Seed-Layer-Free Electroplated Copper Metallization of SHJ Cells Enabled by Chemical Modification of Transparent Conductive Oxides

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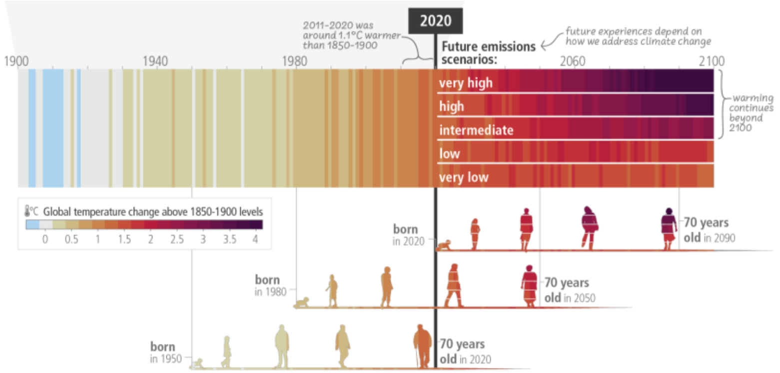
Introduction

Climate Change

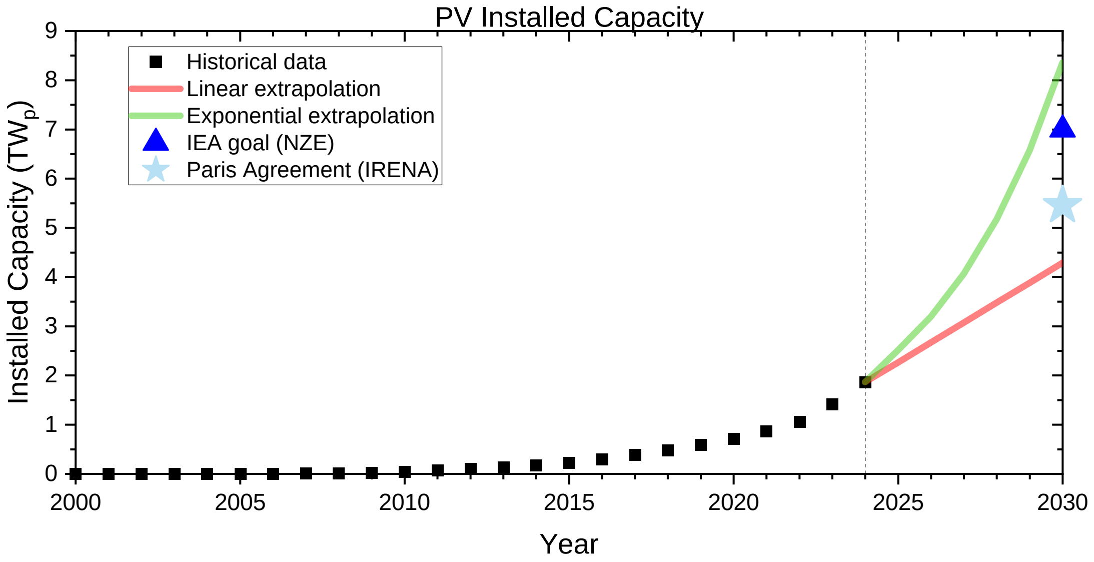
INTERGOVERNMENTAL PANEL ON climate change

Publishes scientific assessment reports on:

- ✓ Greenhouse gas emissions
- ✓ Future climate scenarios
- ✓ Mitigation options
  - ✓ Renewable Energy



PV contribution



International Energy Agency

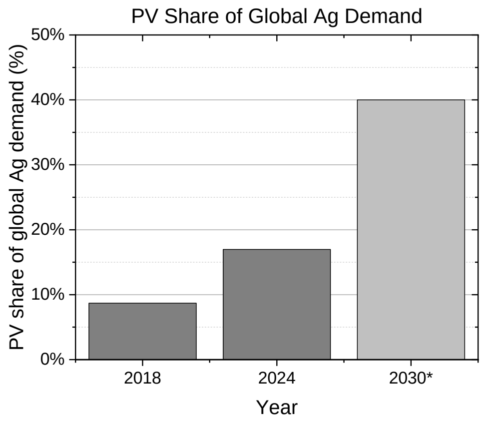
Net Zero Emissions Scenario by 2050

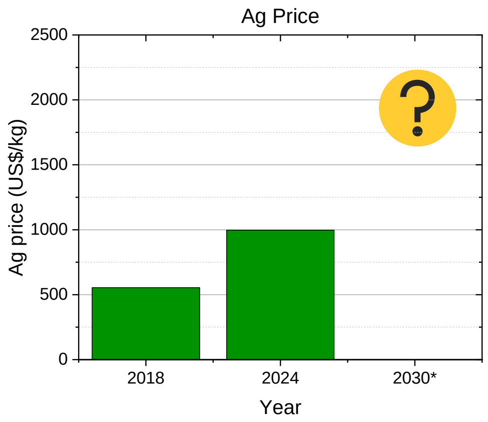
UNITED NATIONS PARIS CLIMATE AGREEMENT SIGNING CEREMONY 22 APRIL 2016

IRENA

Global warming ≤1.5°C

Can Material Supply Support PV Expansion?





pv magazine

PV industry could account for 40% of global silver demand by 2030

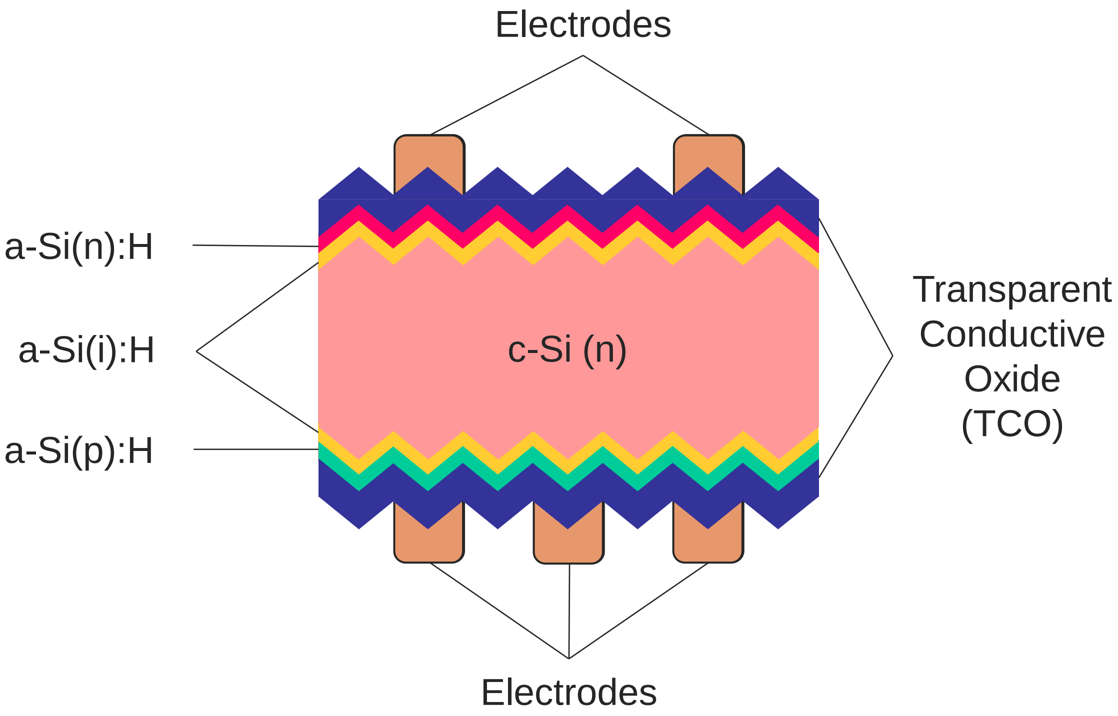
New research from Europe shows that the global PV industry may require up to 14,000 tonnes of silver per year in 2030, with global supply being only 34,000 tonnes. The scientists said more efforts should be made to reduce silver content in TOPCon and heterojunction solar cells.

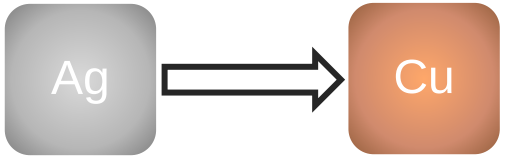
SEPTEMBER 11, 2025 EMILIANO BELLINI

https://www.pv-magazine.com/2025/09/11/pv-industry-could-account-for-40-of-global-silver-demand-by-2030/

The heterojunction (SHJ) architecture

The architecture





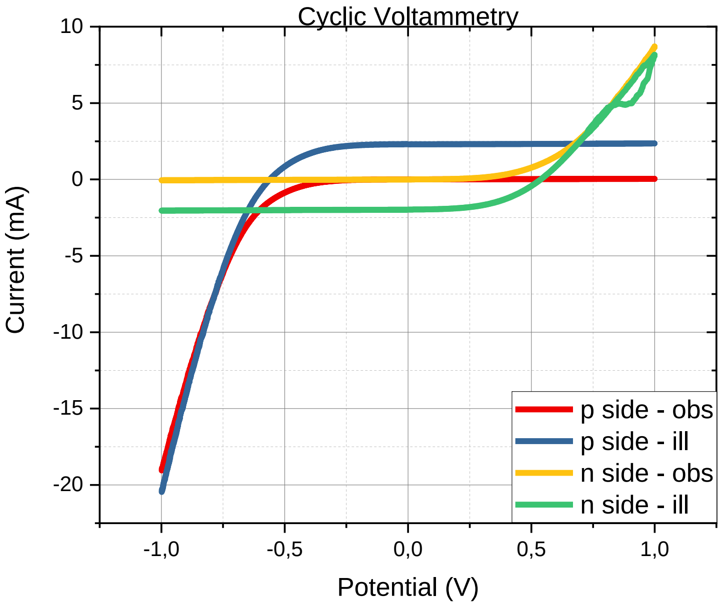
Why EP-Cu on SHJ cells?

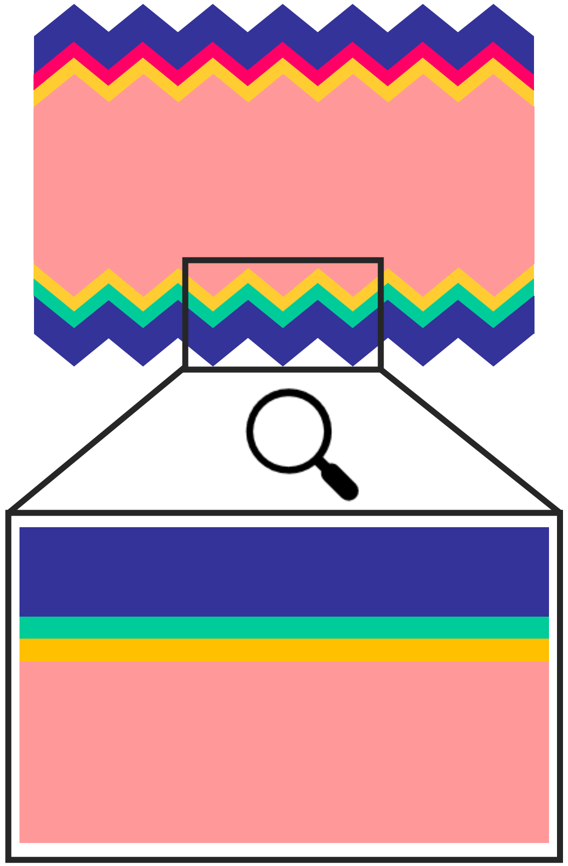
- ✓ **Lower line resistance**
  - ✓ For the same line width, electroplated Cu contacts offer lower line resistance than screen-printed Ag contacts
- ✓ **Intrinsic diffusion barrier**
  - ✓ TCOs, and particularly ITO, are well documented as effective barriers against Cu diffusion in SHJ architectures
- ✓ **Low thermal budget**
  - ✓ Cu plating is performed at low temperatures, fully compatible with the temperature-sensitive SHJ structure
- ✓ **Cost advantage**
  - ✓ Since SHJ requires more Ag than other PV technologies due to its low thermal budget, replacing Ag with Cu offers even greater cost-reduction potential

Cu electroplating on SHJ cells

The process

- ✓ **Front side (n-side)**
  - ✓ LIP (light-induced plating)
- ✓ **Rear side (p-side)**
  - ✓ ECD (electrochemical deposition)



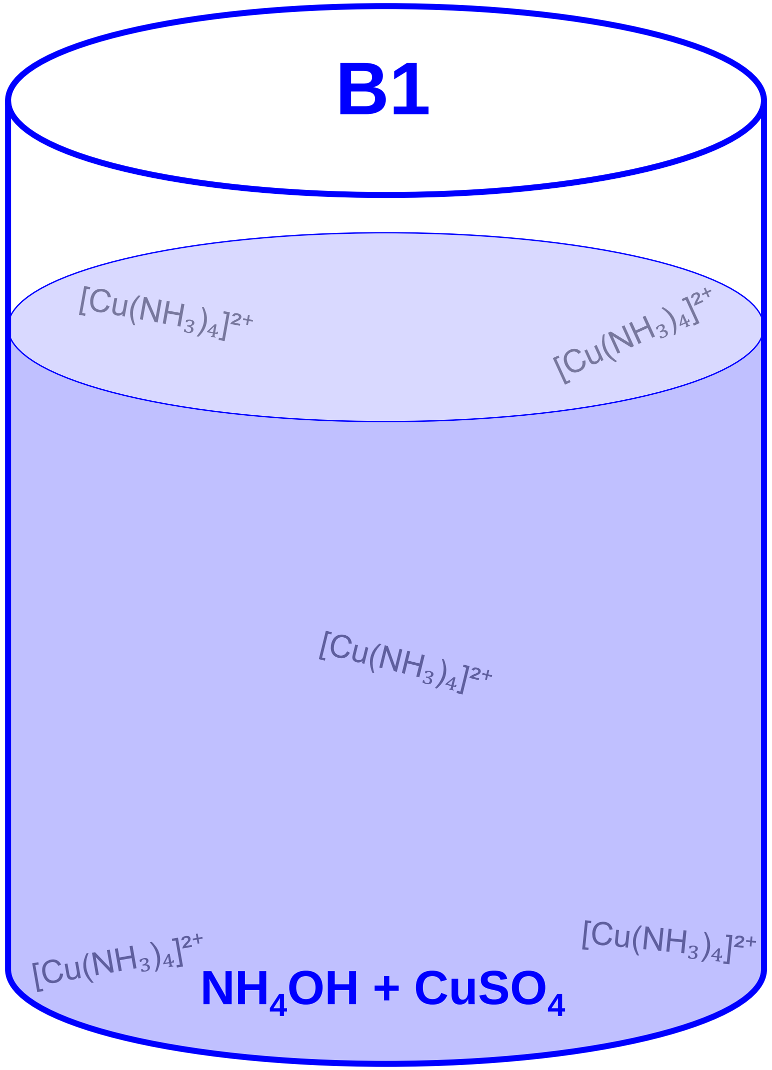


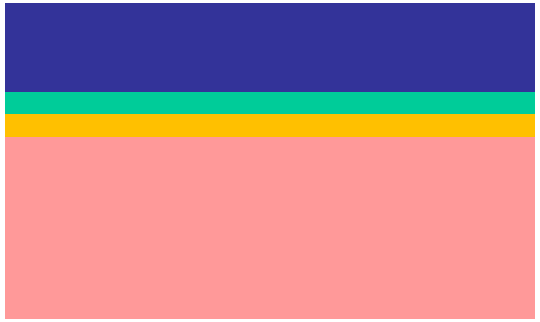
Main challenges:

- ✓ **Selective plating:**
  - ✓ Masking
    - ✓ Photolithography [1]
    - ✓ Dielectric + laser opening [2, 3]
  - ✓ Localized plating [4, 5]
- ✓ **Poor TCO/Cu adhesion:**
  - ✓ Seed layer deposition
    - ✓ Sputtering [6]
    - ✓ Electroplating [7]
  - ✓ Seed-layer-free surface treatment

[1] Shan, Jeff et al. Study of Microstructure and Mechanical Properties of Electrodeposited Cu on Silicon Heterojunction Solar Cells; 2023
[2] Hatt, Thibaud et al. Advances with Resist-Free Copper Plating Approaches for the Metallization of Silicon Heterojunction Solar Cells, 2019
[3] SunDrive. *SunDrive Copper Metallisation Demonstration Project Final Report*. Australian Renewable Energy Agency (ARENA). 2022
[4] Balucani, Marco et al. New selective processing technique for solar cells, 2013
[5] Agata Lachowicz et al. Aging tests of mini-modules with copper-plated heterojunction solar cells and pattern-transfer-printing of copper paste, 2024
[6] Jiun-Yi Tseng, The Impact of Substrate Temperature on the Adhesion Strength of Electroplated Copper on an Al-Doped ZnO/Si System, 2024
[7] Jochen Politze et al. Direct Electroplating on Indium-Tin-Oxide-Coated Textured and Polished Silicon Substrates via Transition Metal Alloyed Interlayers, 2022

Bath 1





- ✓ Aqueous solution containing ammonium hydroxide and copper(II) sulfate (pH ~12)
- ✓ Formation of copper-ammoniacal complexes in solution
- ✓ Chemisorption of copper(II) hydroxide on the TCO surface
- ✓ $Cu(OH)_2$ chemically bounds to the substrate and remains after rinsing

$$Cu^{2+}{}_{(aq)} + 4\,NH_{3\,(aq)} \rightarrow [Cu(NH_3)_4]^{2+}{}_{(aq)}$$

$$[Cu(NH_3)_4]^{2+}{}_{(aq)} + 2\,H_2O_{(l)} \rightarrow Cu(OH)_{2\,(s)} + 4NH_{3\,(aq)}$$

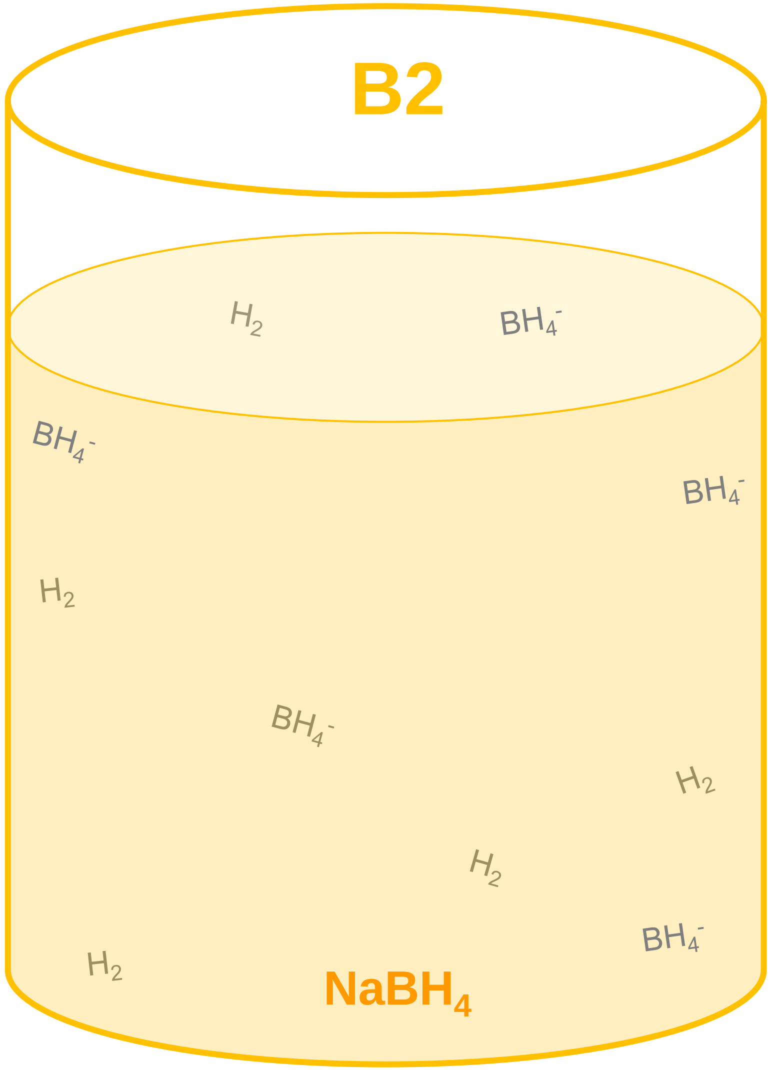
Bath 2

- ✓ Aqueous solution containing sodium borohydride
- ✓ $NaBH_4$ in water produces H_2, and both the hydride ions (BH_4^-) and the evolved hydrogen gas act as reducing agents
- ✓ BH_4^- reduces Cu^{2+} from copper(II) hydroxide to Cu^0
- ✓ Cu^0 catalyzes the reduction of In^{3+} (in In_2O_3) to In^0
- ✓ Reduction can occur directly via BH_4^- (through Cu) or indirectly via H_2 gas from BH_4^- hydrolysis

$$NaBH_4 + 2\,H_2O \rightarrow NaBO_2 + 4\,H_2 \uparrow$$

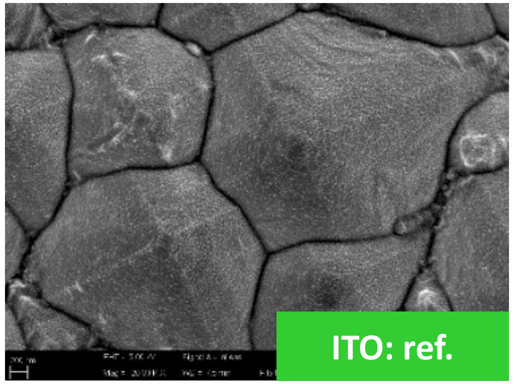
$$Cu^{2+} + 2e^- \rightarrow Cu^0$$

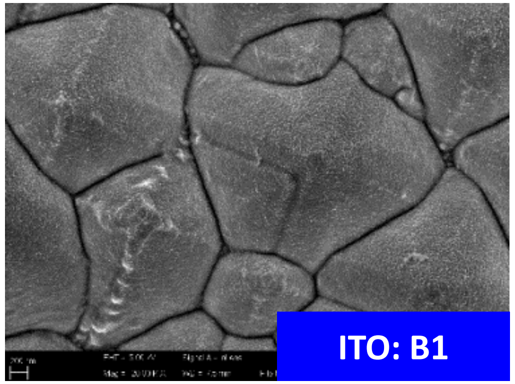
$$In_2O_3 + 3\,H_2 \xrightarrow{Cu^0} 2\,In^0 + 3\,H_2O$$

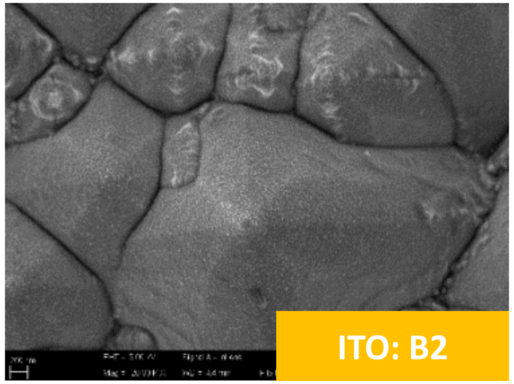


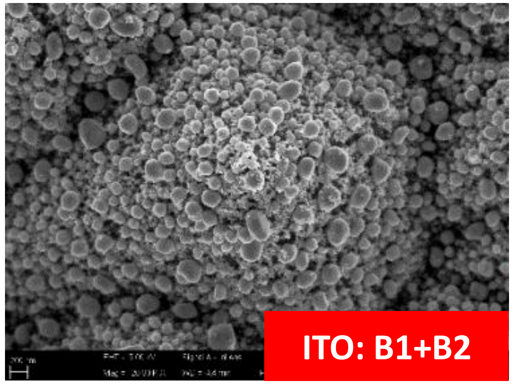
TCO Surface Chemical Treatment

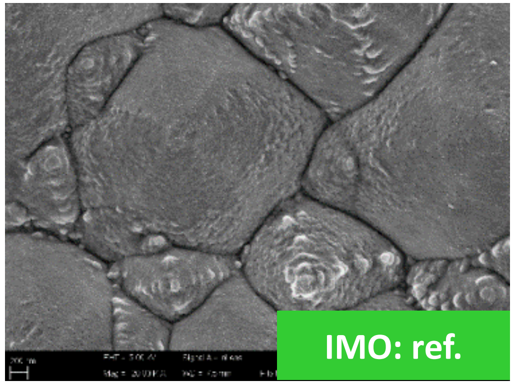
SEM

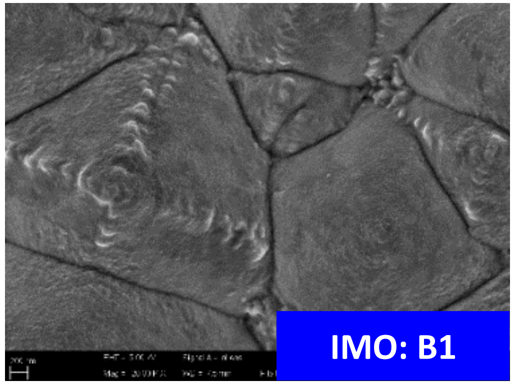


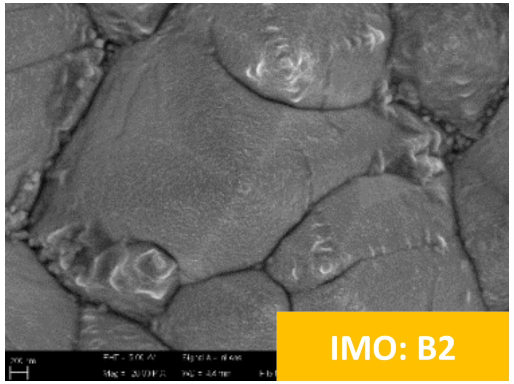


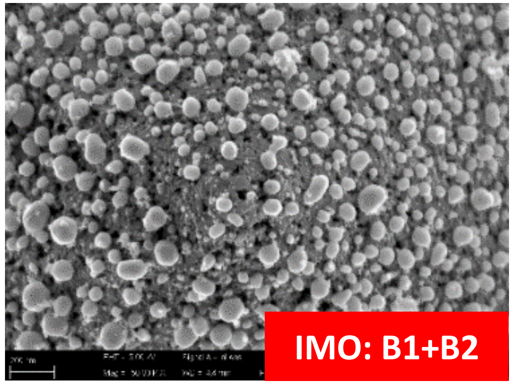






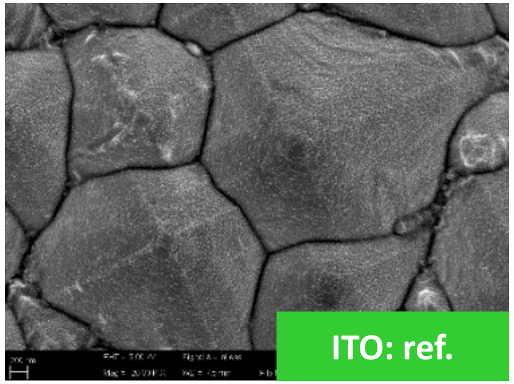


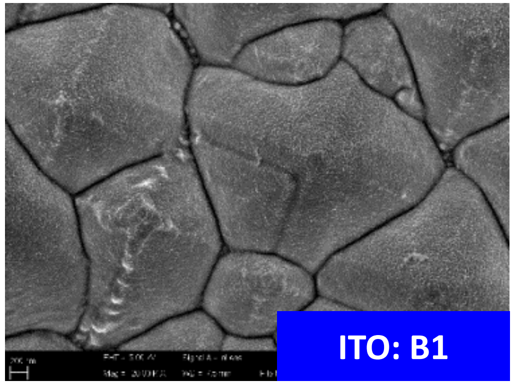


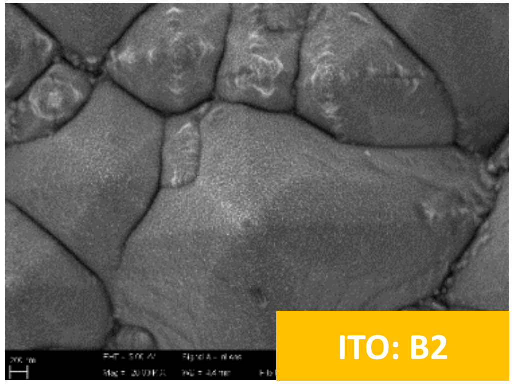


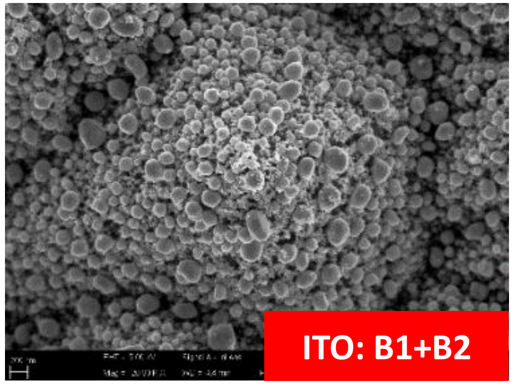
ITO Surface Chemical Treatment – B1+B2

SEM

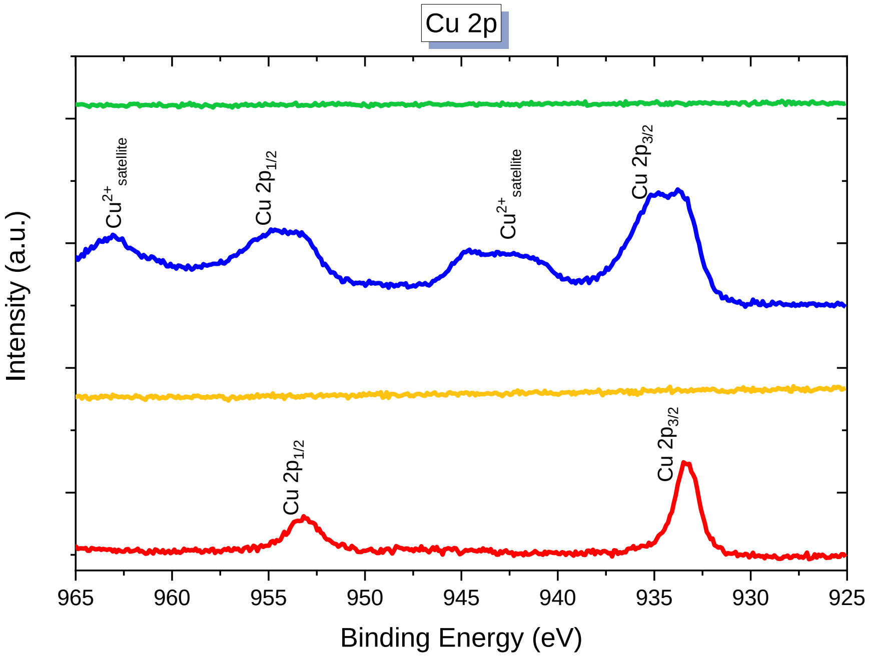


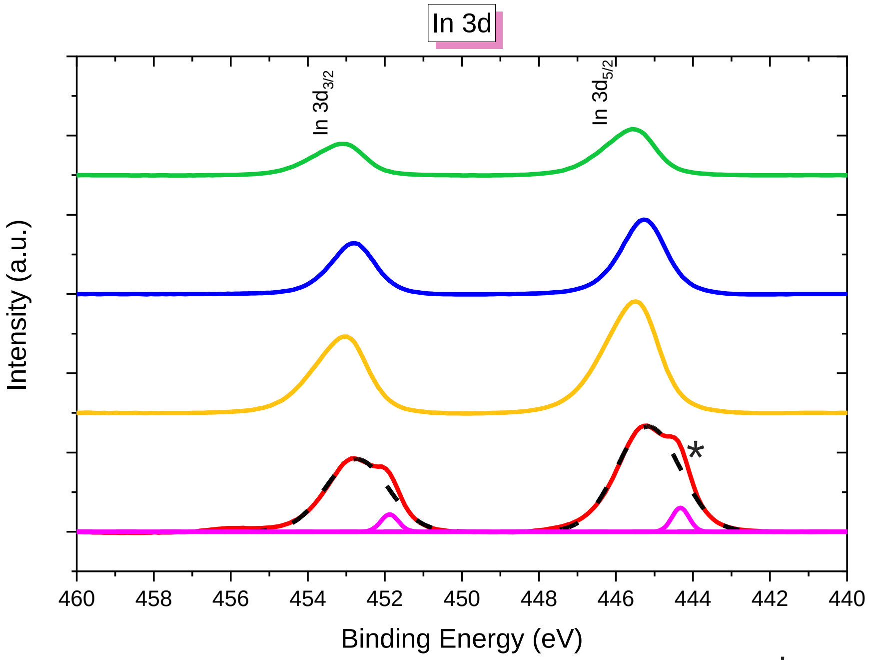






XPS

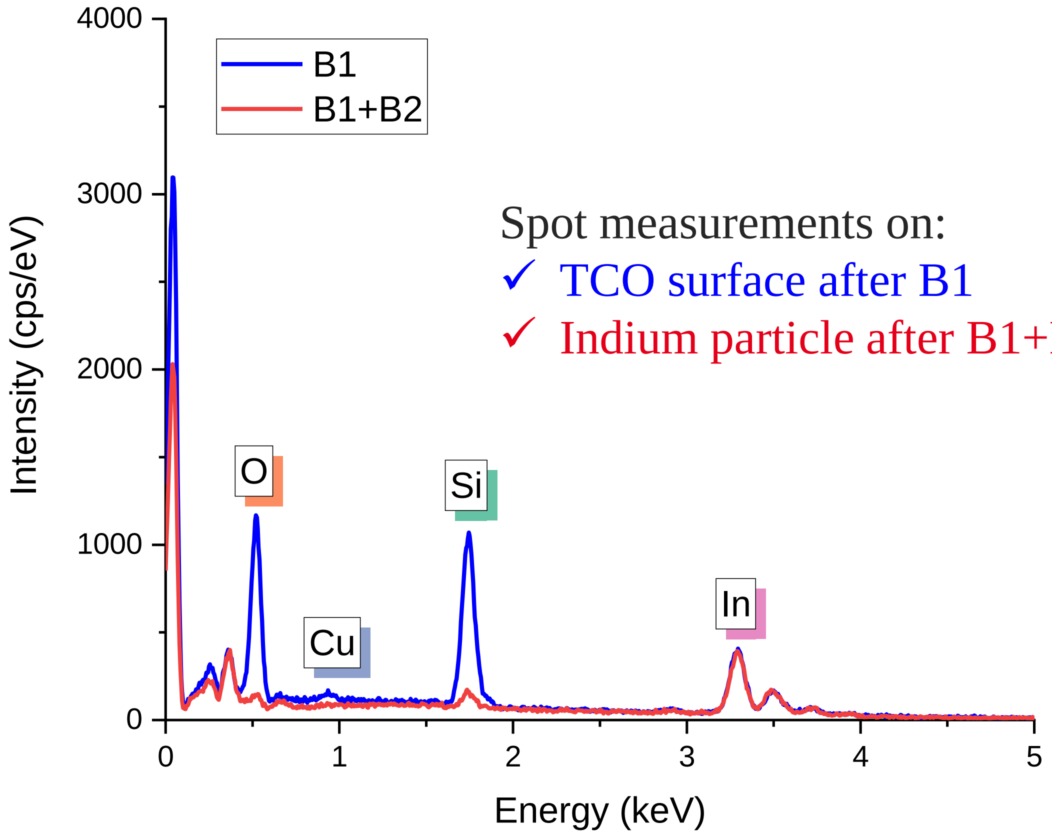




* After argon plasma etching

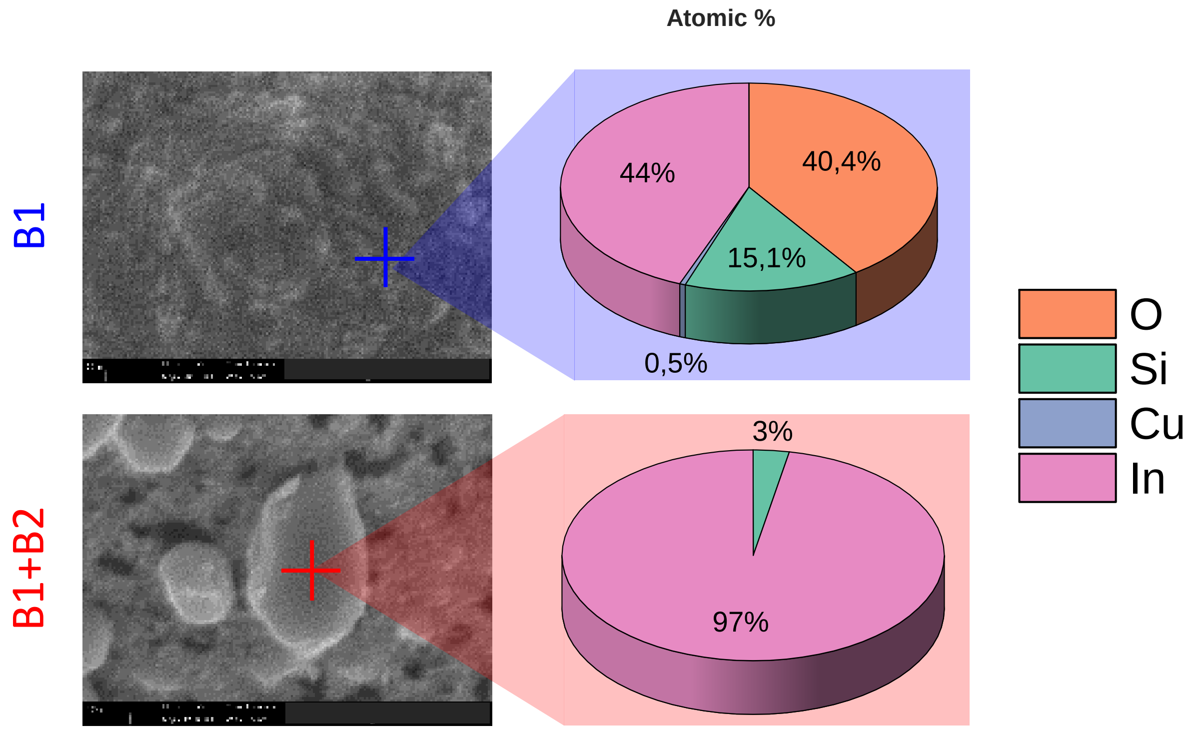
ITO Surface Chemical Treatment – B1+B2

SEM/EDX



Spot measurements on:

- ✓ TCO surface after B1
- ✓ Indium particle after B1+B2



EDX analysis confirms that the particles observed by SEM are composed mainly of indium.

Optimization of Seed-Layer-Free Electroplating

Experimental workflow

ECD on p-side performed under dark conditions

Bath 1
- ✓ Solution: fixed
- ✓ Duration: fixed
- ✓ Temperature: fixed

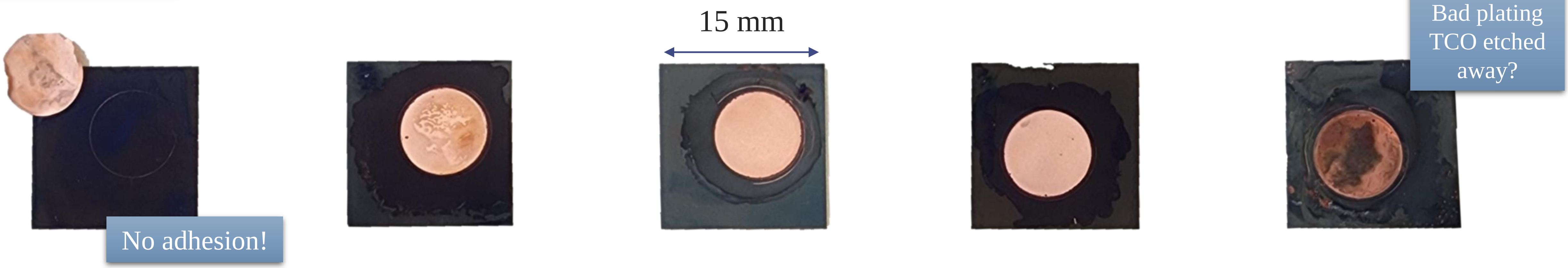
→

Bath 2
- ✓ Solution: fixed
- ✓ **Duration: variable**
- ✓ Temperature: fixed

→

Cu Electroplating
- ✓ pH 0
- ✓ $[Cu^{2+}]$ = 0,84 M
- ✓ J = 20 mA/cm²
- ✓ q = 25 C/cm²

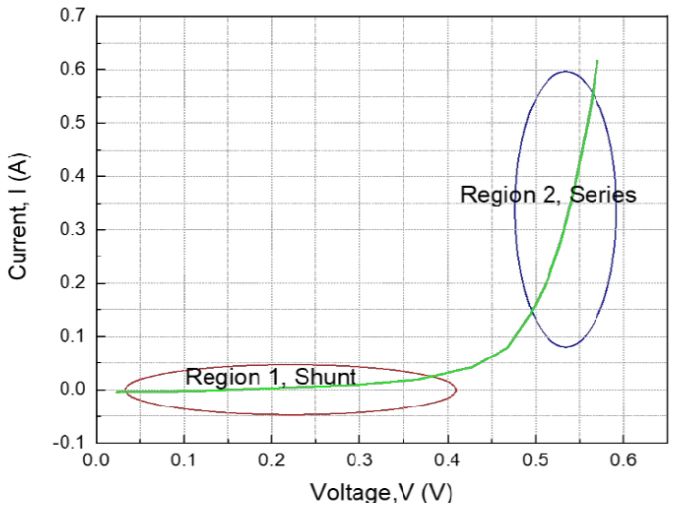
First results



Bath 2 duration

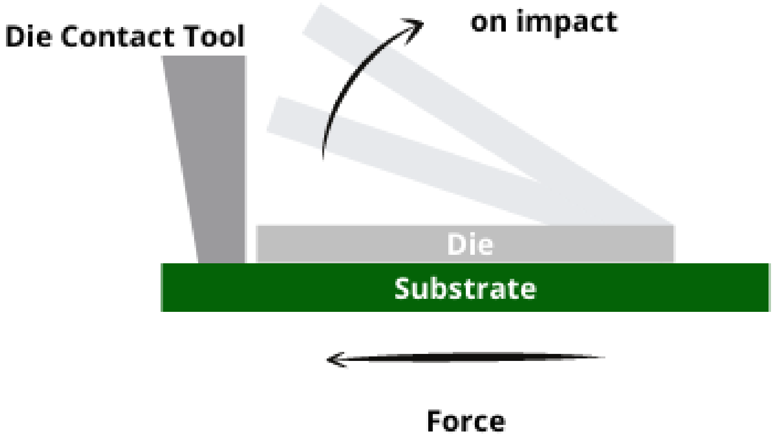
Samples Characterization

Electrical Contact
(Dark IxV)



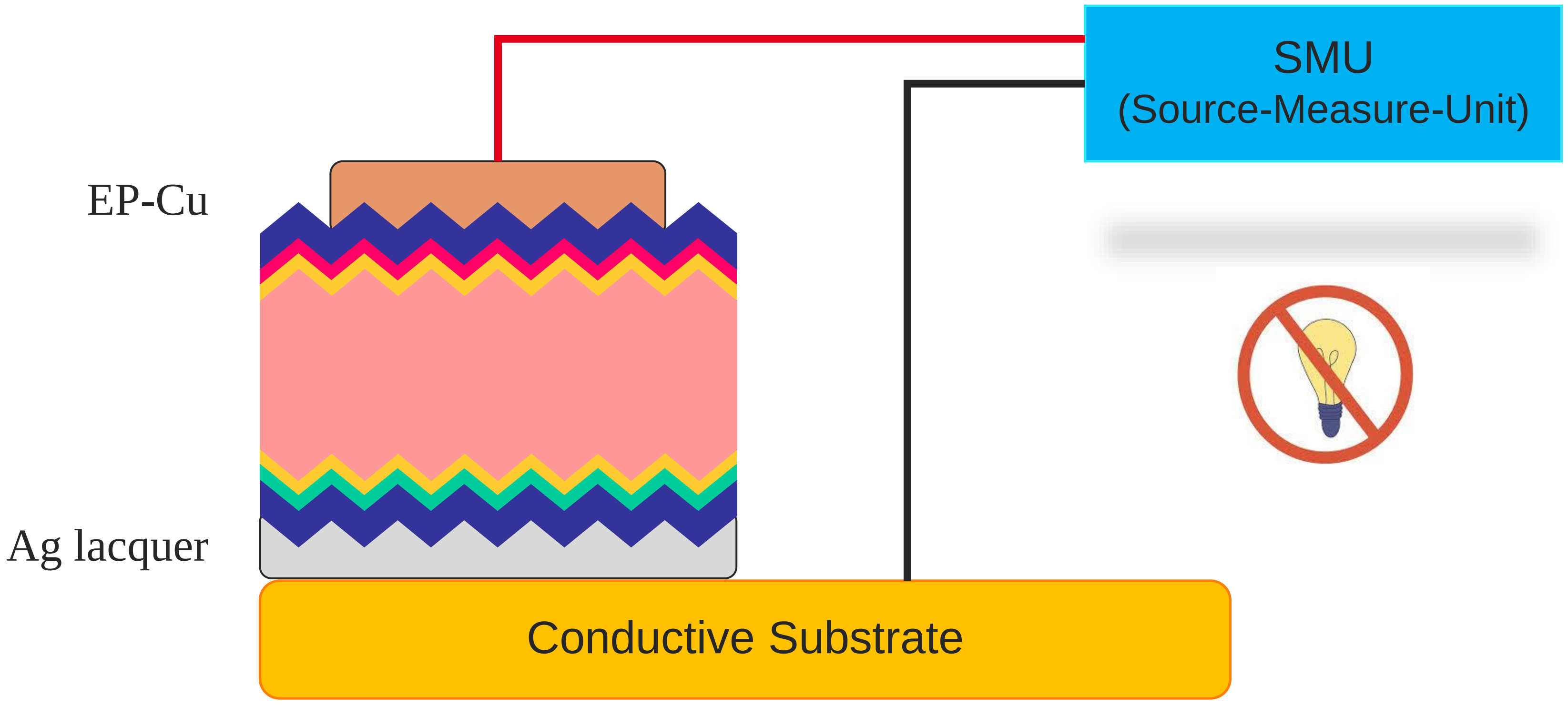
The concentration factor on the mixture of Ag paste and H 3 PO 4 solution as a dopant paste for contact formation in silicon solar cells, 2023

Mechanical Adhesion
(Shear Strength Test)

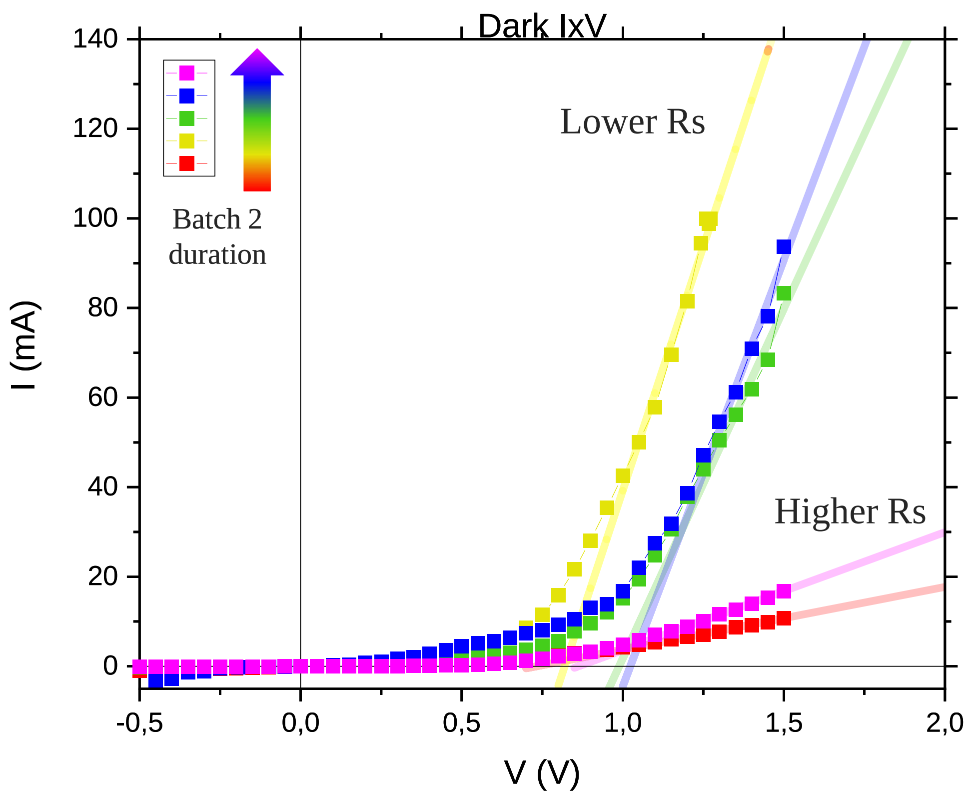


https://www.reltronix.com/semiconductor-testing/mechanical-test/die-shear/

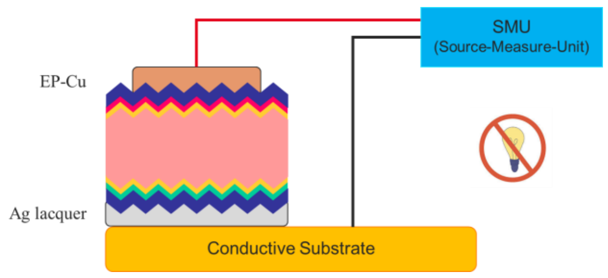
Electrical Contact – Dark IxV



Electrical Contact – Dark IxV

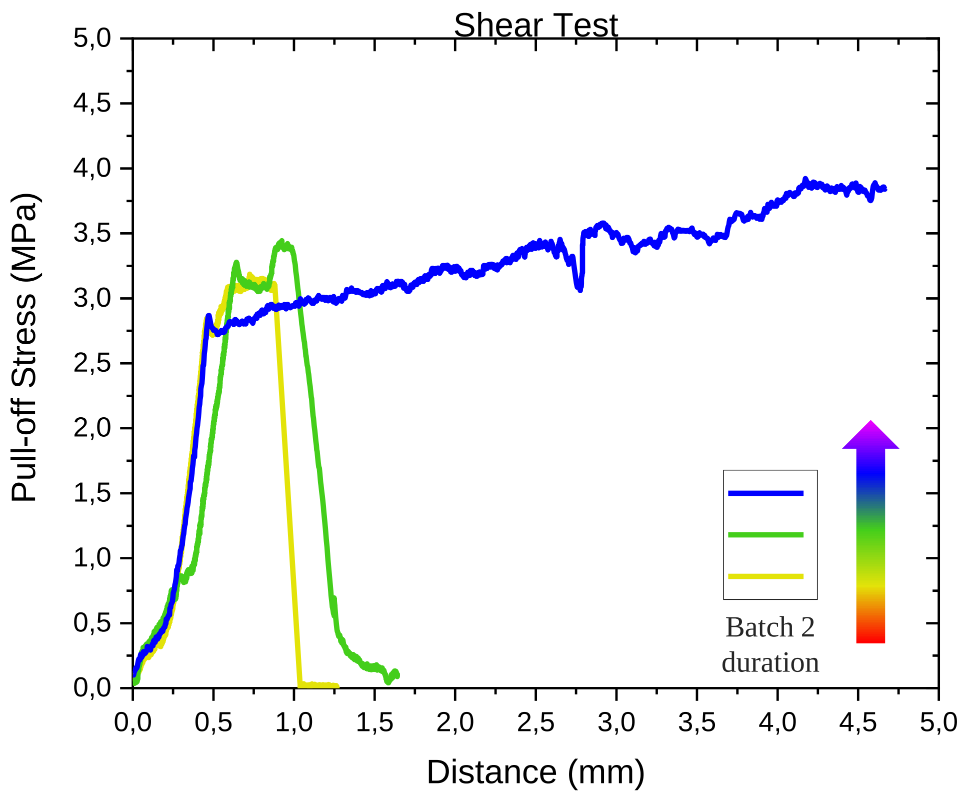


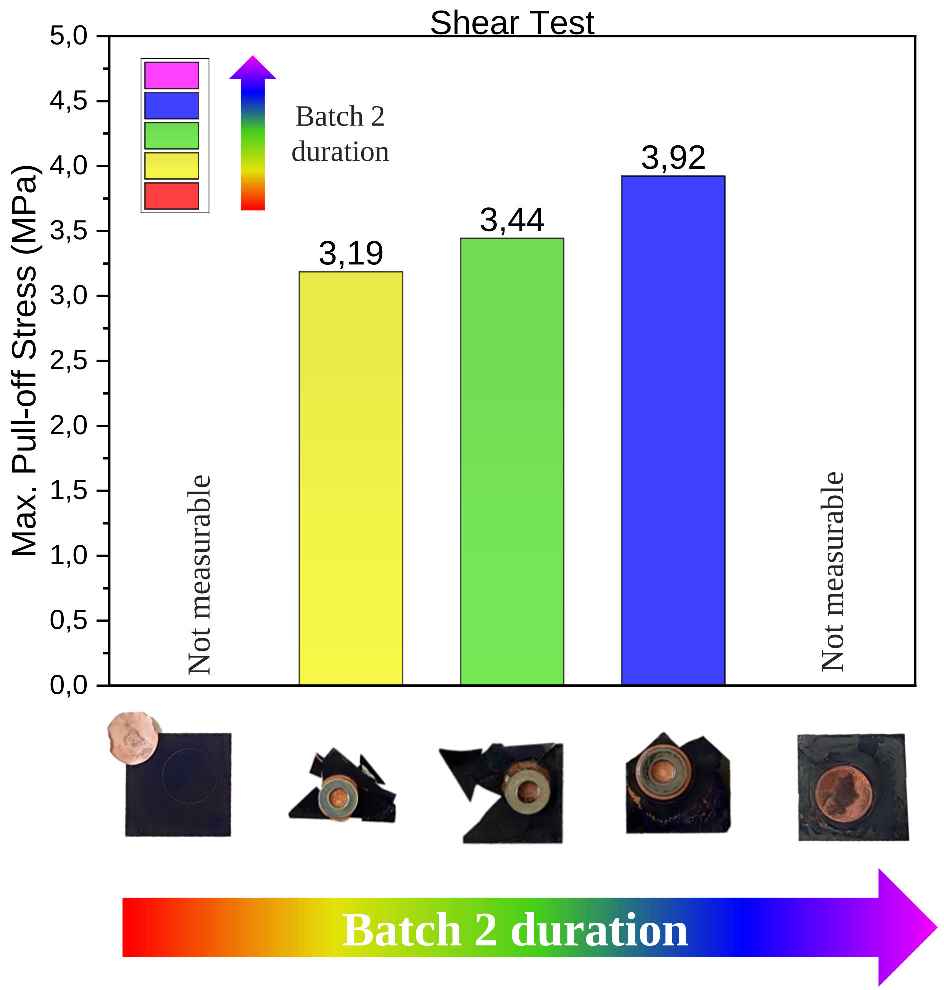
Electrical contact was enhanced by TCO surface treatment prior to Cu EP. Best performance was achieved for intermediate bath 2 durations.



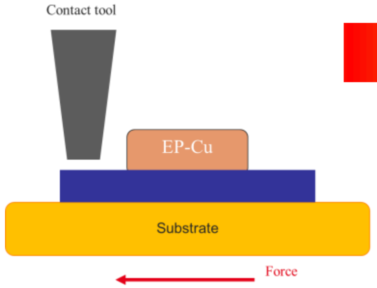
Multiple measurement points on the same sample to assess repeatability and homogeneity

Mechanical Adhesion - Shear Strength Test





Substrate fracture occurring before Cu delamination is a strong indicator of good adhesion, suggesting the actual maximum pull-off stress could be even higher.

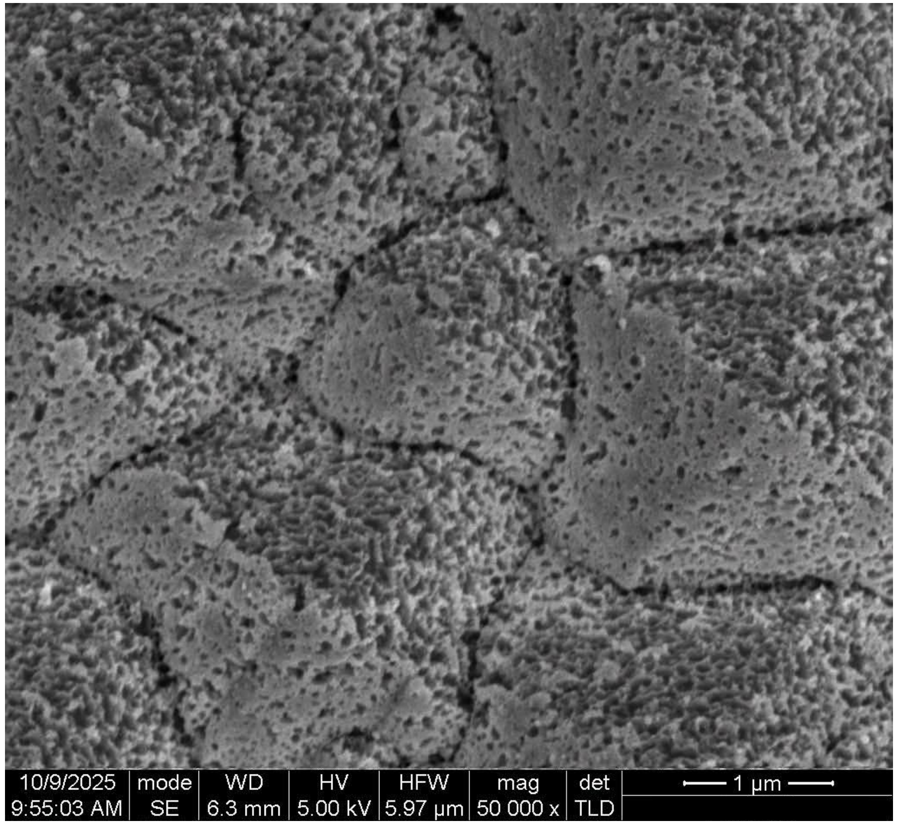


TCO/Cu interface after Shear Strength Test

SEM

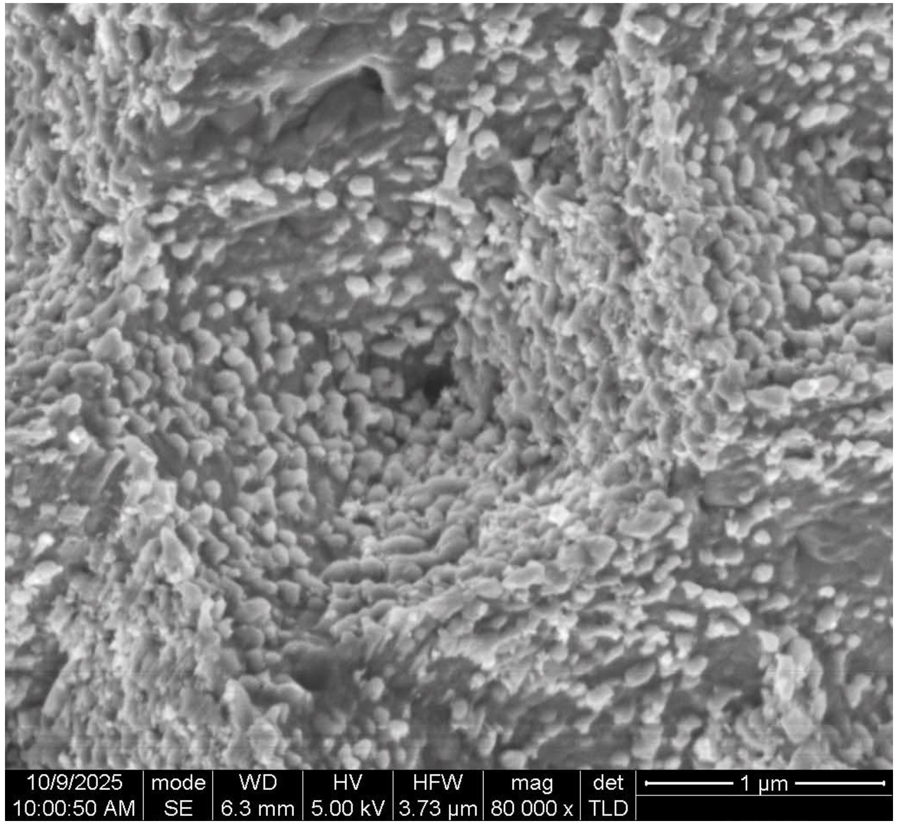
TCO side

Voids on TCO surface after particle detachment



Cu side

Indium particles adhered to Cu layer



Indium particles exhibit enhanced bonding with the plated Cu, indicating that the failure occurs predominantly at the TCO interface.

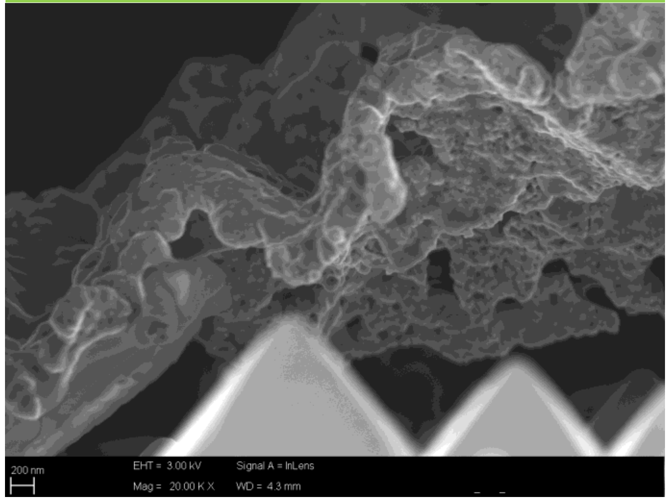
Conclusions

- ✓ Wet-chemical treatment enables **direct Cu metallization on ITO without seed or barrier layers**
- ✓ Homogeneous Cu growth with **strong adhesion**
- ✓ Batch process allows treating multiple cells at once - **industrial compatibility**
- ✓ **Simple chemical process:** no PVD, electrical contacts or potentiostat required (masking still needed)
- ✓ **Proof of concept** demonstrated on small-scale samples
- ✓ **Patent** filed for the surface treatment process

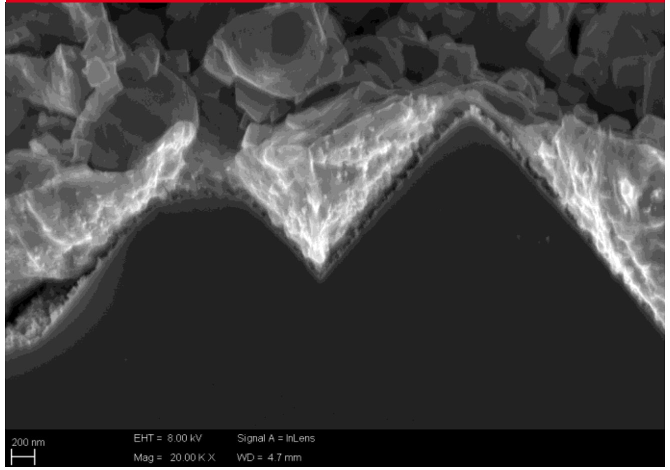
Perspectives

- ✓ **Benchmarking** against alternative seed layer approaches
- ✓ Scaling up to **larger samples**
- ✓ Full **process optimization** to enhance adhesion and electrical performance
- ✓ Extension to **other TCOs** (e.g., IMO)
- ✓ Porosity and barrier function assessment to evaluate and control **Cu diffusion**

Untreated TCO surface



Treated TCO surface



Thank you for your attention!

Special thanks to colleagues from CEA-INES and ICMPE

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