithm of D-versus-$1/T$ (K) curves (lines) for the diffusion of copper, gold, silver, and aluminum in silicon. Also noted are D values at 500°C.

Callister, W.D., Rethwisch, D.G., Materials Science and Engineering, 9th Edition, 2014, John Wiley and Sons



CuBert™

Screen Printable with the same printing technology used in the industry.

Air Fired in the same belt furnaces used in the industry.

Etches through silicon nitride coating.

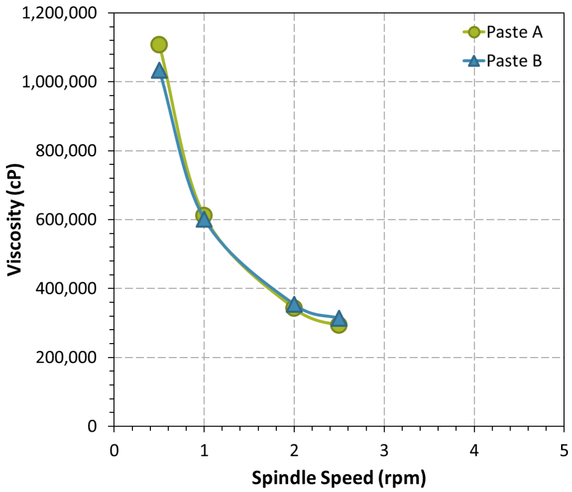
No Additional diffusion barriers.

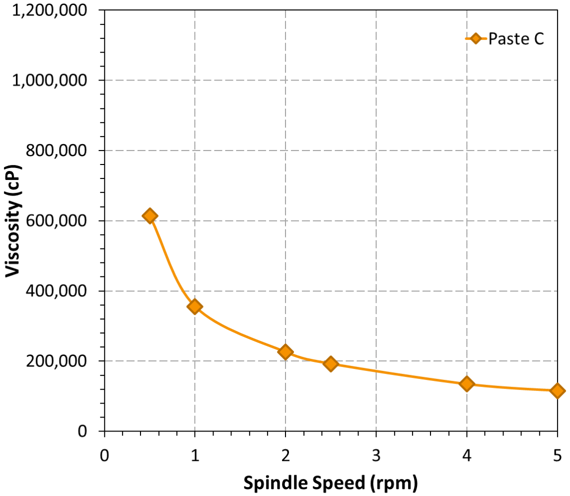
No changes to processing.

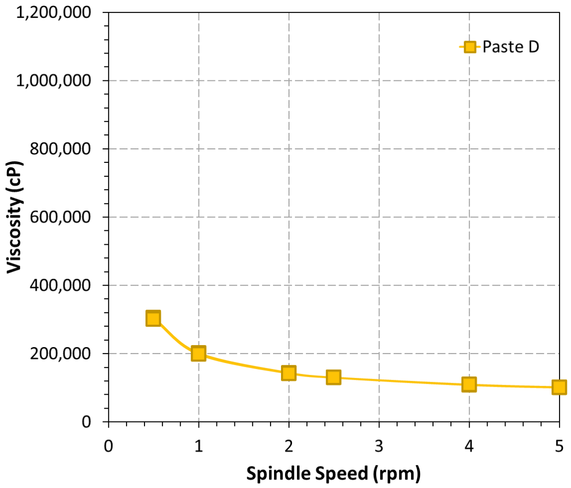
No new equipment to add.

Rheology

Rheology is controllable and is being optimized for fine line printing (< 30 µm).



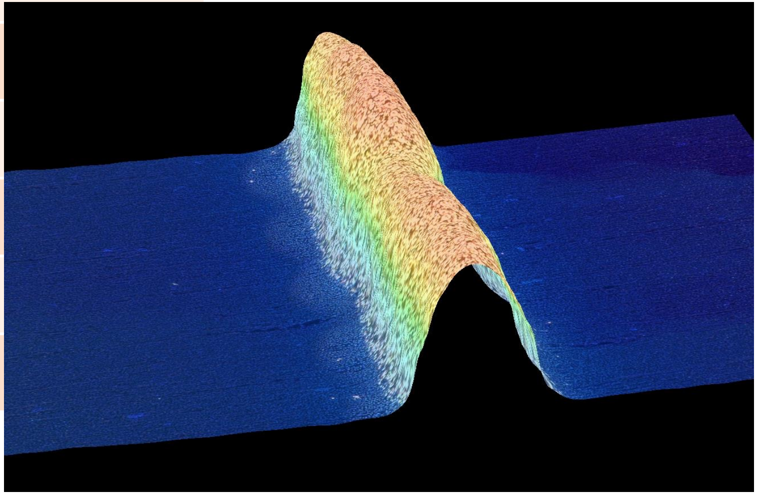




Screen printing

Fine line screen printing using screens employed in industry.

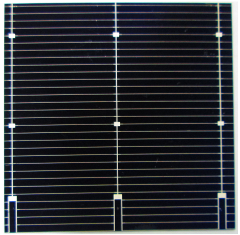
Screen Parameter	Value
Mesh	400-500 mesh, 18 µm wire
Screen tension	16-19 N/cm
Emulsion thickness	12-20 µm
Print gap	1.2-2.0 mm
Print speed	75-150 mm/s
Squeegee pressure	6-10 kg
Squeegee durometer	70-80

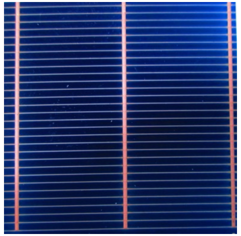


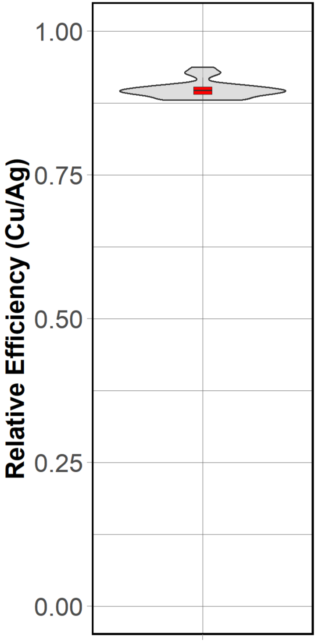
Prior Results

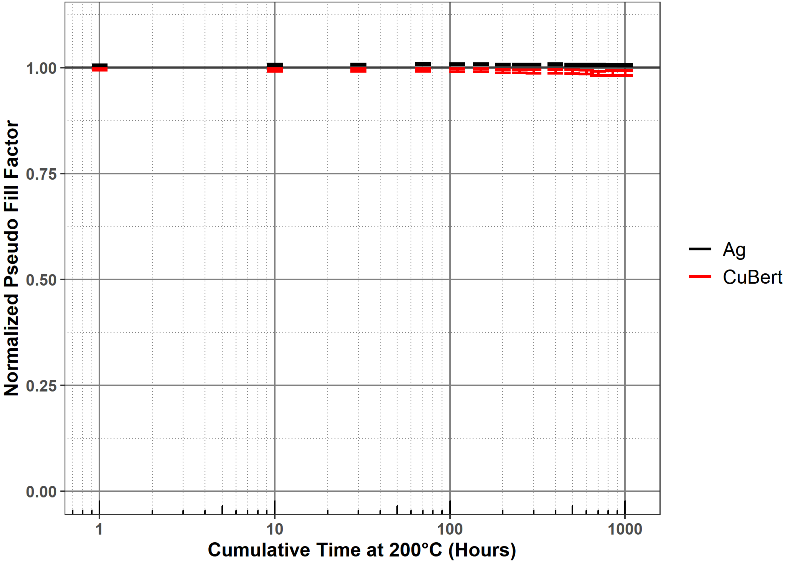
16 cm^2 PERC Sections: Performance and Durability

Silver vs. Copper paste metallized PERC cells. (50 sections)









Dry heat studies used to study the performance of the inherent diffusion barrier.

Aim of DuraMAT Project.

- Identification of degradation pathways.
- Optimization of formulations and processing windows.
- Create a durable module with CuBert™ metallized silicon cells.

Contents

BERT THIN FILMS LLC → Georgia Institute of Technology → NREL NATIONAL RENEWABLE ENERGY LABORATORY

Formulation & Printing → **Firing & Initial Measurements** → **Characterization & Encapsulation**

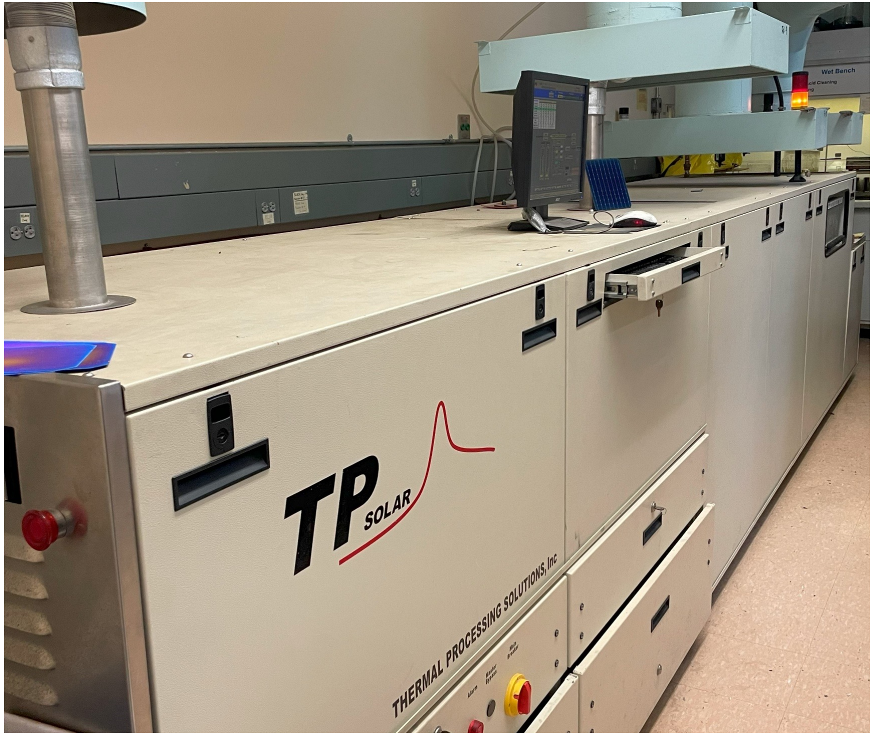
BTF Prints

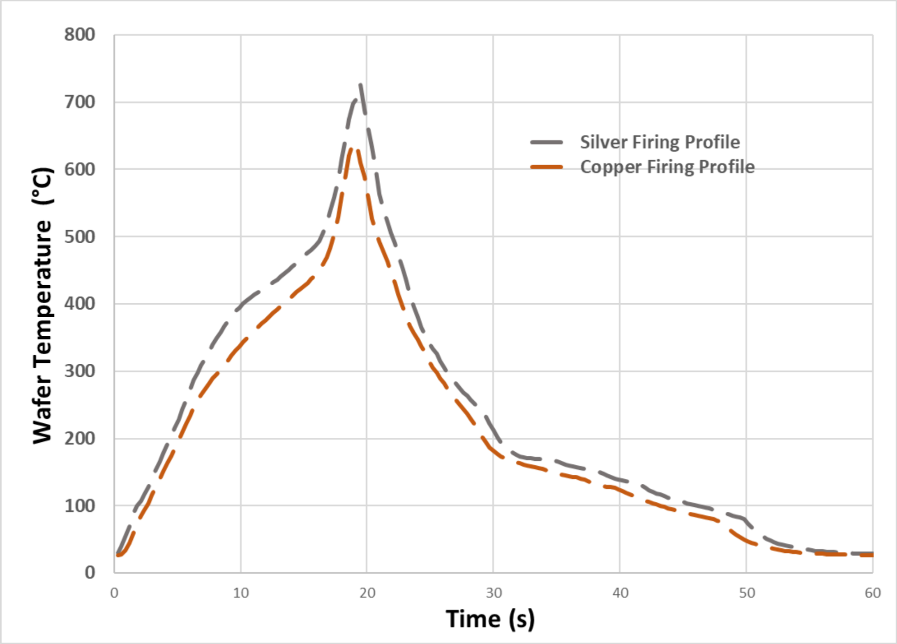
Set 1 (May 2023): **125 cells, 5 pastes**
- Fired at 590, 610, 630 °C peak wafer temperatures.

Set 2 (September 2023): **54 cells, 2 pastes**
- Fired at 604, 611, 622, 633 °C peak wafer temperatures.

Set 3 (November 2023): **200 cells, 2 pastes**
- Fired at 620, 630, 640 °C peak wafer temperatures.

Firing





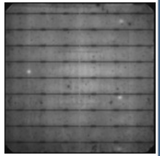
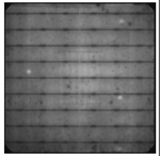
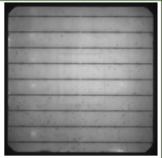
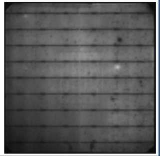
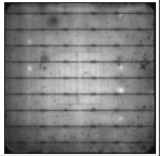
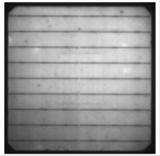
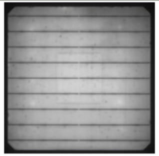
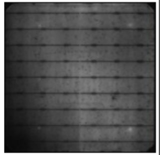
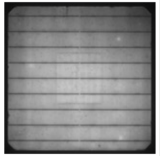
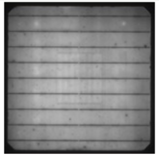
- Example of firing profiles for cells at Georgia Tech.

Firing Optimization

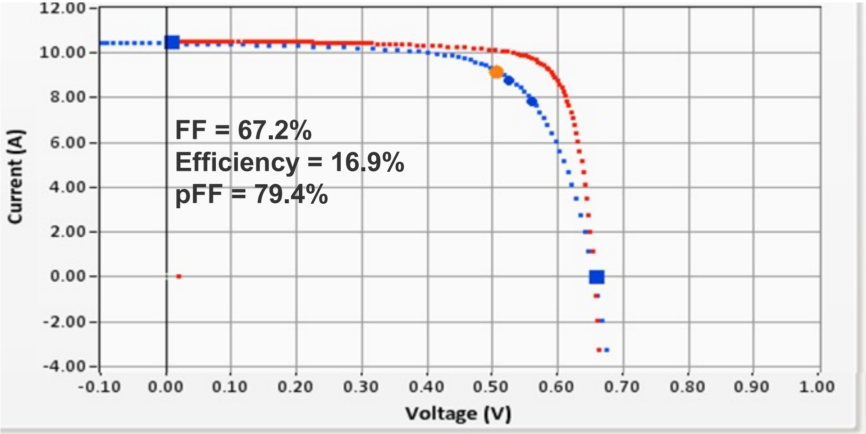
- Firing at GIT.
- Photoluminescence imaging at NREL.

Changes from Set 1 to 2:

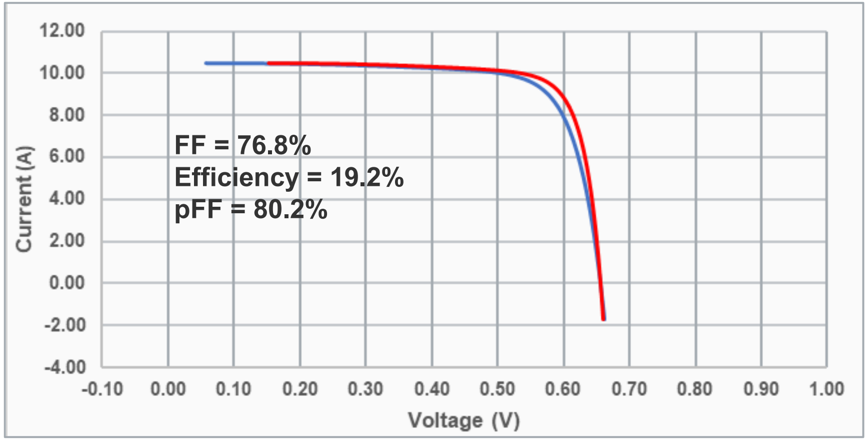
- Set 2 used a homogeneous emitter to avoid misalignment between the printed fingers and the selective emitter.
- Optimization of the furnace settings for the rear aluminum and front copper contacts.

	Set 1			Set 2	
	Paste E	Paste B		Paste E	Paste B
590°C	pFF = 81.1% 	pFF = 81.9% 	604°C	pFF = 81.6% 	pFF =82.5% 
610°C	pFF = 80.1% 	pFF = 82.8% 	611°C	pFF = 82.0% 	pFF = 82.5% 
630°C	pFF =73.3% 	pFF =78.2% 	622°C	pFF = 80.9% 	pFF = 81.5% 
			633°C	pFF = 79.0% 	pFF = 81.4% 

Firing Optimization



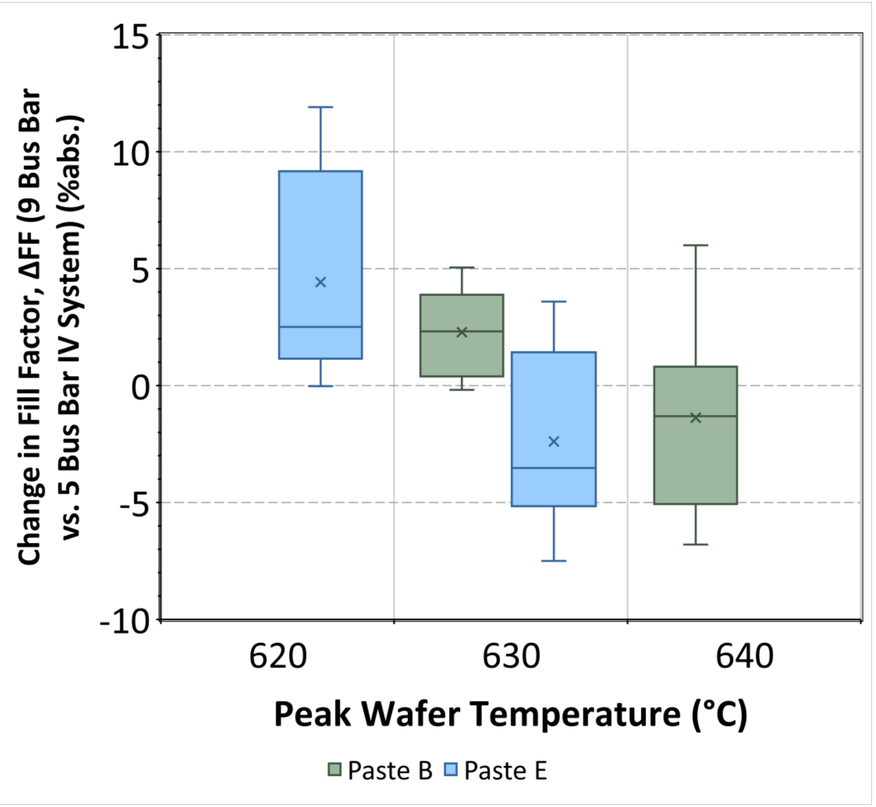
Set 1 Champion Cell



Set 3 Champion Cell

Issues

- Firing non-uniformities remain.
- Cells manually handled a lot.
- 9 busbars printed, but 5 busbar IV system used to dial in processing.



- **Cells 5 Bus Bar IV system measured the same week as firing.**
- **9 Bus Bar IV system measured ~2 months after firing.**

Contents

DuraMAT Tasks

- Damp heat testing to study the impact of the formulation and process on:
  - Diffusion
  - Oxidation

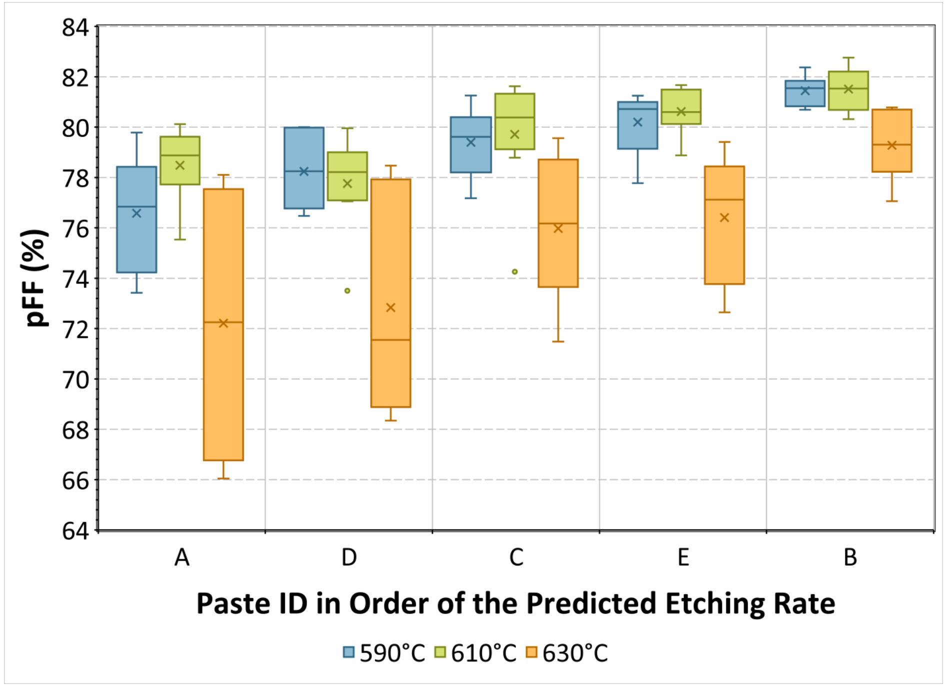
Task	Description	Deliverable
Initial	Baseline deliverable, fired cells using current paste formulation	100 cells
1.0	Review of prior studies	PPT review
2.1	Formulation and process	100 cells

Baseline

Initial cells:

- M6 sized PERC cells.
- 5 formulations with varying etching rates.
- 3 firing conditions.

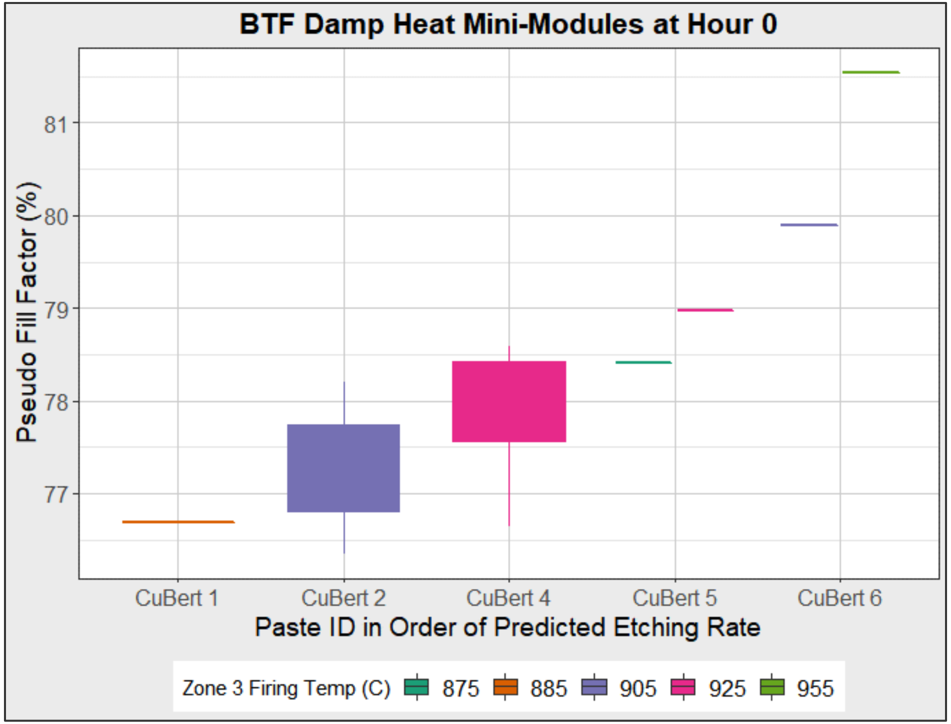
Cells were used to optimize firing conditions and narrow down formulations.



Pseudo Fill Factor (pFF) of 100 cells printed at BTF and fired at GIT.

Mini-Mini Modules

- Set 1.
- 16 cm^2 PERC cells printed and fired at BTF.
- **Structure:** Glass/TPO/Backsheet.
- **Rear:** Sn60Pb40 coated copper ribbons soldered to the rear silver tabs.
- **Front:** Smart Wire Connection Technology. (Sn42Bi57Ag1 coated copper wires connected to the copper metallization).



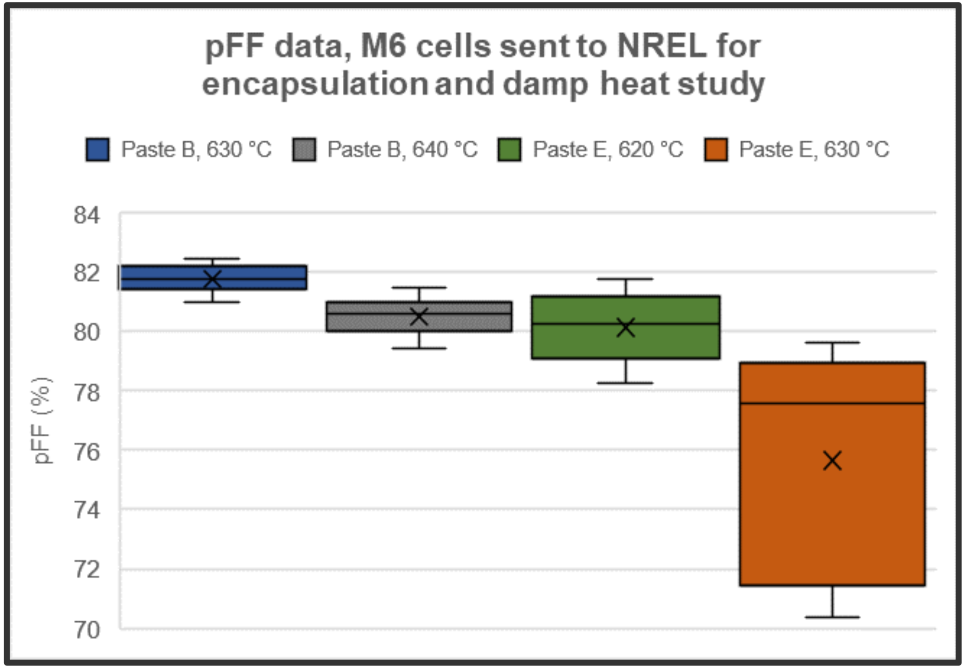
Mini-mini modules prepared and tested at BTF.

Set 3, Dec 2023

M6 Sized PERC Cells:

- 200 cells printed and fired.
- 2 formulations: Varying etching rates to force over-etching.
- 40 cells using two firing conditions (paste dependent) sent to NREL.

Cells are currently being measured and encapsulated by NREL.

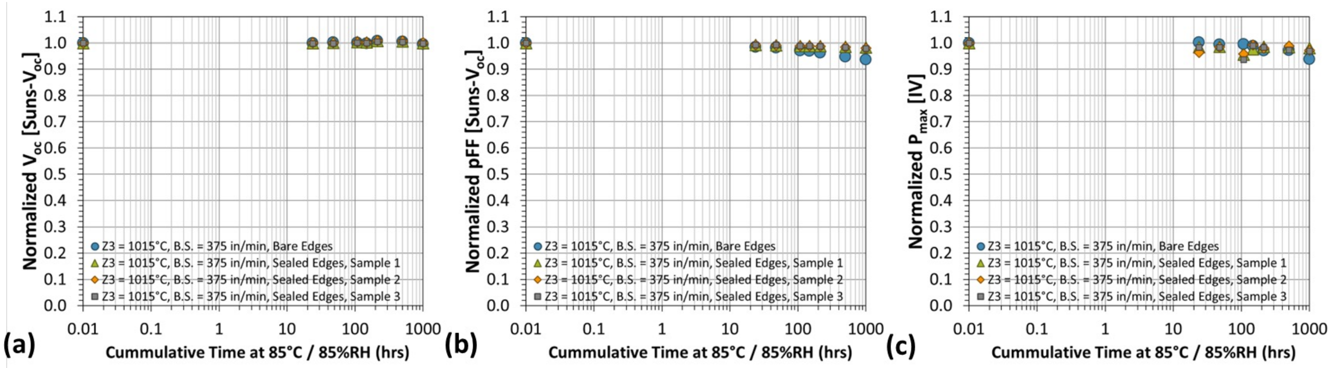


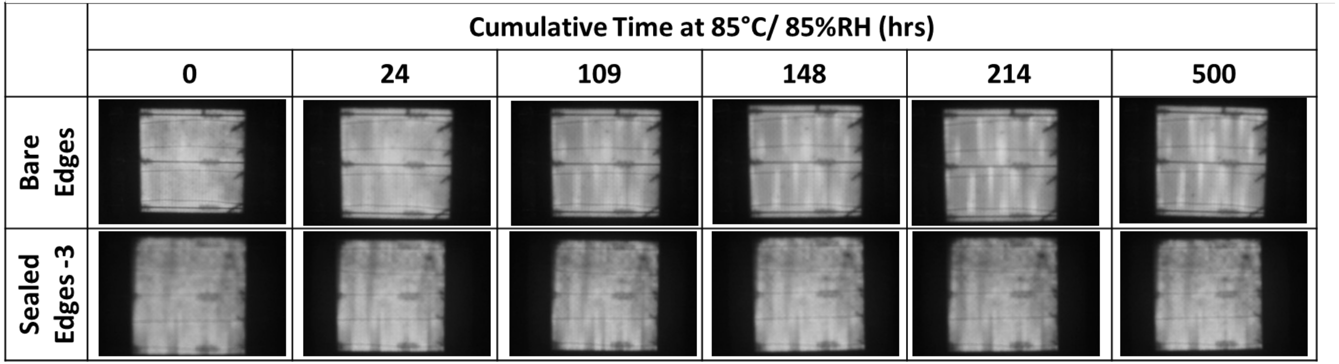
pFF of 40 cells printed at BTF, fired at GIT and sent to NREL for encapsulation.

Mini-Mini Module: Damp Heat Results, Set 2.

Damp Heat Tests at BTF.

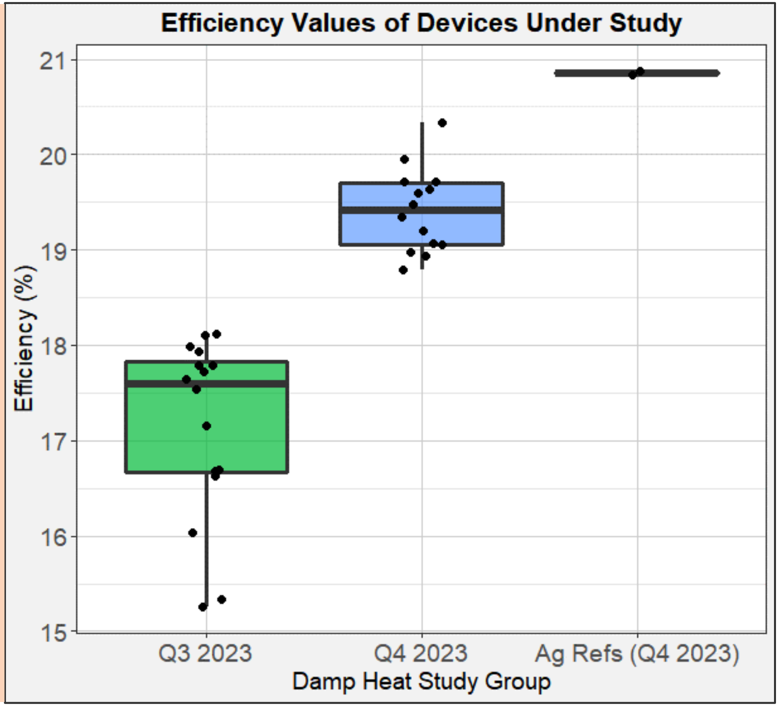
- **Structure:** Glass/TPO/Glass.
- Cracking at edges impacted pFF values.





Efficiency Improvements

Mini-Mini Modules



16 cm^2 PERC Cells

IMPROVEMENTS:

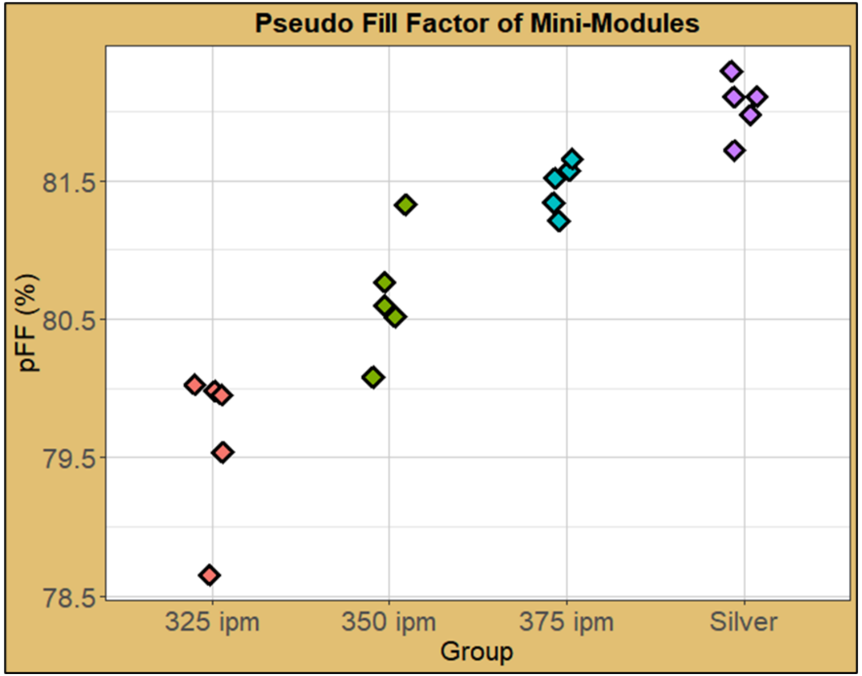
- Formulation / Printing.
- Firing Optimization.
- Interconnection Improvements.

Mini-Mini Modules, Dec 2023

Fifteen mini modules sent to NREL:

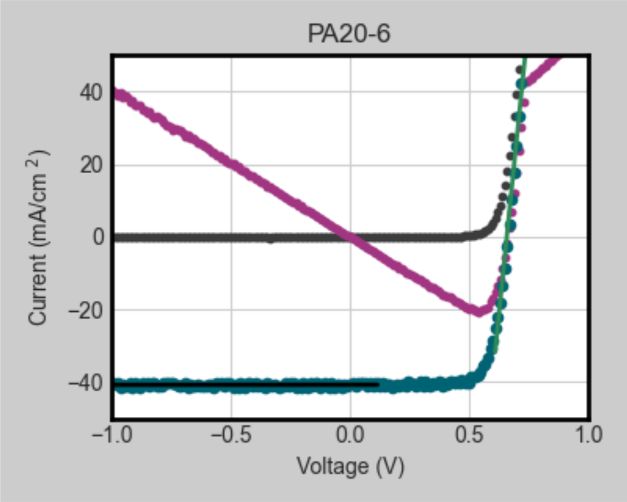
- 16 cm^2 PERC cells.
- 1 Cu paste formulation.
- 3 firing conditions used to vary the etching rate to study failure modes.
- **Structure:** Glass/TPO/Glass.
- **Rear:** Sn60Pb40 coated copper ribbons.
- **Front:** Smart Wire Connection Technology. (Sn42Bi57Ag1 coated copper wires).
- **Edges:** PIB desiccated sealant.
- Silver metallized cells printed and fired by the manufacturer of the wafers was also encapsulated and tested.

Modules are currently undergoing damp heat testing at NREL.



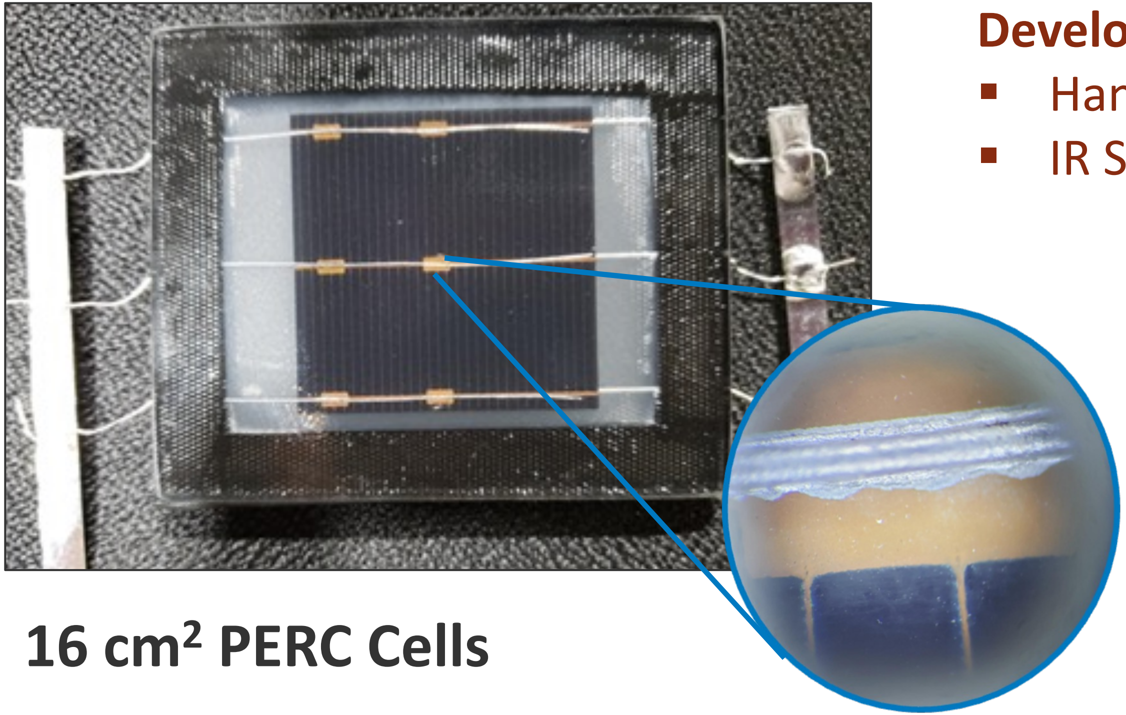
Initial pFF measurements of encapsulated mini-mini modules.

2024: Mini-Mini Module Improvements Leading to Efficiency Increases.



Cell ID	Voc	Jsc	FF	Eff	Vmax	Imax	Pmax	Rs	Rsh	Area	Points	NPLC	App Ver
Ag5-10 G(	0.6542	41.95	0.7993	21.94	0.5377	40.799	21.94	1.32	-5657.2	15.6	200	0.01	1.1
PA20-6	0.657	40.72	0.7695	20.59	0.5377	38.285	20.59	1.54	39938.43	15.6	200	0.01	1.1

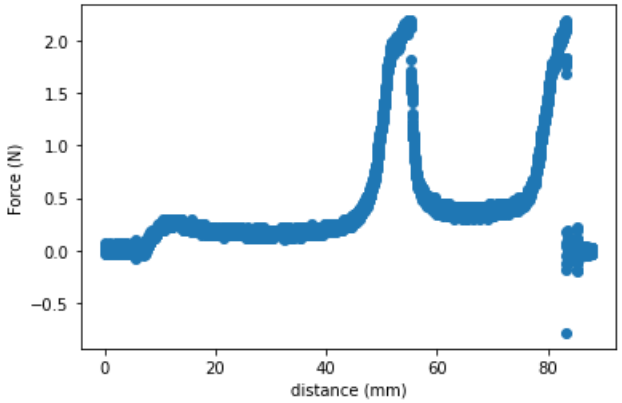
Soldering



16 cm^2 PERC Cells

Development of Copper Pastes:

- Hand Soldering.
- IR Soldering.



Contents

Future Work

- Encapsulation of cells at NREL.
- Damp Heat / Dry Heat testing.
- Material characterization of the Interface.
- Solderable M6 sized cells.

Conclusions

- Demonstrated screen printed and air-fired copper pastes.
- 1,000 hours damp heat results on mini-mini modules show durability of the copper contacts.
- Copper pastes were shown to be a viable and less expensive metallization alternative.

DuraMAT
Durable Module Materials Consortium

Thank You

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