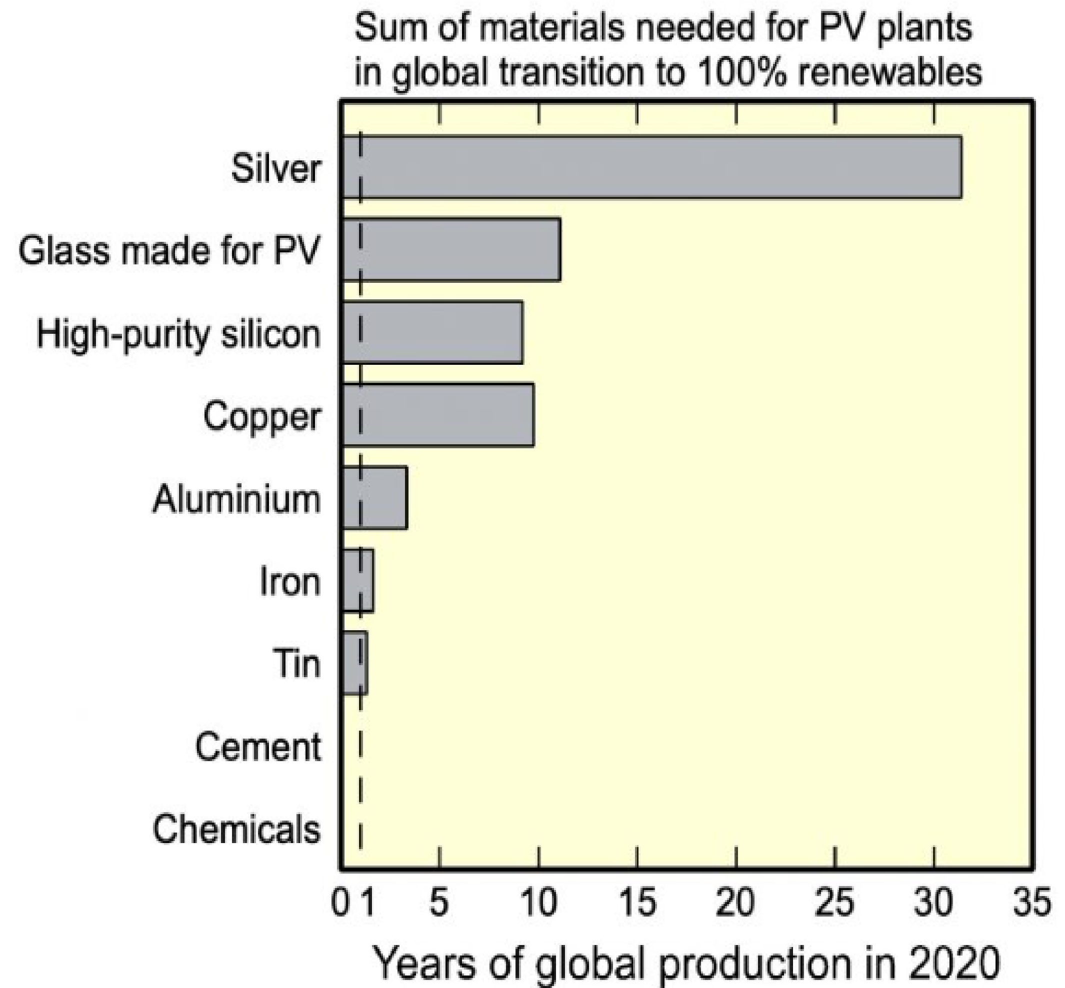
A review on metallization of silicon solar cells using Copper

Why to reduce silver usage?

- 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!!



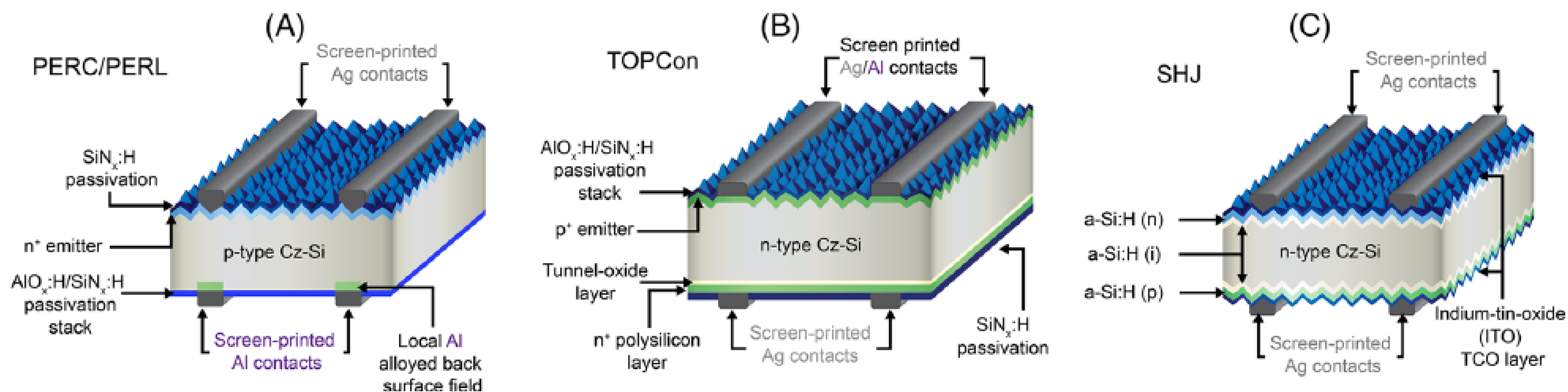
https://www.changeanyway.com/is-solar-electricity-sustainable/

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.

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

Paste Constituents

Components	Materials	Purposes
Metal powder	Doped copper (aluminum, magnesium, etc.), copper alloys (CuSn, CuAg, CuNi, CuZn, etc.)	To have conductive property
Polymer resin	Ethylcellulose	To enable printing of copper-containing particles
Glass frits	Lead oxide (PbO_x), silicon oxide (SiO_2), alumina (Al_2O_3), boron trioxide (B_2O_3), zirconia (ZrO_2), zinc oxide (ZnO), bismuth oxide (Bi_2O_3), strontium oxide (SrO), titanium oxide (TiO_2), and lanthanum oxide (La_2O_3)	To pass through a passivation layer and promotes adhesion to the substrate
Solvents	α-Terpineol, toluene, ethanol	To tune viscosity characteristics

Table 1. Components and possible materials of the copper paste for high-temperature annealing.

IntechOpen

Encapsulation materials for Copper-containing particles

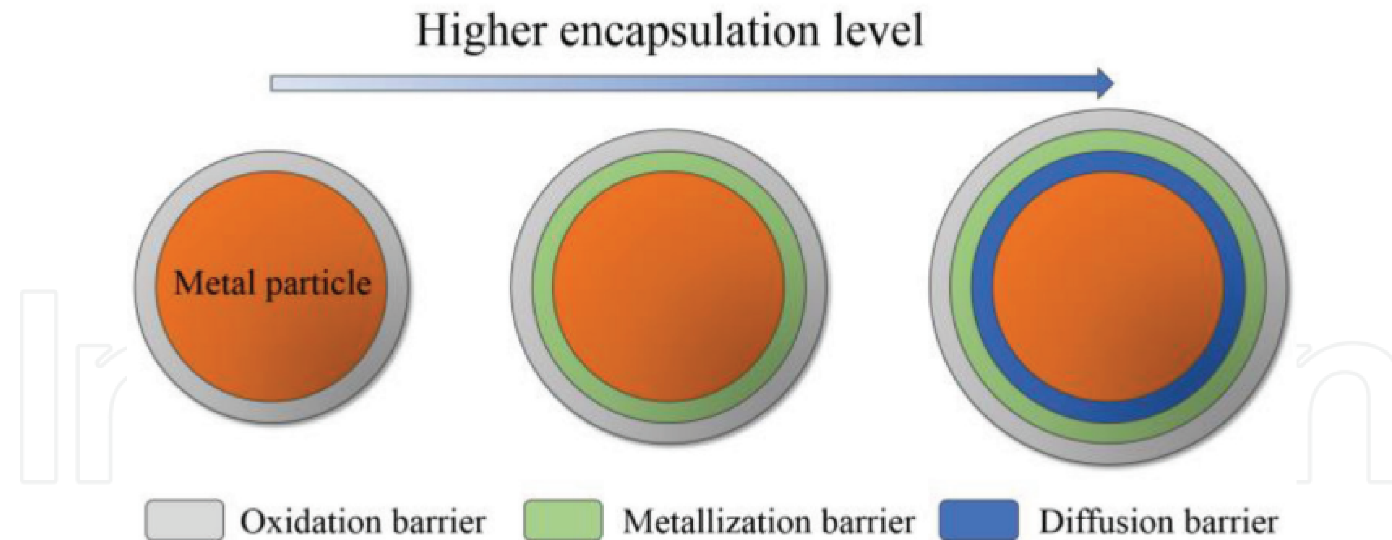


Figure 3. Cross-sectional views of encapsulated copper-containing particles with single and multi-barrier layer.

Encapsulation layer	Oxidation barrier	Metallization barrier	Diffusion barrier
Possible materials	Silver (Ag), nickel (Ni), and zinc (Zn)	Nickel (Ni), titanium (Ti), titanium nitride (TiN), tungsten (W), titanium-tungsten (TiW), cobalt (Co), tungsten doped cobalt (Co:W), molybdenum (Mo), tantalum (Ta), and chromium (Cr)	

Table 2. The possible materials of each encapsulation layer for copper-containing particles.

Challenges in preparing Cu paste

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

Different types of Cu paste available till now

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]

Cost

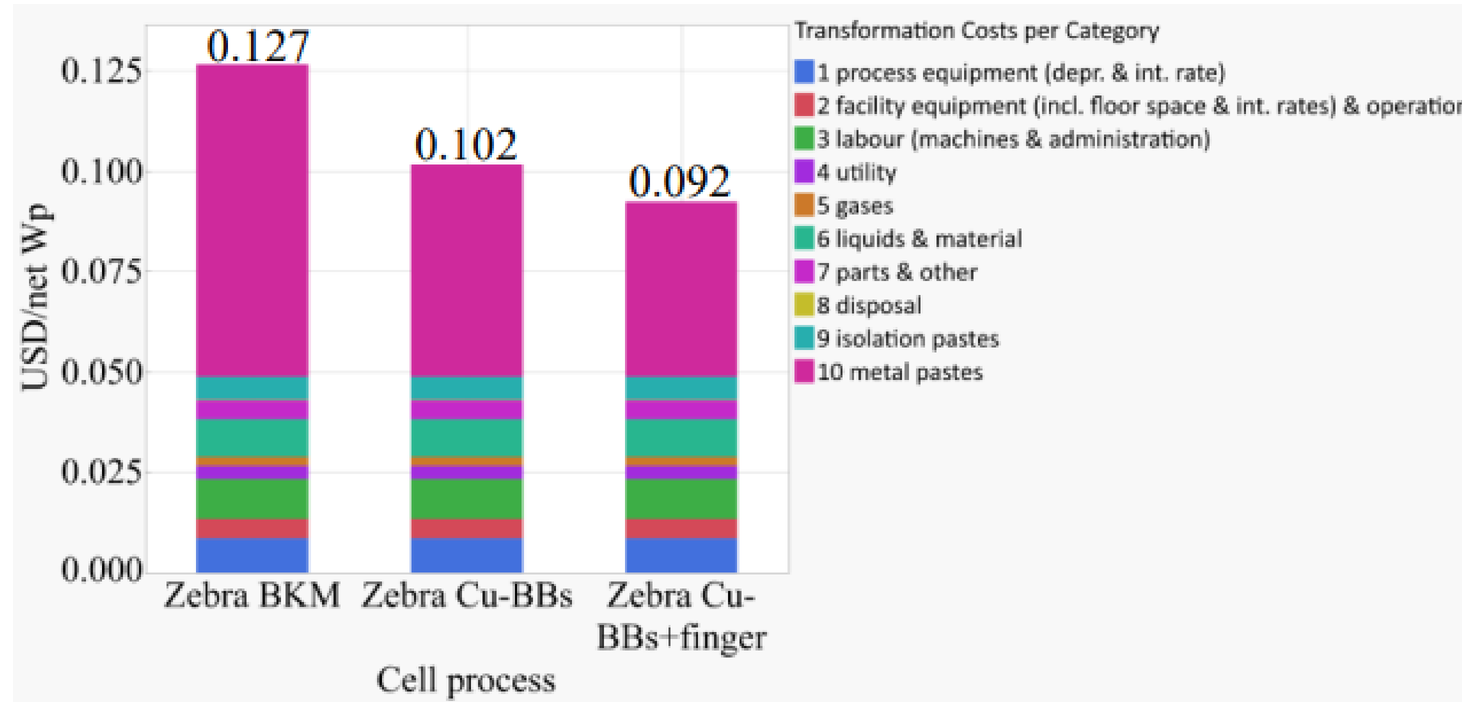


Figure 1: Total cost of ownership (USD/W_P), without wafer material costs, for a ZEBRA cell, in the case of Ag paste for fingers and busbars, Ag paste for fingers but Cu busbars and Cu for fingers and busbars. Cost of ownership calculations were carried out internally by using the following input parameters: 5 GW_P /year Zebra M6 cell line in Europe, cell efficiency of 23.8%, Ag paste price of 783 USD/kg and Cu paste price 50% of Ag paste.

This calculation shows that by replacing the Ag busbars with Cu busbars, the cost of ownership can be reduced by 13%, and if Cu paste is used for both the busbars and fingers, a total 19% reduction in cost can be achieved.

Comparison of cost for Silver (Ag) and Copper (Cu) paste

Year	2020	2023	2030	2033
Ag cost ($/kg)	$600	$750	$1,500	$2,000
Cu cost ($/kg)	$8	$8	$16	$20
Global PV production	135	300	1000	1700
Global PERC Production (GW)	120	240	240	250
Global TOPCon Production (GW)	0	36	600	1020
Ag Consumption PERC (mg/W)	19.5	13	10	9
Ag Consumption TOPCon (mg/W)	22.8	21.6	18	14.4
Total Ag consumption (Tonnes)	2340	3898	13200	16938
Ag costs global ($B)	**$1.40**	**$2.92**	**$19.80**	**$33.88**
Cu Consumption PERC (mg/W)	20	20	20	20
Cu Consumption TOPCon (mg/W)	22.8	22.8	22.8	22.8
Cu costs global ($B)	**$0.02**	**$0.04**	**$0.30**	**$0.57**
Paste cost/kg				
$100	**$0.24**	**$0.56**	**$1.85**	**$2.83**
$150	**$0.36**	**$0.84**	**$2.77**	**$4.24**
$200	**$0.48**	**$1.12**	**$3.70**	**$5.65**

Copper Electroplating

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

-Highest efficiency achieved for copper plated bifacial SHJ cell[1]

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

-Challenges in electroplating[2]

- Complicated plating process
- Copper-induced degradation
- Reliability

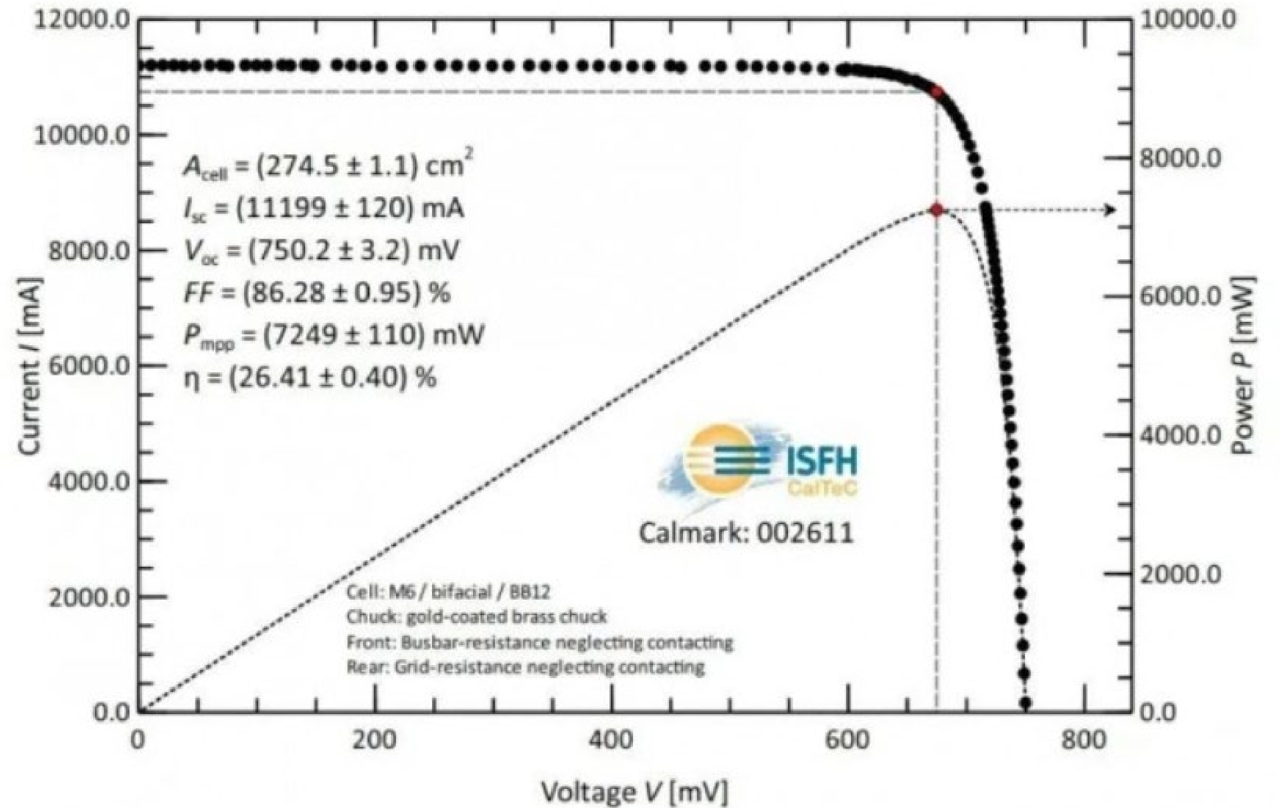
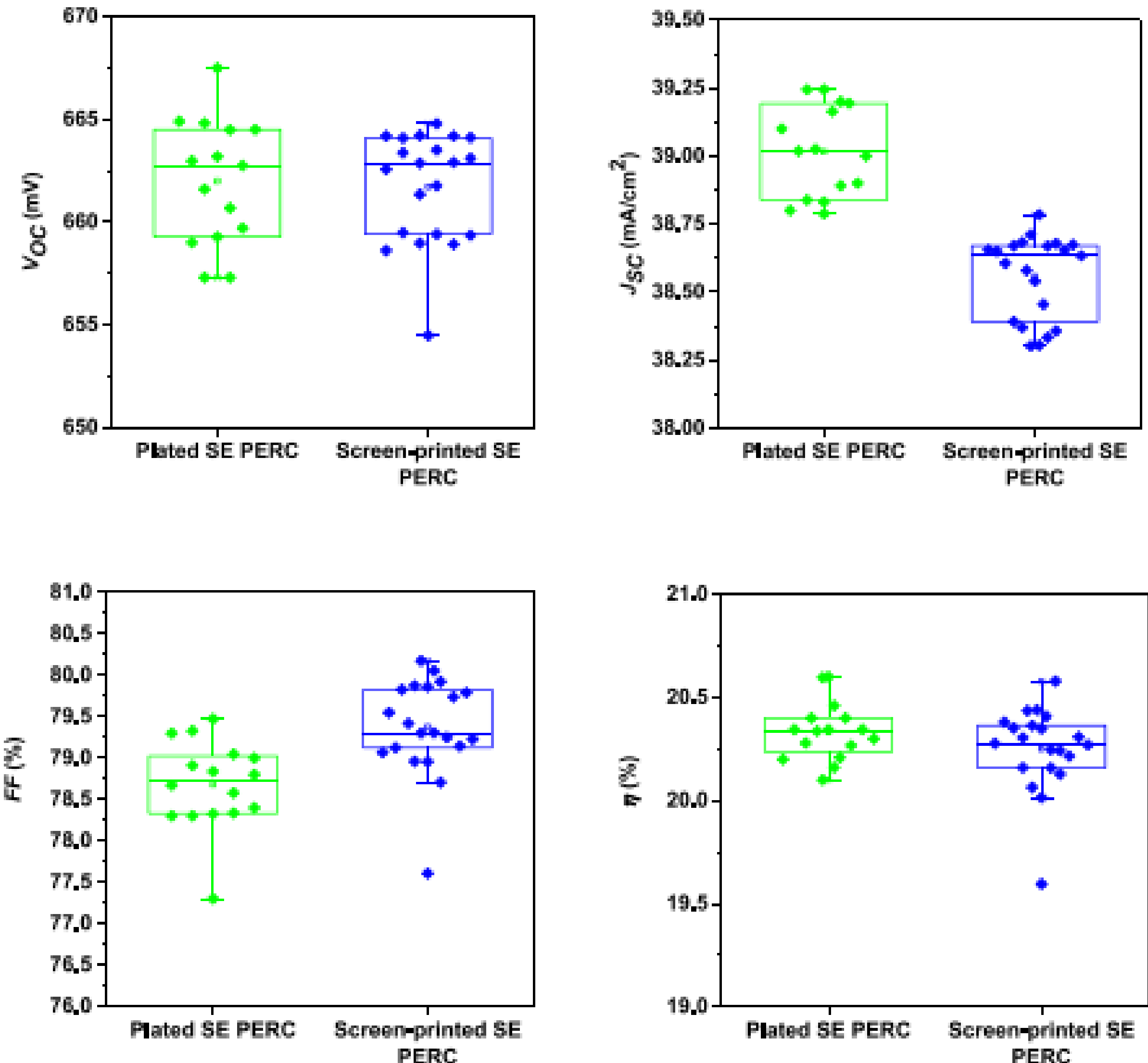


Fig. Measured IV characteristics under standard test conditions

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 in future!

PERC by Copper Electroplating

- Application of 266-nm picosecond (ps) laser ablation and copper (Cu)-plated metallization to p-type selective emitter (SE) passivated emitter and rear cells (PERC)
- Successful alignment of laser-ablated openings to the heavily doped SE regions resulted in a comparable cell efficiency of Cu-plated SE PERC cells to screen-printed controls, with a maximum cell efficiency of 20.6% being achieved for the Cu-plated cells



Ref: Hsiao et al., *IEEE Journal of Photovoltaics* 8, no. 4 (2018): 952-959.

PERC by Copper Electroplating + Low temperature paste

p-Cz (Ga), 156mm-sq, 180um, 1.8 Ohm-cm

Texturing front and polishing rear	
$POCl_3$ target 130-140 Ohm/sq emitter + junction isolation	
Clean and oxidation (target 120Ohm/sq)	
PECVD SiNx on the front + PECVD stack on the rear	
Rear laser ablation, Al sputtering and co-firing	
Front laser ablation fingers and BB	Front laser ablation – only fingers
LIP Ni - LIP Cu - immersion Ag plating	
	Cu BB Printing
Full stack sintering	

Fig. p-type PERC cell process. To the left is shown the standard plating process; to the right is shown the modified process, using the copper paste for the busbars.

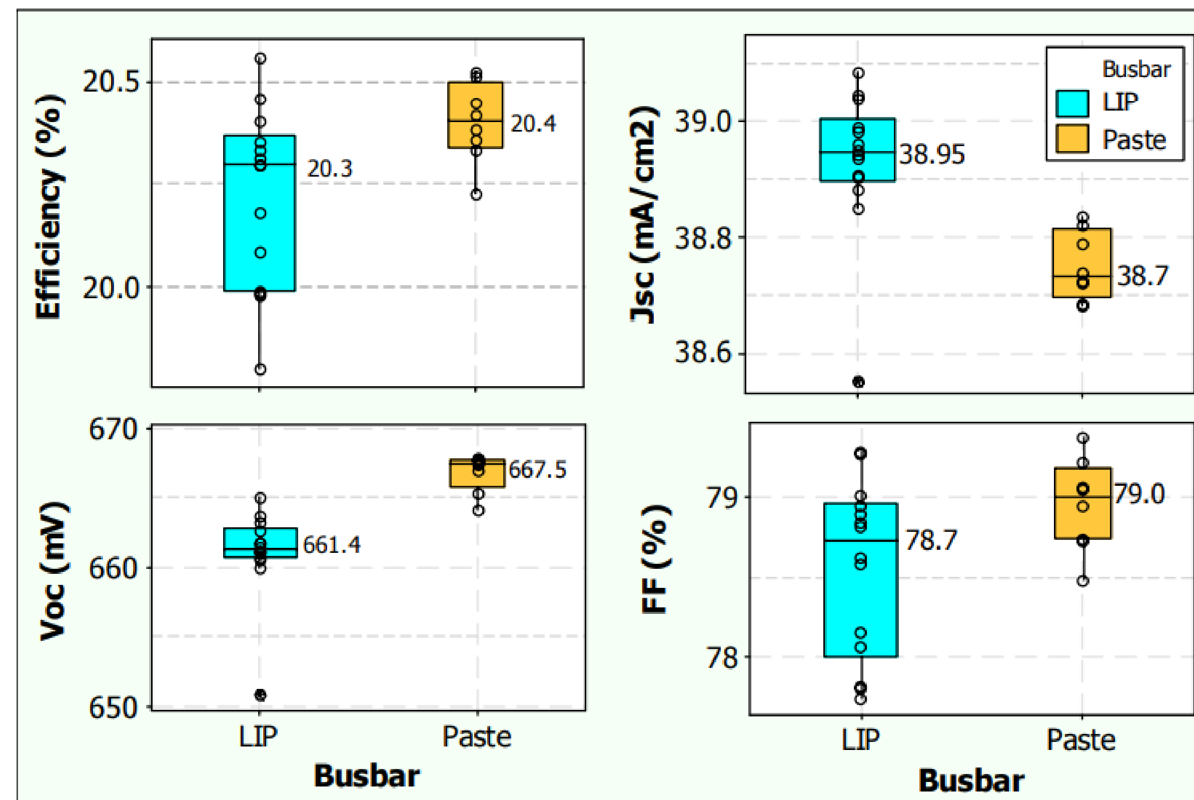


Fig. Cell parameters for PERC cells, with each cell represented by a single symbol. The fingers of all cells are produced by laser ablation and subsequent light induced plating of copper. Those groups to the left (blue boxes) have busbars also formed by light induced plating. Those to the right (orange boxes) have busbars formed by screen printing of the copper paste. Median values are listed on the charts.

Damp Heat Induced Degradation of SHJ Solar Cells With Cu-Plated Contacts

Experiment:

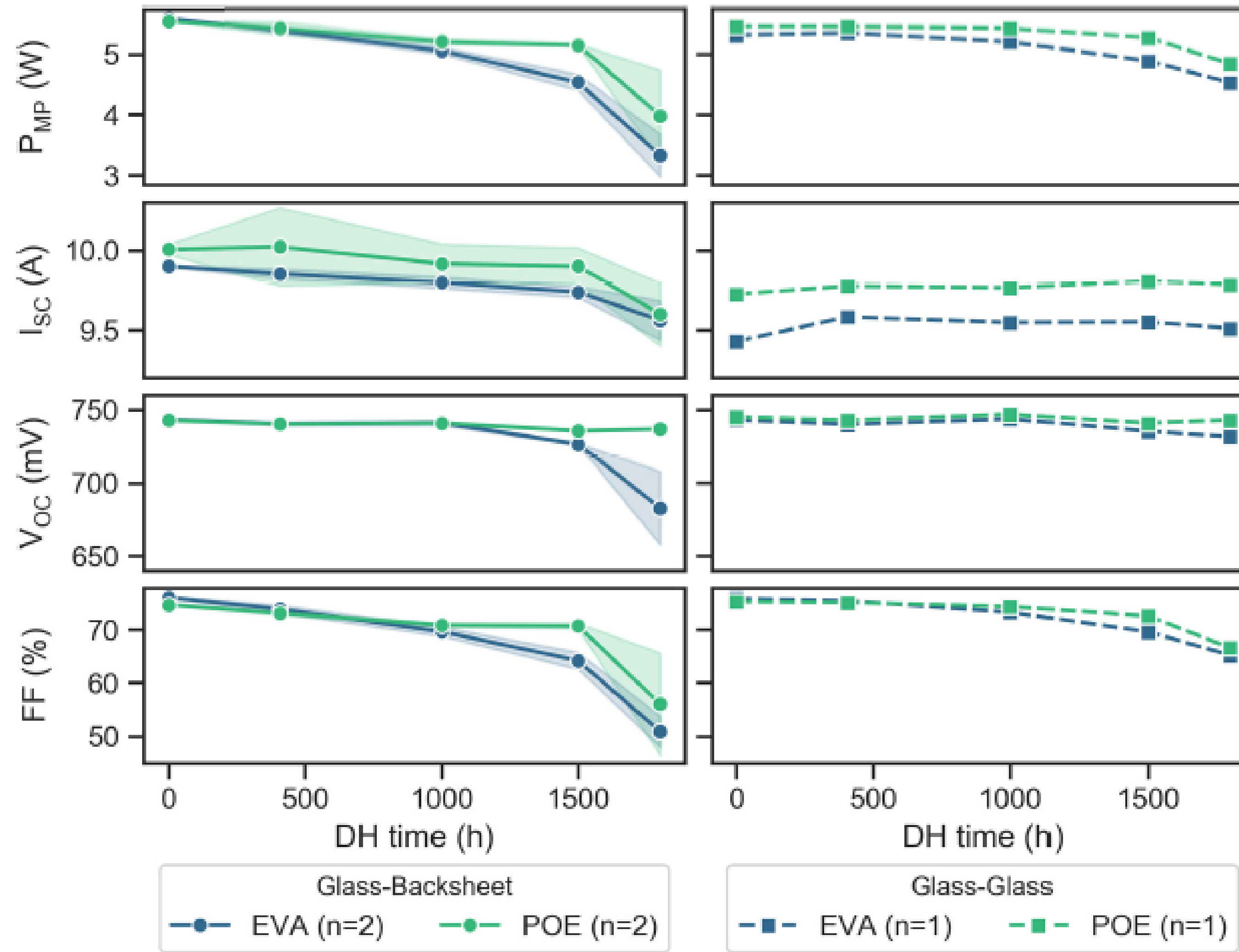
- One-cell modules containing SHJ solar cells with Cu-plated contacts to extended damp heat tests at 85 °C/85% relative humidity.
- SHJ cells were laminated with
    - Two common encapsulants: ethylene vinyl acetate (EVA) and polyolefin elastomer (POE)
    - Two constructions: glass–backsheet and glass–glass

Observation:

- Degradation in all components of solar cell maximum power (P_{MP}): current, voltage, and fill factor, and find evidence of increased carrier recombination and nonideal diode behavior with increasing stress.
- For glass–backsheet constructions, EVA samples generally degrade more than POE by a factor of approximately 1.5x P_{MP}
- Different encapsulants produce different degradation patterns.
- Similar trends are observed in glass–glass modules, but to a lesser degree.
- Some degradation unrelated to the contacts is to be expected and confirms the observation of increasing recombination.

Ref: Karas et al., "Damp heat induced degradation of silicon heterojunction solar cells with Cu-plated contacts." IEEE Journal of Photovoltaics 10, no. 1 (2019): 153-158.

Damp Heat Induced Degradation of SHJ Solar Cells With Cu-Plated Contacts



Copper In-diffusion

Cu can easily diffuse into Si and generate near-mid band-gap defect states, causing device failure![1,2]

- **Promising diffusion barrier for SHJ cells with electroplated Cu contacts**
  - ITO and IWO[3]
  - 50- to 100-nm-thick SiO_x capping layer deposited on TCO[4]
  - In combination with polyolefin encapsulation, Cu-electroplated SHJ devices with SiO_x capping layers were shown to retain >99% of their initial maximum output power after 6,000 h of damp heat testing in a climate chamber at 85C and 85% relative humidity conditions.[4]
  - Ni barrier layer to avoid Cu diffusing into the Si bulk, and have found their way into the solar industry in the past[5]
- **Diffusion barriers in low temperature Cu paste**
  - ITO[6], polymer coating[7] act as barrier layers
- **Diffusion barrier in high temperature Cu paste**
  - Coating of copper powder with nano-silica[9]