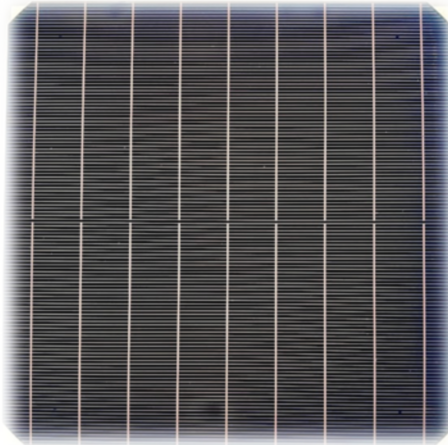
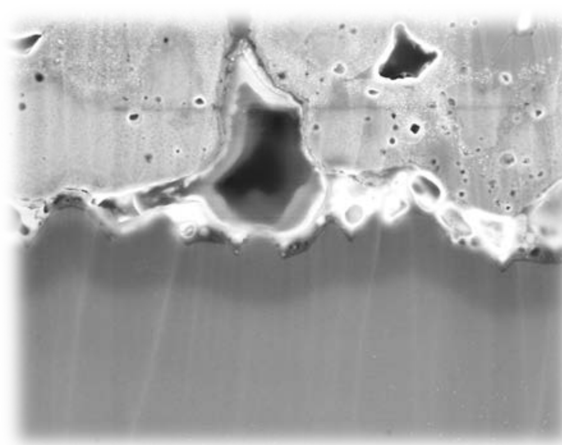
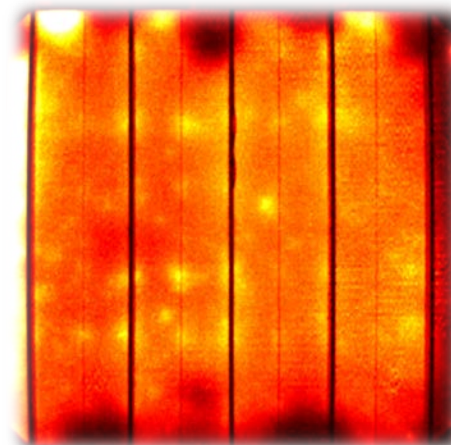

Evaluating the performance and reliability of screen-printable fire-through copper paste on PERC solar cells

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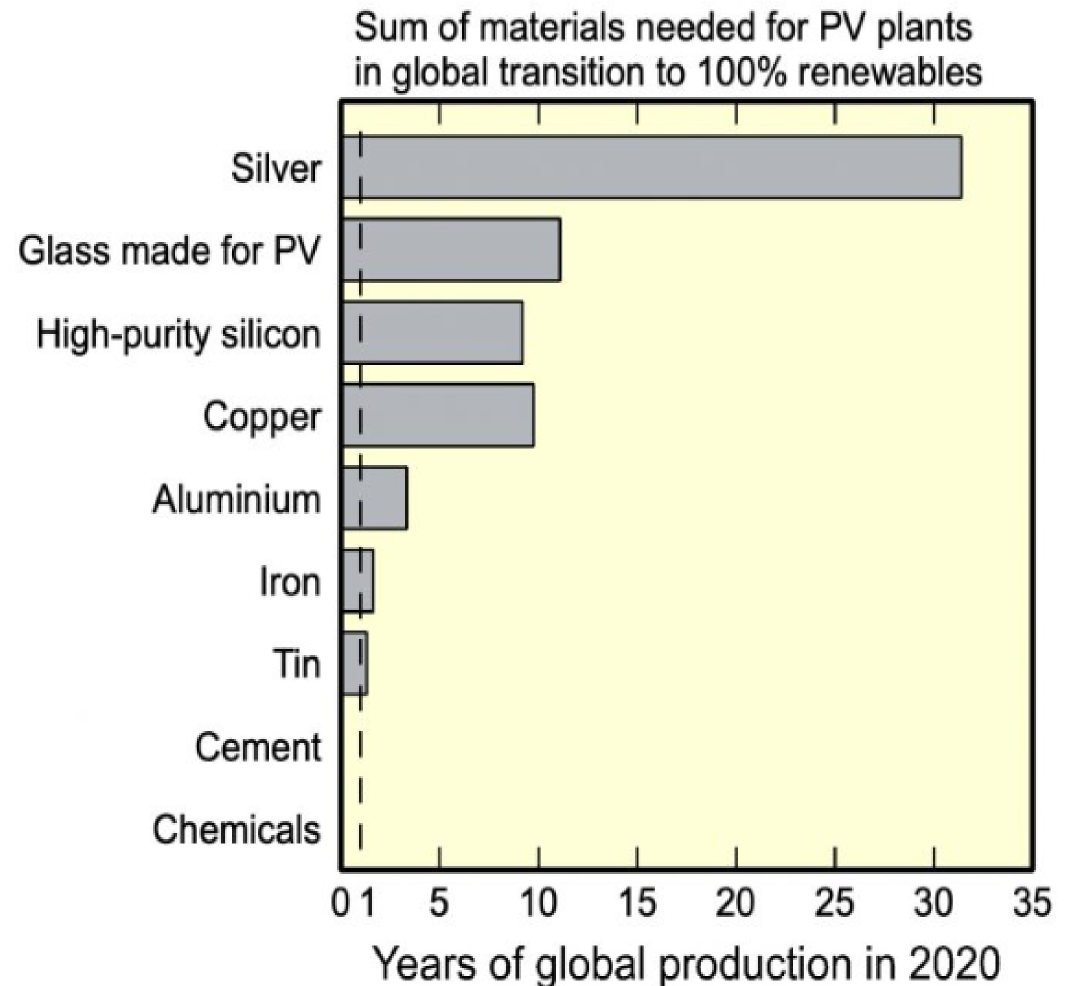
[3]Georgia Institute of Technology, Atlanta, USA

14th Silicon PV 2024, France

Motivation

- Silicon PV is responsible for >170 GW of renewable energy
- 40 TW of energy needed for transition of our planet to 100% renewables
- Global production for Ag needs to continue for the next 30 years for global transition to 100% renewables.

Silver is the most-expensive non-silicon material used in current c-Si technologies



https://www.changeanyway.com/is-solar-electricity-sustainable/

Why do we need an alternative material?

A bifacial Silicon Heterojunction solar cell demands ~210 mg usage of silver paste (9 busbars, 24.5%, bifacial, M6 size wafer)

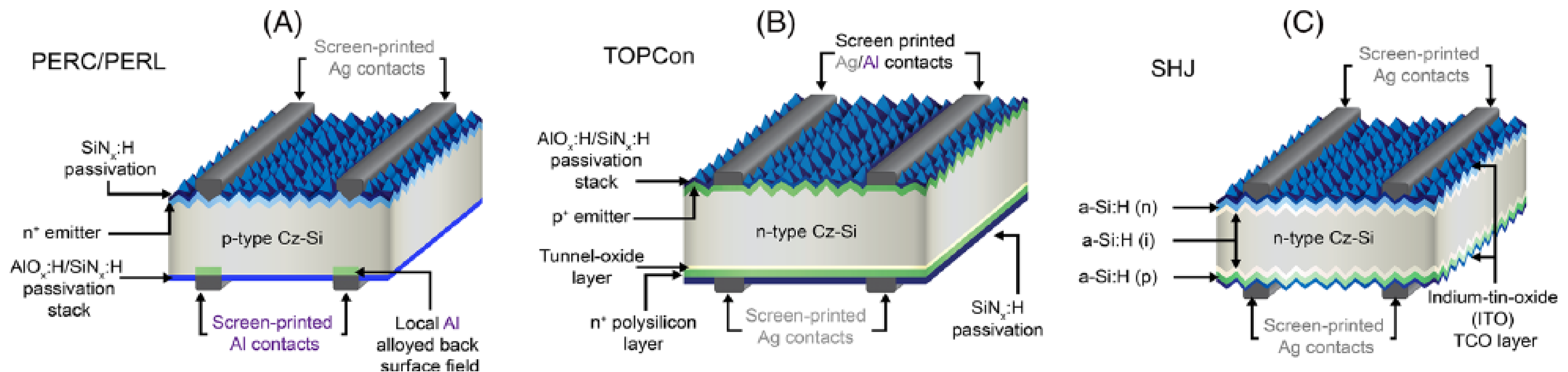
Copper (Cu) is an excellent alternative to Ag

- ☑ 100 times cheaper than Ag
- ☑ Exhibiting similar electrical resistivities
  - (ρ_{Ag}=1.6 μΩ·cm; ρ_{Cu}=1.7 μΩ·cm)
- ☑ 1000x more abundant

Silver consumption in solar cells and modules

Parameter (unit)	PERC	TOPCon	SHJ
Silver consumption per cell (mg/cell)	90.1–96.1[2]	130–162.6[2,38]	198–242[2,39]
Typical module power, 144 × half-M6 cells (W)	440–450[2,40]	450–460[2,40]	465–470[2,40]
Silver consumption at module level (mg/W)[a]	14.4–15.7	20.4–26.0	30.3–37.4

Note: Cell format is assumed as M6 (166 × 166 mm).
[a]Silver consumption is based on silver consumption per cell × 72 cells over the typical module power.



Ref: Hallam et al., *Progress in Photovoltaics: Research and Applications* 31, no. 6 (2023): 598-606.

Electroplating or Screen Printing?

*Electroplating is the most common technique for **copper** metallization on silicon solar cells!*

-Highest efficiency achieved for copper plated bifacial SHJ cell C. Yu et al., Nature Energy 8, 1375 (2023)

- 26.41% (certificated by ISFH)
- M6 size wafer (274.5 cm2)

-Challenges in electroplating:

- Plating process, waste
- Copper-induced degradation
- Reliability

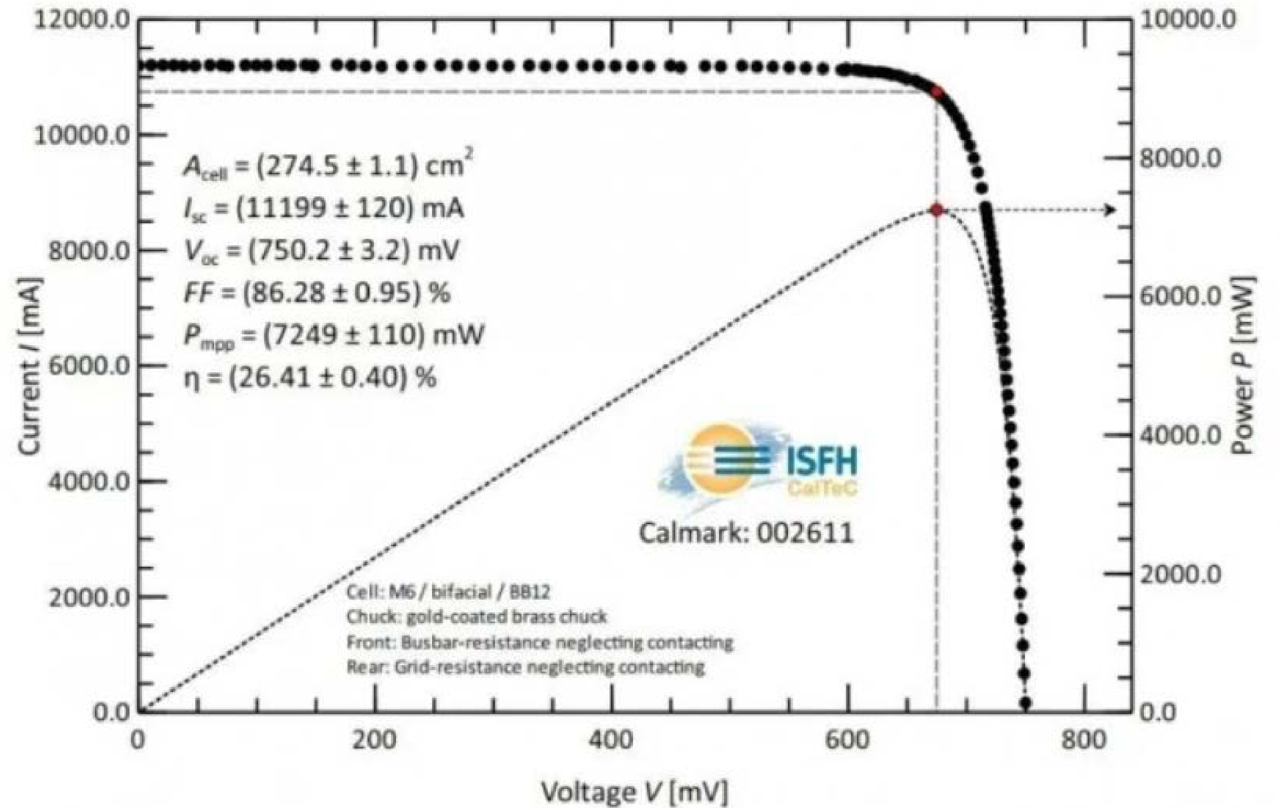


Fig. Measured IV characteristics under standard test conditions

Screen printing is the most dominant metallization technology (>95%) for c-Si solar cell mass production and will continue to be the mainstream metallization technology

Challenges in preparing Cu paste

Pastes include

- Metal powders: For metallization
- Glass frits: To etch through the ARC
- Organic binders and solvents : For processability of the pastes.

Firing of pastes need high temperatures (>600 °C)

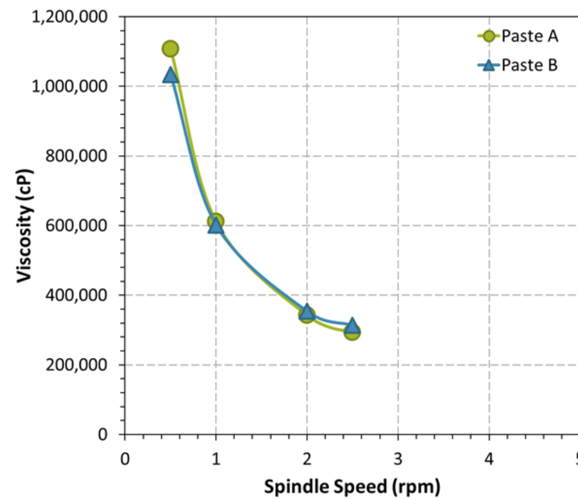
- To remove the organics,
- To etch the ARC
- To sinter the metals.

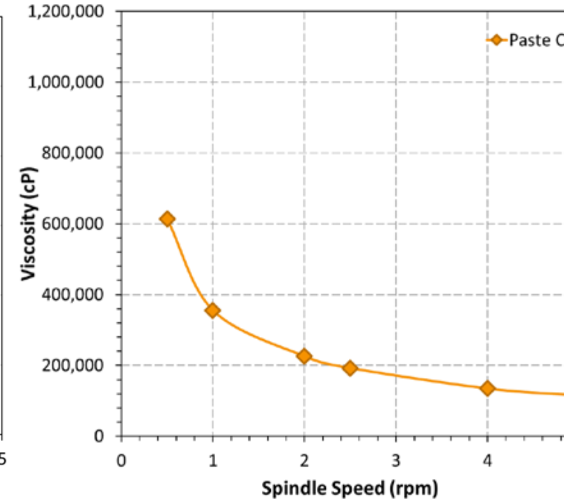
At high temperatures

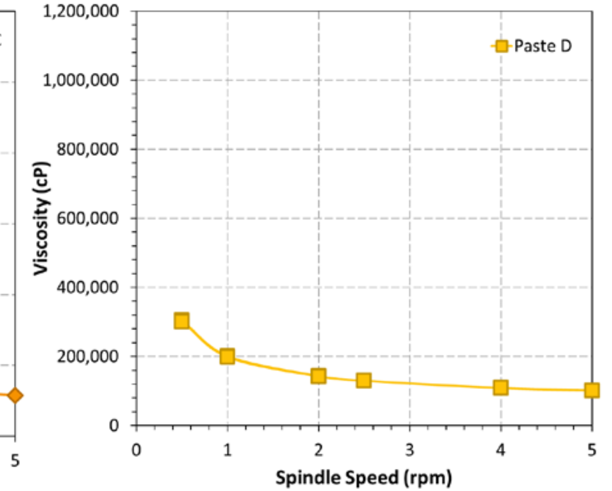
- Copper can oxidize leading to high resistivity
- Copper can diffuse into Si and cause deep level impurities
- **Need of Cu diffusion barrier: laser ablation, deposition, silicide barrier formation, etc. ?**

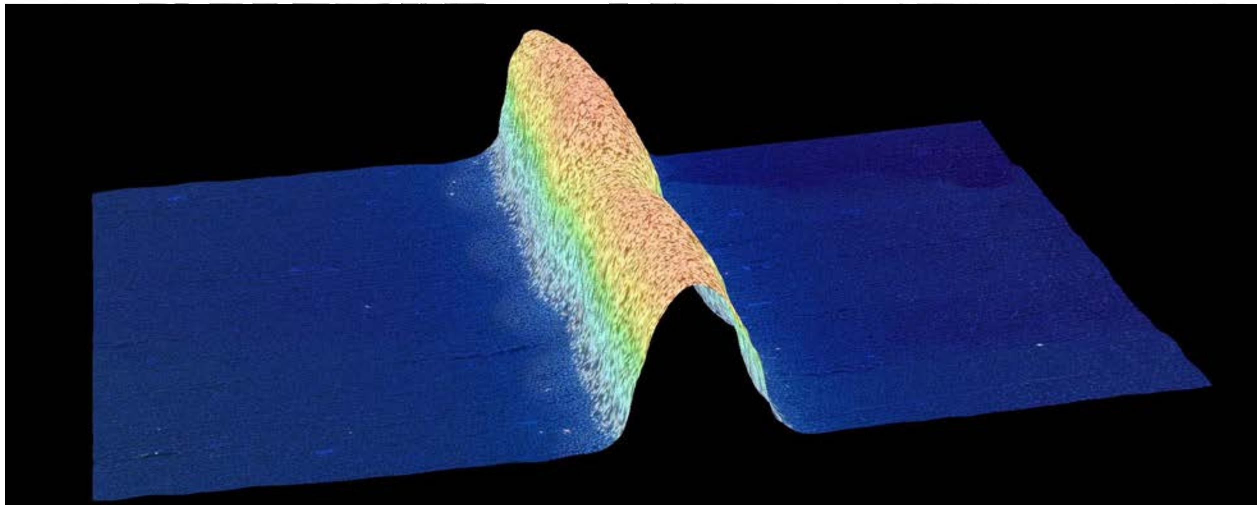
Rheology of Copper Paste

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









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

PERC Cells with **fire-through Cu paste** by Bert Thin Films

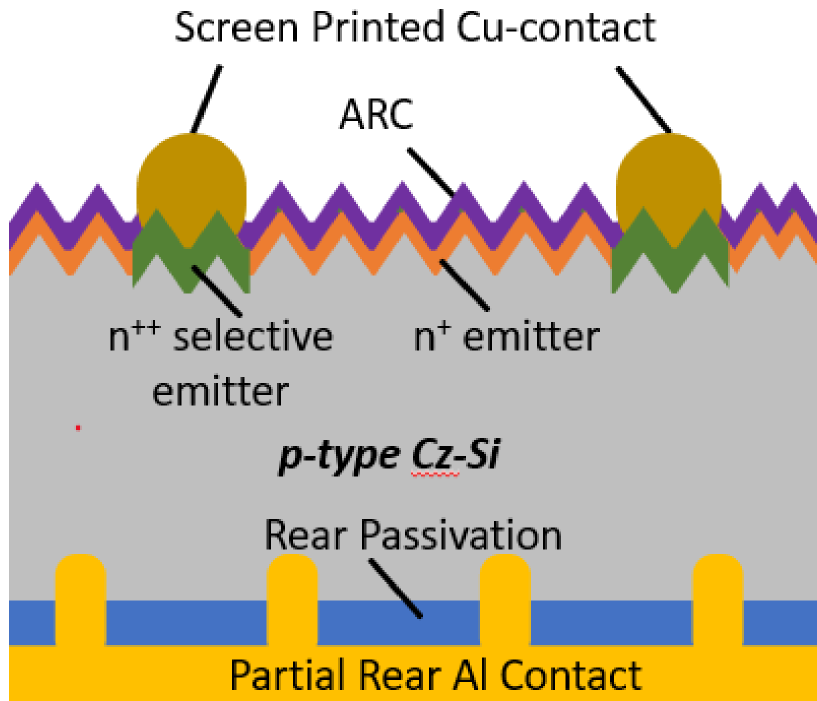


Fig. Schematic Structure of selective emitter PERC Cell

Table: Details of cell structure

Parameter	Selective Emitter	Homogeneous Emitter
Cell Size	166x166 mm^2 (M6)	166x166 mm^2 (M6)
SiNx thickness	70-80 nm	70-80 nm
Emitter Sheet Resistance	150-160 Ω/□	70-80 Ω/□
Selective Emitter	SE 110-120 Ω/□	none
Backside Condition	Polish + laser opening Al print/AgAl print	Polish + laser opening Al print/AgAl print
Busbar Number	9	9
Width of Finger Pattern	65 µm	55 µm
Width of Bus Bar Pattern	0.45 mm	0.45 mm

Firing process

- *Al contact at rear side is printed, dried and fired*
- *Cu paste is printed and dried*
- *Front Cu contact fired (peak temperature varied between 550°C to 630°C)*

Early Studies on Contact Formation (16 cm^2 devices)

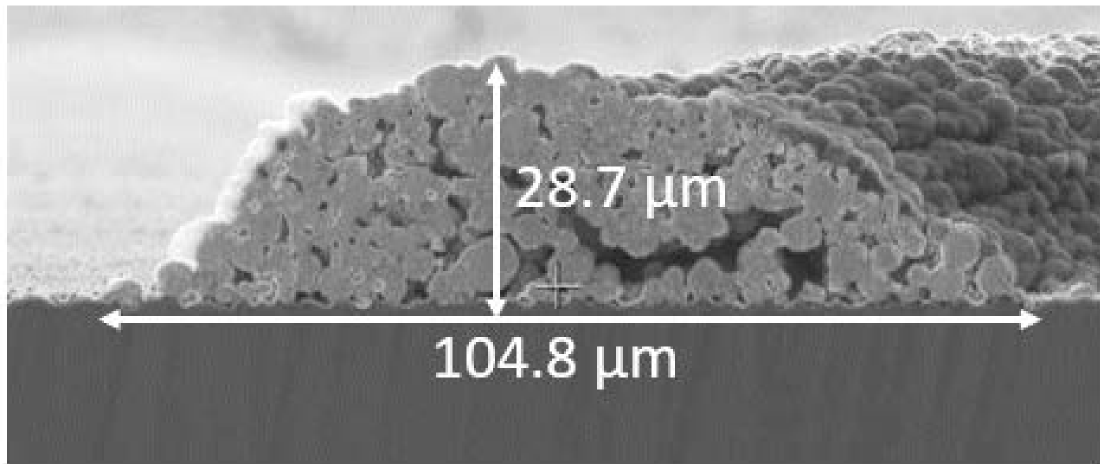


Fig. Cross-sectional SEM-Image of Cu finger

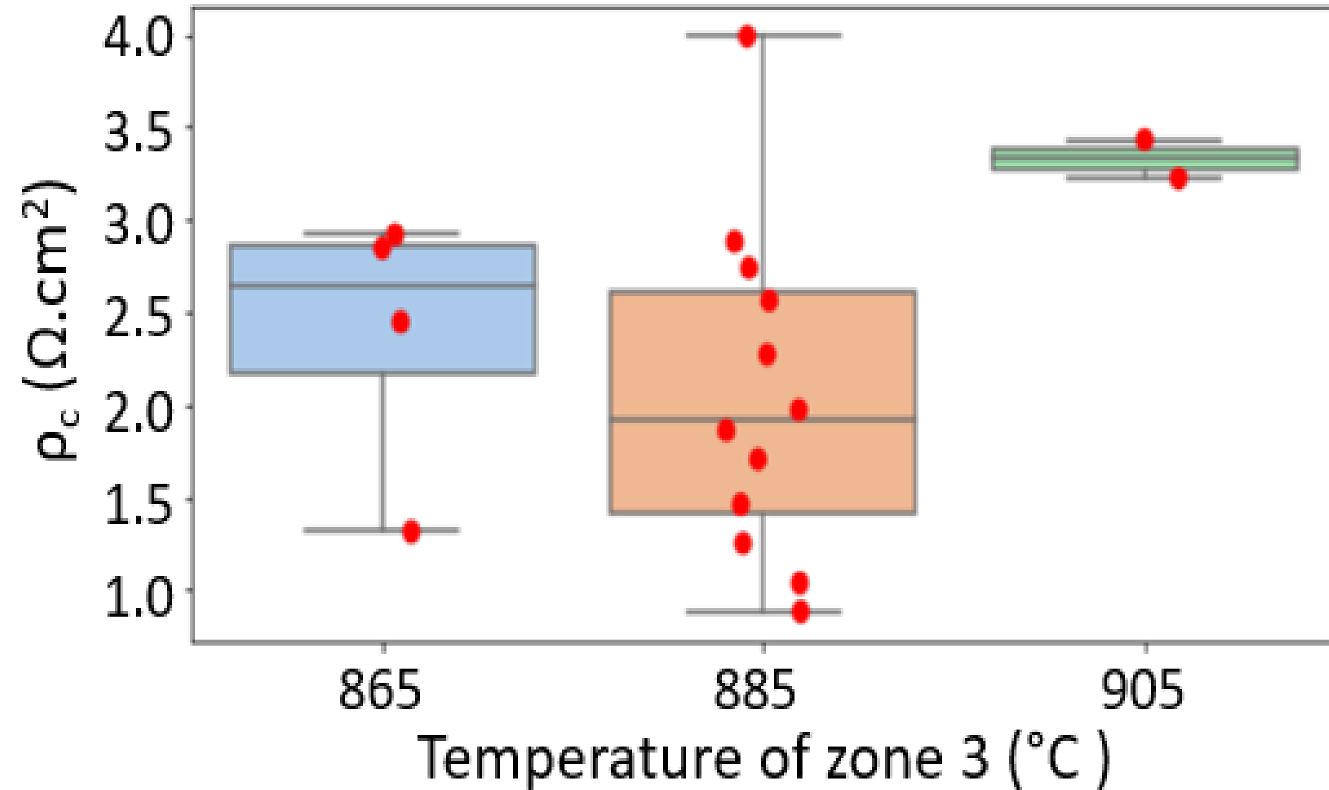
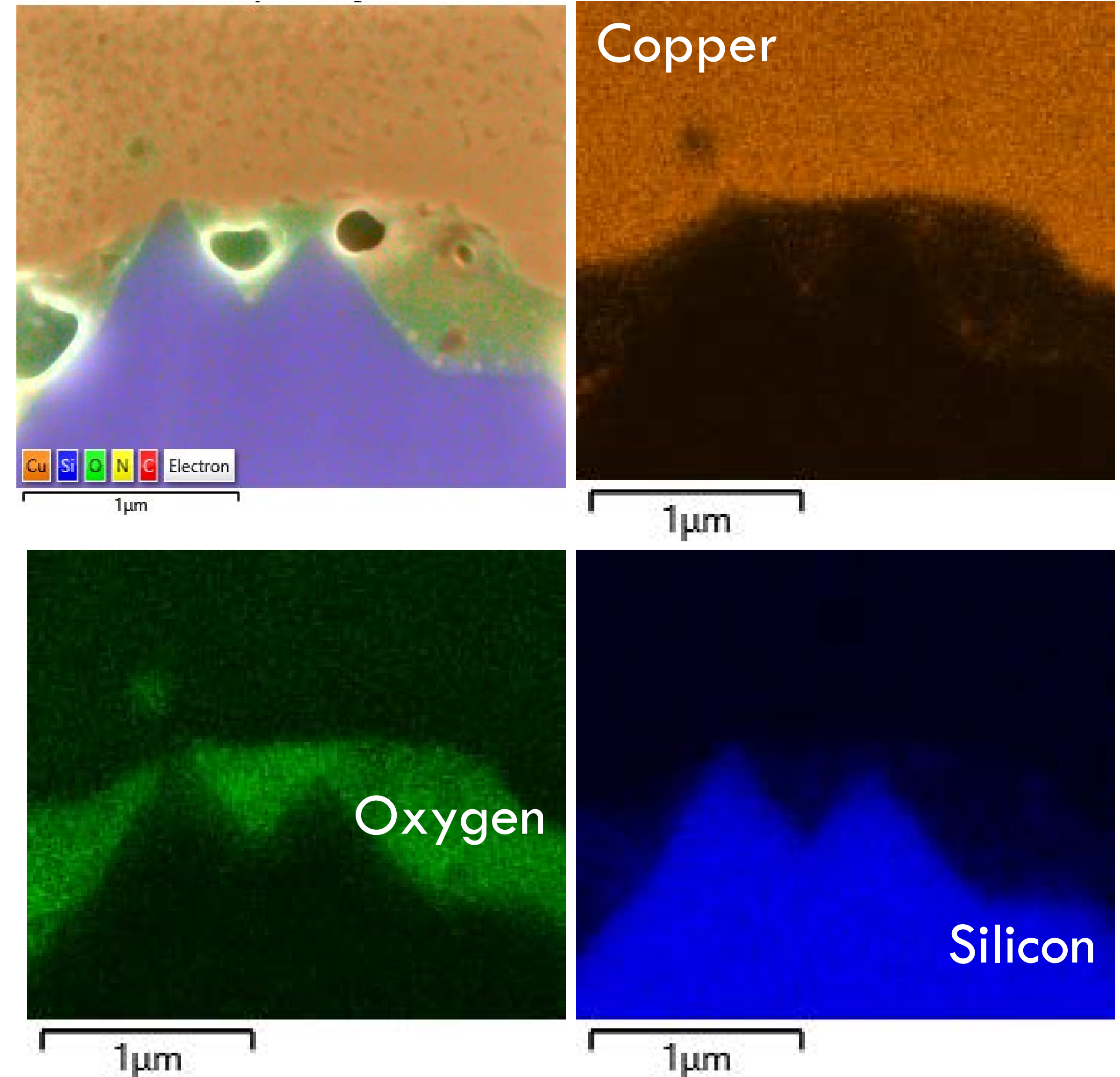


Fig. Contact resistance (ρ_c) after firing at different temperatures for initial versions of the Cu paste (Firing done in a 3-zone furnace, Temperature of zone 1 &2 was 450°C with belt speed =250 inch/min)

Interface Studies by Energy Dispersive X-ray Spectroscopy (EDS)

Observations:

- Thick oxide layer between Copper and Silicon
- This layer likely acts as Cu diffusion barrier
- Interface chemistry controls electronic properties



Early pastes: J-V parameters for M6 sized PERC Cells

Observations:

- Mean Voc is ~ 5mV lower for 630 °C, but the Rs is lowest and hence, FF and efficiency is highest

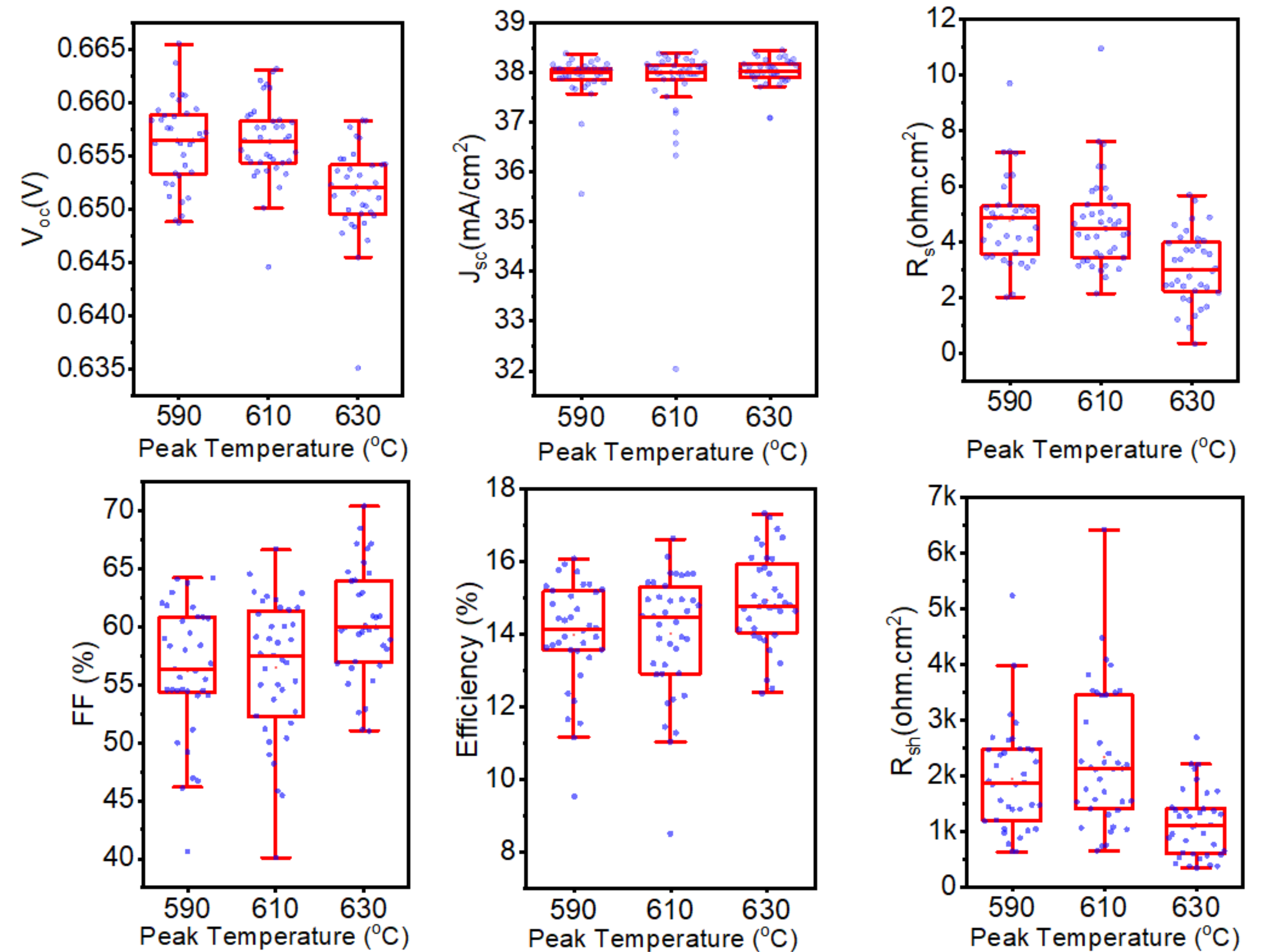
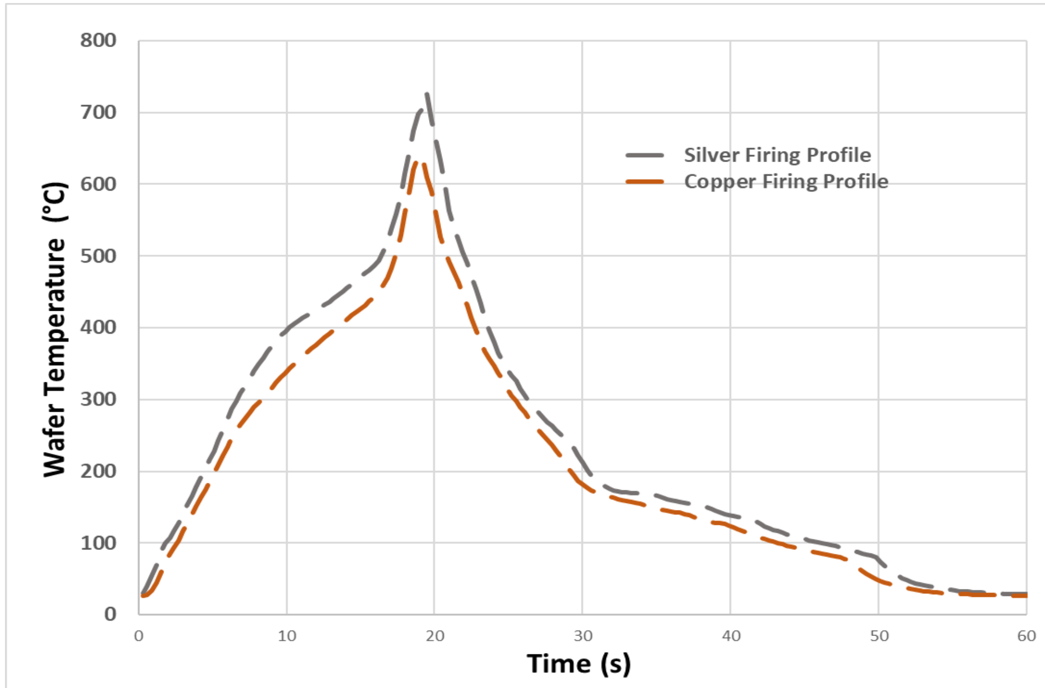


Fig. Distribution of IV parameters for M6 Size cells fired at three peak temperatures namely, 590°C , 610 °C and 630 °C

17+ Year Old Furnace (M2)



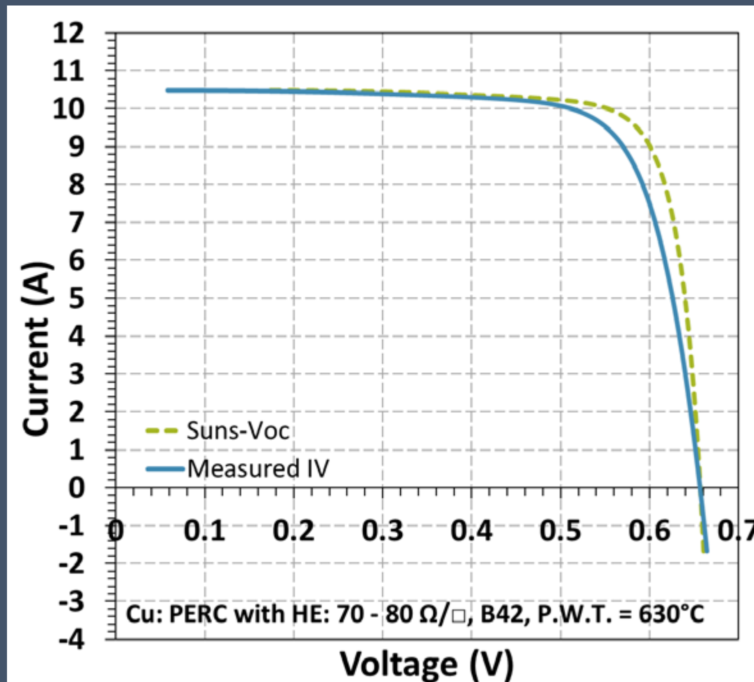
Champion Cell on M6 size wafer:

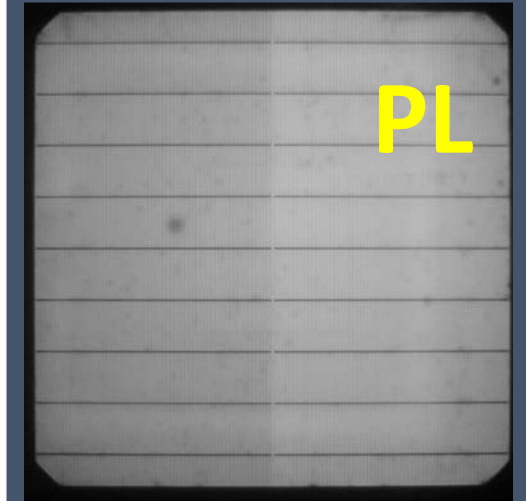
J_{sc} = 38.32 mA/cm^2

V_{oc} = 0.657 V

FF = 76.14%

η = 19.17%





- **Designed for smaller wafer sizes.**
- **Temperature uniformity limiting performance.**

Biased PL imaging reveals firing non-uniformities; Series Resistance Mapping

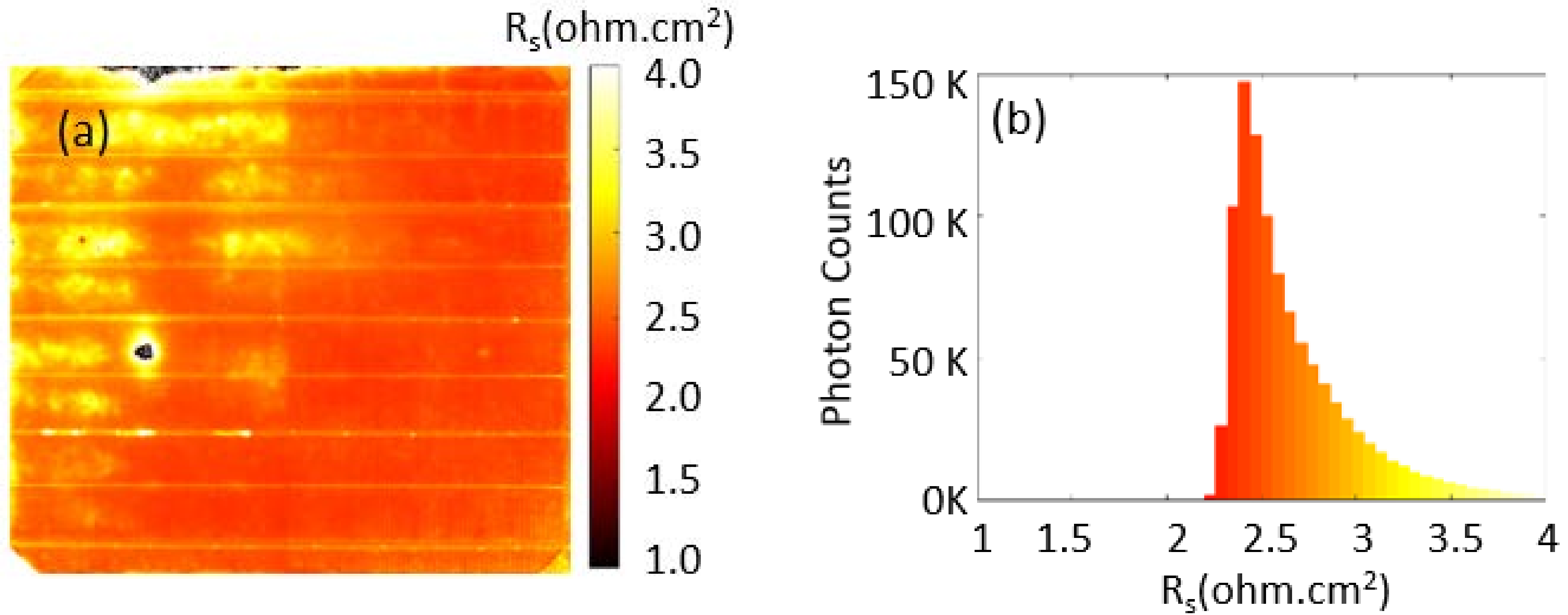
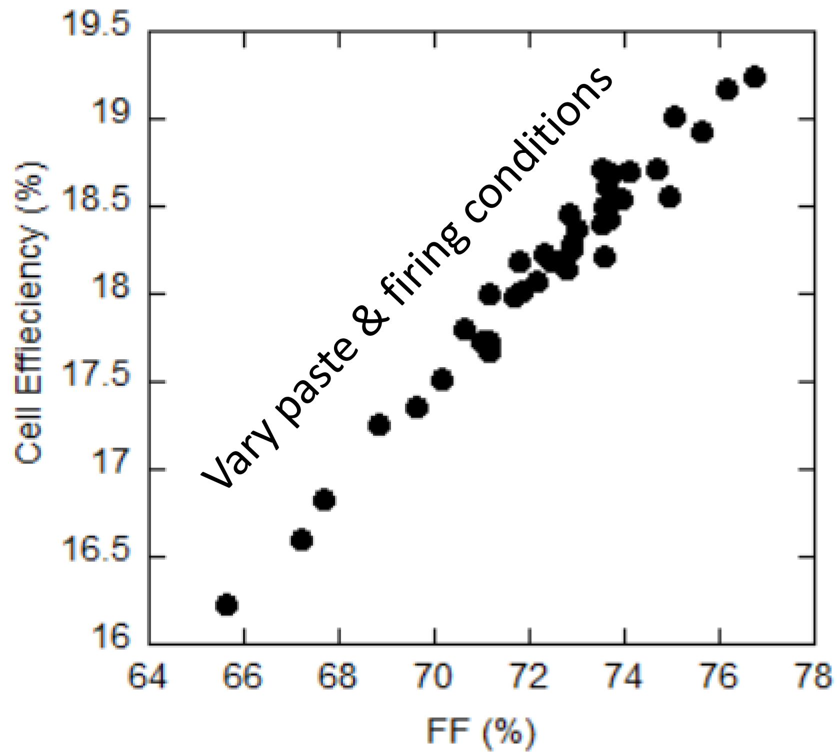


Fig. (a) R_s map obtained from biased PL images at two different intensities
(b) Histogram showing the distribution of R_s over the entire surface

Improved paste study: Initial Cell Efficiency correlates with Fill-factor variations. FF controlled by J_{02} and R_{ser}

FF varies within 9% abs. in series studied.
(12% relative, >> than V_{oc}, J_{sc})

V_{oc} varies within 10 mV (1.5% relative)
Short circuit current varies within 1.5 % relative.



FF is affected by R_{series} between 0.3 and 1.7 Ohm-cm^2 and Pseudo-FF (varies ~ in the same range as FF plus 4% abs)

FF vs pFF

FF vs Rseries

FF vs Rshunt

Pseudo-FF (%)

Series R (Ohm-cm2)

Shunt R (Ohm-cm2)

FF (%)

FF and pFF are controlled by J_{02} junction recombination; anticorrelate with J_{01}

pFF vs Jo2

FF vs Jo2

FF vs Jo1

FF , pFF (%)

J_{02} (nA/cm^2)

J_{01} (fA/cm^2)

Reliability Studies: earlier pastes, Damp Heat

Observations:

- In Devices with Cu paste 1, Voc degraded severely by 7.44% after 500 hrs of Damp heat (DH) testing.
- In Devices with Cu paste 2, Voc degraded by 1.67% in the first 500 hours but didn't decay further in 1500 hours.

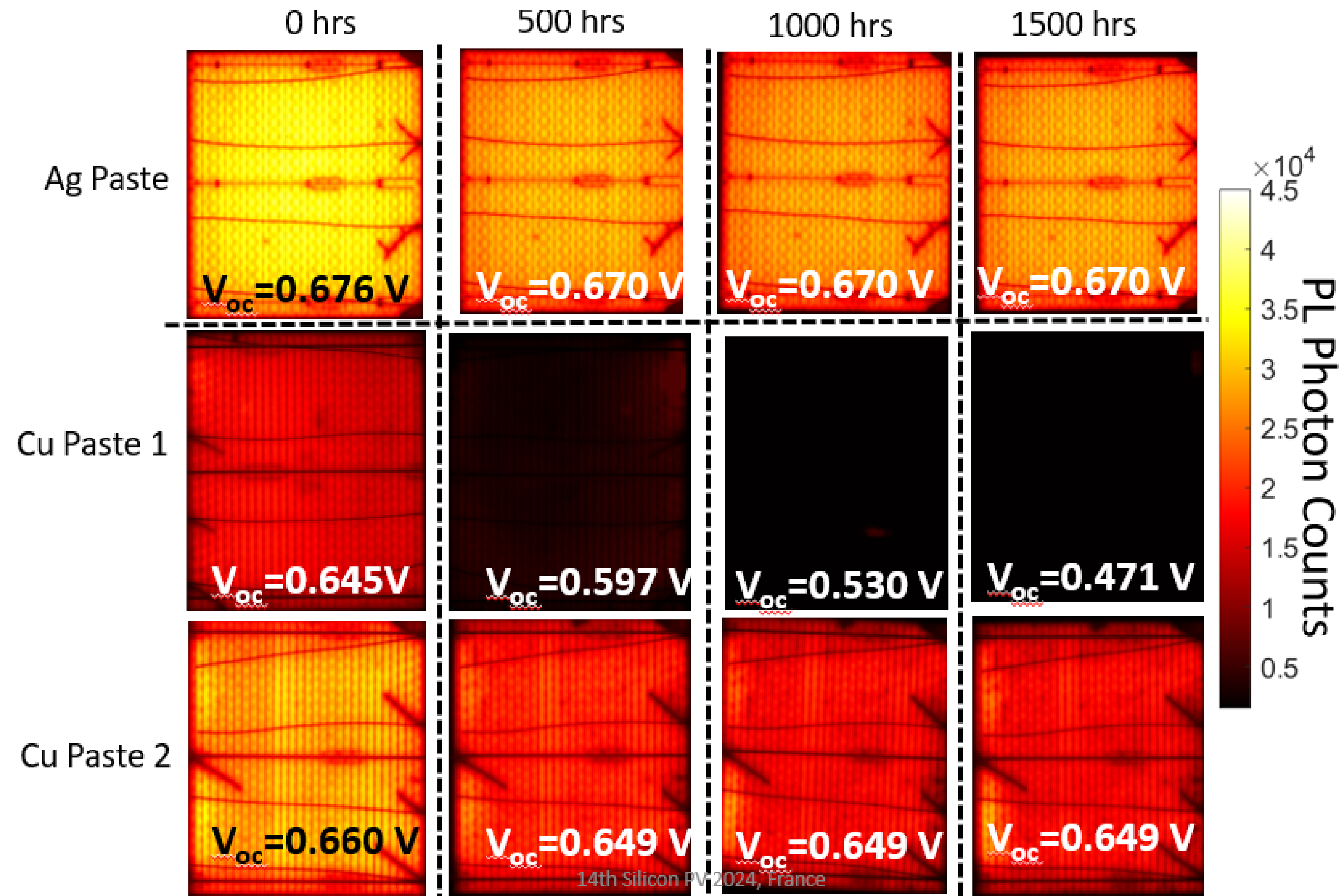


Fig. Open –Circuit PL imaging and Voc degradation after DH (85 deg C/85% Humidity)- 4 cmx4cm modules

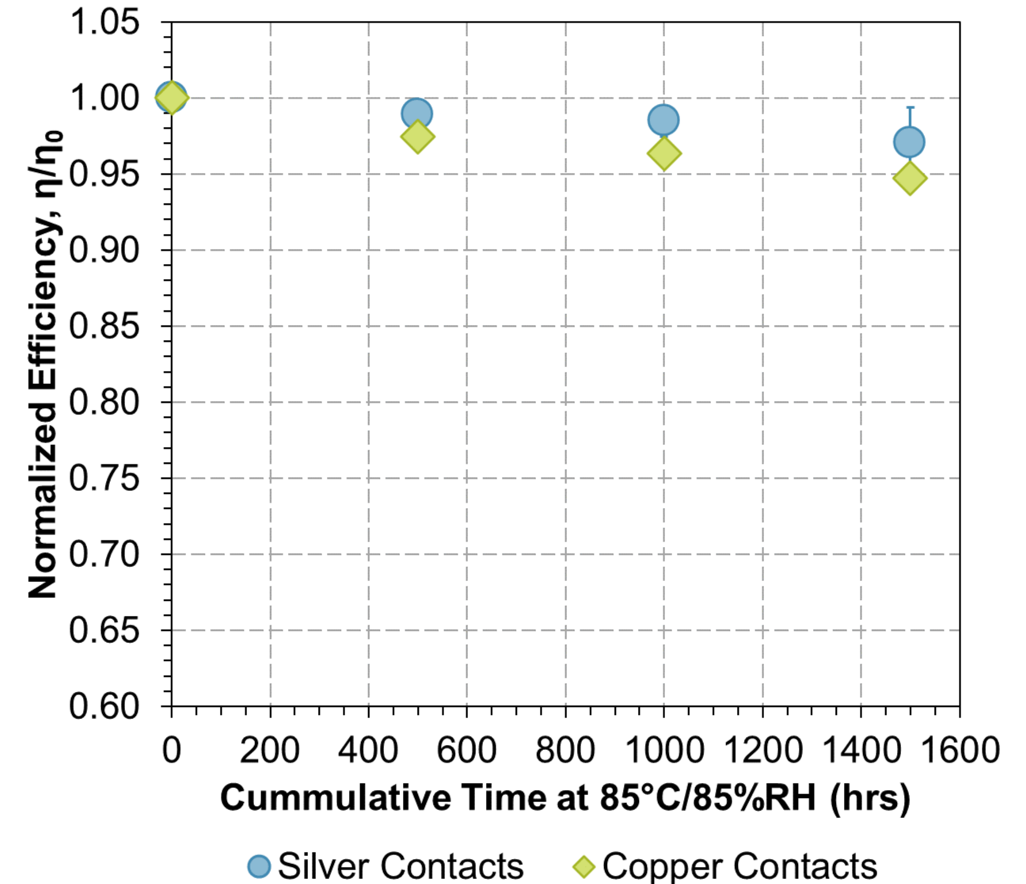
Damp Heat – improved pastes

Copper contacts were compared to commercially sourced silver contacts in micro-modules.

Measured at NREL.

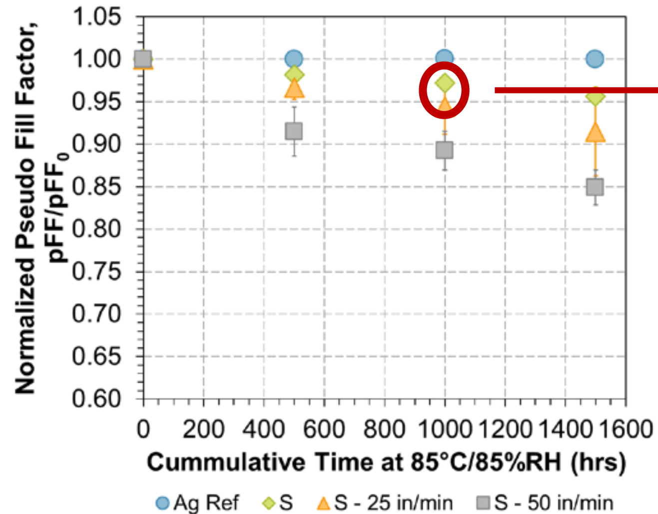
- 16 cm^2 cells encapsulated in to 6.4 cm × 8.3 cm micro-modules.
- 24 µm Screen Opening.
- Glass/Glass module structure with Thermoplastic Polyolefin (TPO).
- 5 micro modules per condition.
- Smart Wire Connection Technology (SnBiAg solder) used for the front.
- Manually soldered (SnPb) coated ribbons used on the rear.
- Modules used a desiccated polyisobutylene tape sealant on the edges.

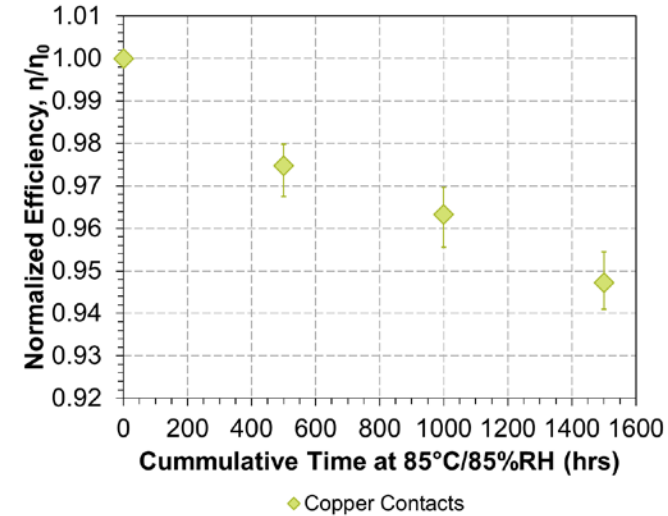
	Cumulative Time at 85°C/ 85%RH			
	0 hrs	500 hrs	1000 hrs	1500 hrs
Sample 1				
Sample 2				
Sample 3				
Sample 4				
Sample 5				



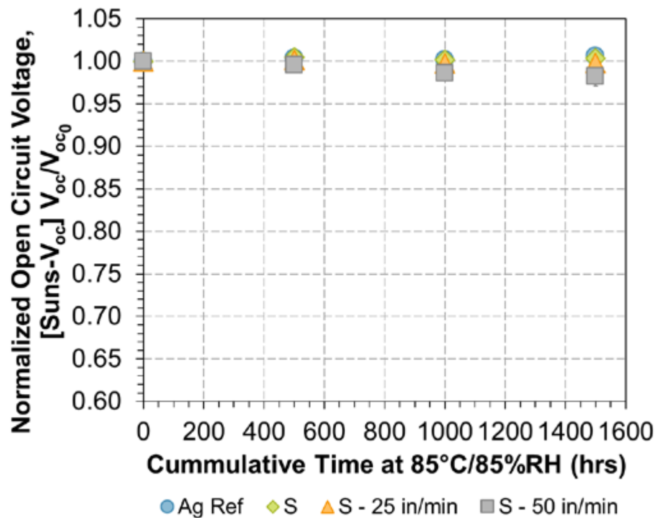
Yellowing of encapsulant for all (including silver contact) samples observed over time.

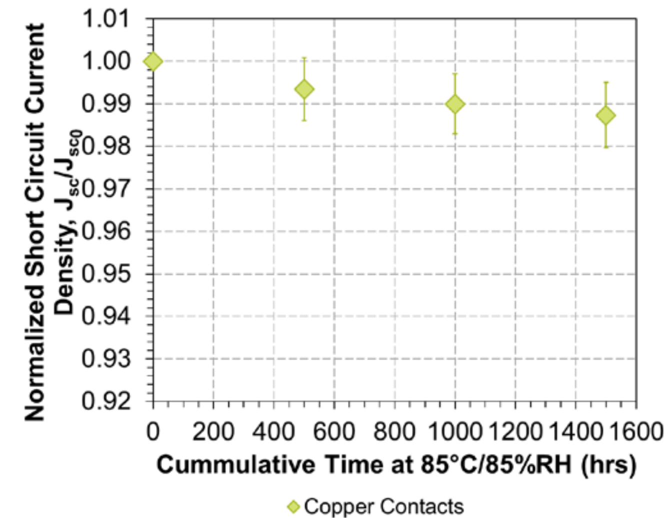
Improved paste Cu-printed cells in a minimodule: Minimodules degrade 3.5% relative after 1000h Damp Heat Test





Efficiency dropped by 3.5% relative in 1000h DHT

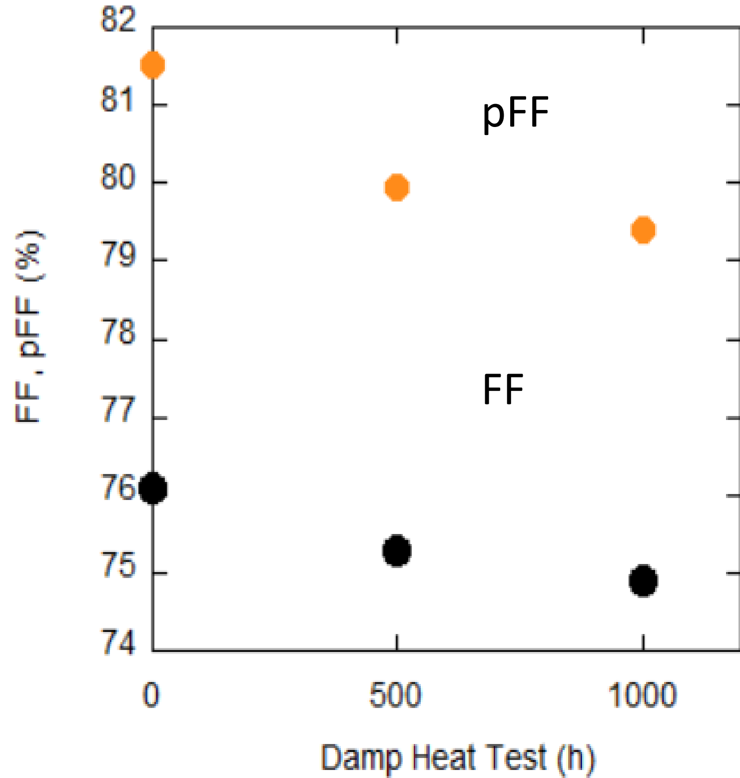




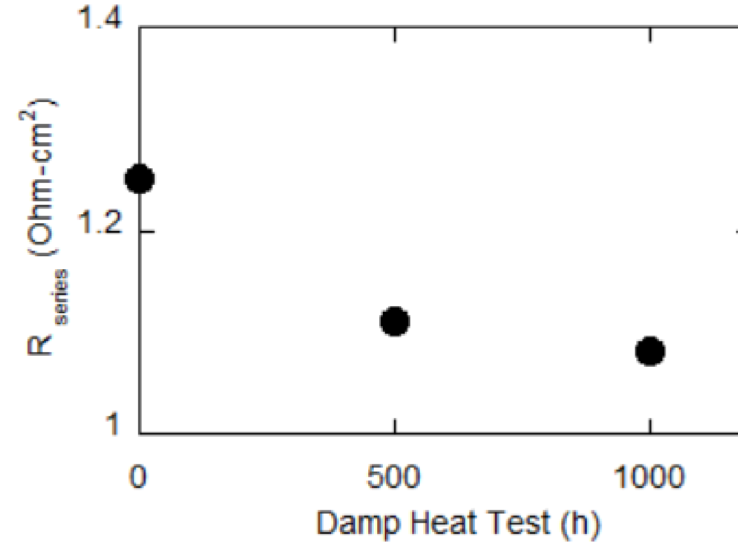
Jsc drops by 0.5 mA/cm2 (2%)

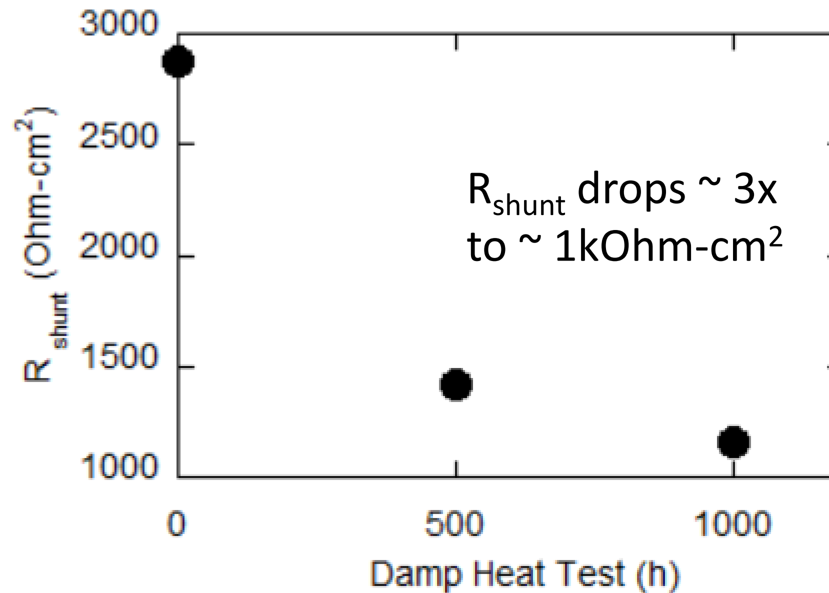
Minimodule degradation is governed by Fill-factor change. FF is again controlled mostly by J_{02}

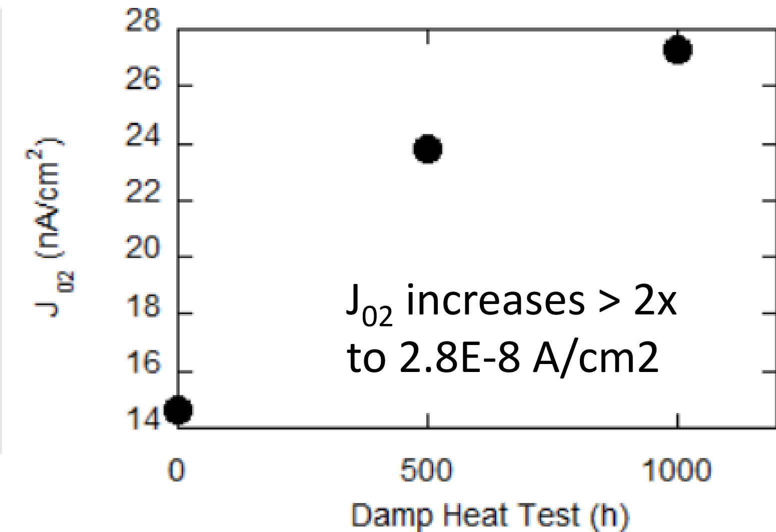
Both FF and pFF degrade to similar extent (1% - 3% relative):
FF/pFF ratio is almost constant



Rseries is ~ unchanged near 1.2 Ohm-cm²







Conclusions

- Successful demonstration of large area selective emitter PERC solar cells using Cu fire-through paste with FF ~75% and ~19%
- Paste chemistry results in oxide-based Cu diffusion barrier, leading to good reliability of the devices: 1000h DHT → 3.5% efficiency drop. The additional series resistance still needs to be lowered.
- Printed and fired cell performance is governed mostly by pFF, especially J_{02} ; same for DHT degradation.
- Further improvement in printing and firing optimization for lower series resistance and higher FF.

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