A Breakthrough in Plating for Solar Cell Metallization

M. Balucani[1,2] S. Quaranta[1]

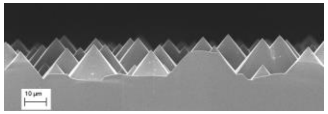
[1] DIET-Sapienza University of Rome, Via Eudossiana, 18 - 00184 Roma (ITALY),
[2] Rise Technolgy S.r.l., Lung.re P. Toscanelli 170 – 00121 Roma (ITALY),

Agenda / Outline / Overview

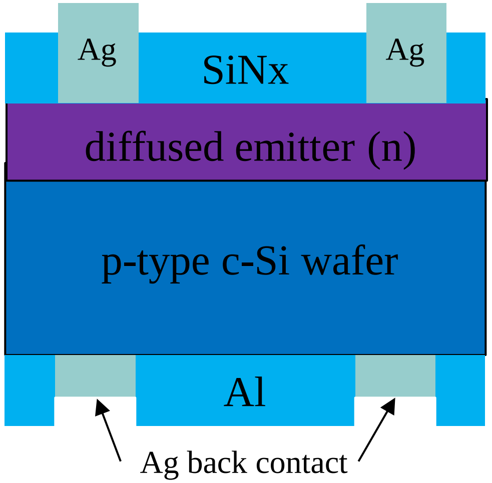
- **Introduction**
  - **Solar cell and cost pressure**
- **History and State of the art**
  - **Plating Techniques**
  - **Technology Key Issues of Plating in Solar Cell**
  - **Localized Plating**
- **Our Approach** **(A Breakthrough in Plating for Solar Cell Metallization)**
  - **DLD/DLM**
    - **Main results achieved**
    - **On going work (H2020 AMPERE Project)**
- **Acknowledgement**
- **Conclusions**

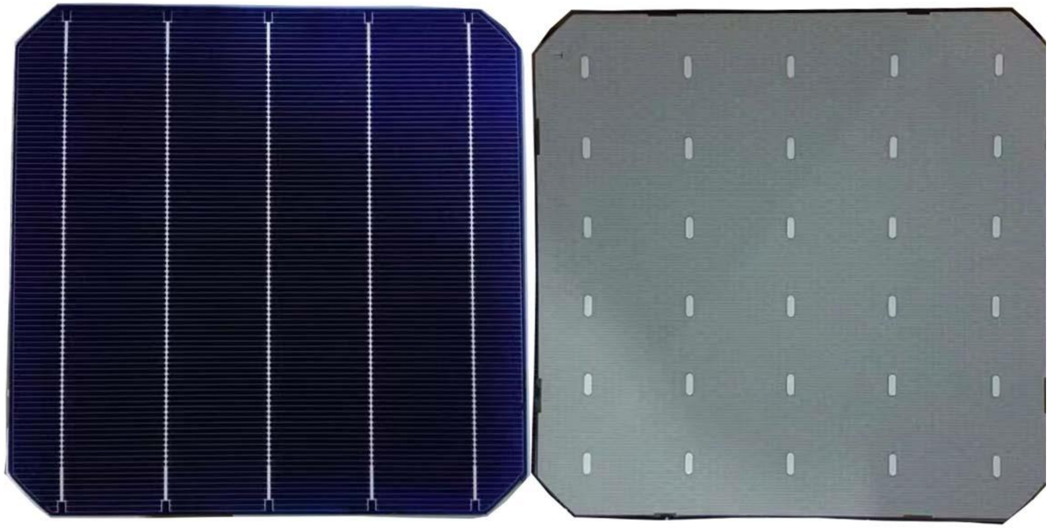
Introduction

- Solar Cell *World wide production capacity > **110GW***



A solar cell, or photovoltaic cell, is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect, which is a physical and chemical phenomenon. It is a form of photoelectric cell, defined as a device whose electrical characteristics, such as current, voltage, or resistance, vary when exposed to light.





ITRPV 2018

	Market Share	Efficiency	trend for such technolgies
Al-BSF	75%	16.0 < η < 20.0%	- (2028 ~ 7%)
PERC/PERL/PERT	22%	19.0 < η < 22.5%	+ (2028 ~ 60%)

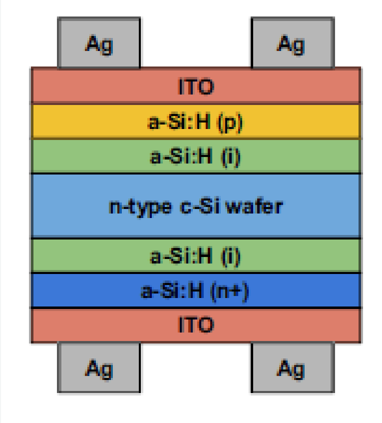
M. Balucani et al.

Introduction

- Silicon HeteroJunction (SHJ) Solar Cell *$\eta >$ 22.0%*

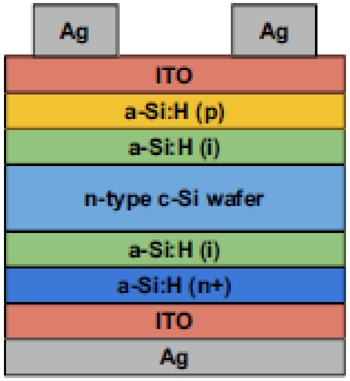
Ref. SHJ

$\eta \geq 22.4\%$



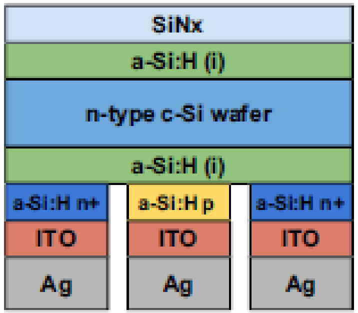
PVD SHJ

$\eta \geq 22.7\%$



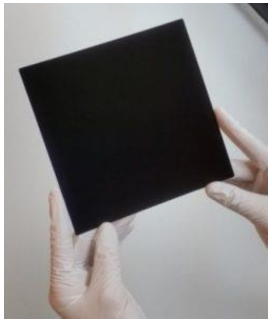
IBC SHJ

$\eta \geq 23.3\%$



η_{record}=26.63%

size (180 cm^2)



Kaneka Corporation

AMPERE

AUTOMATED PHOTOVOLTAIC CELL AND MODULE INDUSTRIAL PRODUCTION TO REGAIN AND SECURE EUROPEAN RENEWABLE ENERGY MARKET

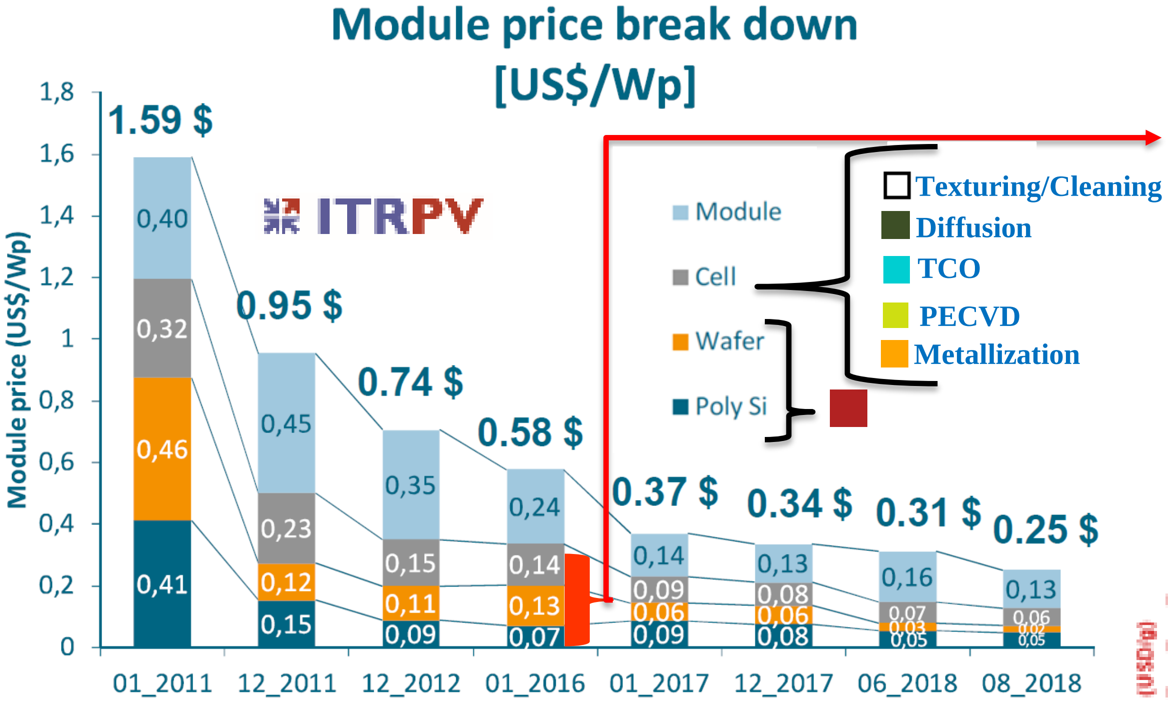
April 2020 η=22.5% bifacial cell

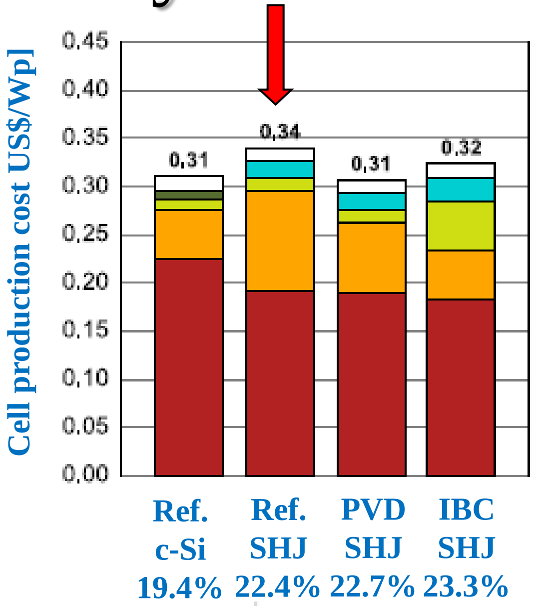
at industrial level full scaled automated cell line100MW

Look to solutions for η=23.5%

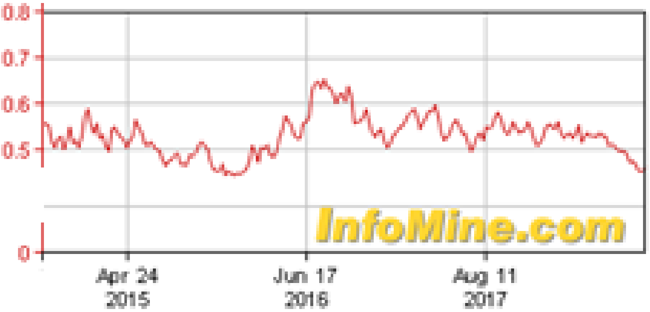
Introduction

- Cost Pressure Increasing Tremendously in SC



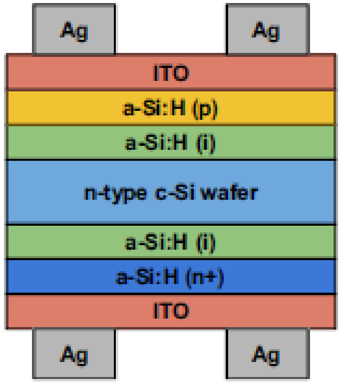


15% < Metallization influence cost ($/Wp) < 30%
on Solar cell production cost



Introduction

- Ag $/g influences Tremendously solar cell cost



Low temperature Ag paste ≈ 0.7$/g

Sheet resistance post curing is not bulk Ag: (Temp < 200° C)

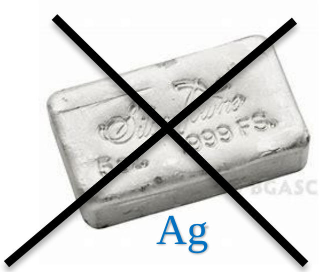
$$5\,\frac{m\Omega}{\square} < R_{sq\ @25\mu m} < 25\,\frac{m\Omega}{\square}$$

$$8.5\cdot\rho_{Ag\ bulk} \qquad 42.5\cdot\rho_{Ag\ bulk}$$

Specific contact resistance $1 m\Omega\cdot cm^2$ to $4 m\Omega\cdot cm^2$

Bi-facial SHJ Ag/cell (5BB) ≅ 0.2g → 0.14$/cell $\xrightarrow{22.5\%}$ 0.073 $/Wp →0.34$/Wp → 21.4%

↑η ⟷



→

6.19 $/Kg $\approx \frac{A_g\ price}{100}$, $\rho_{Cu}=1.1\cdot\rho_{Ag}$

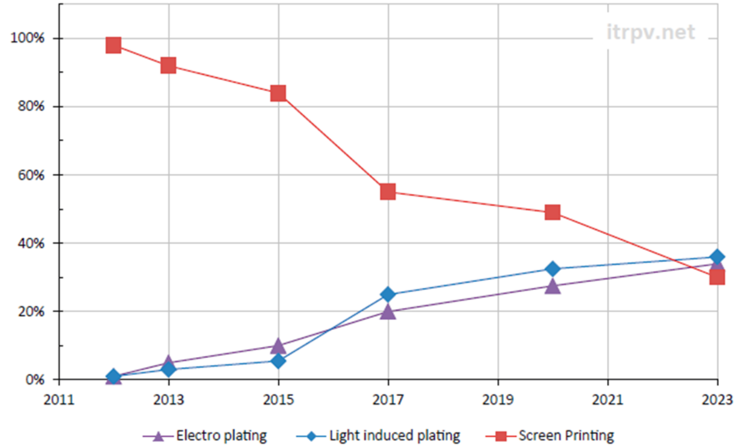
Electroplating the only industrial solution

History and State of the art

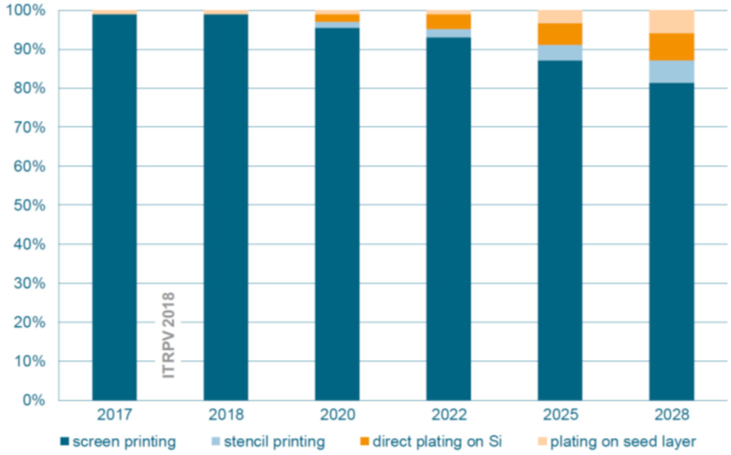
Plating Technique in Solar Cell

Before the introduction of alternative metallization techniques, technical issues in reliability and adhesion have to be solved. Appropriate equipment also needs to be available. **(ITRPV)**

ITRPV 2013
Market share

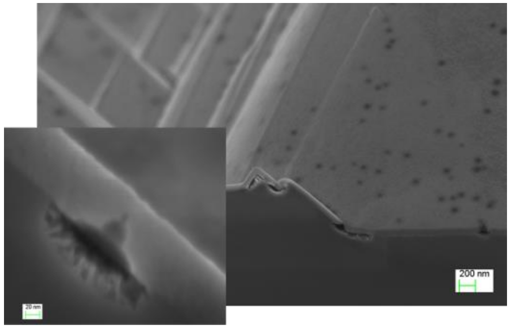


ITRPV 2018
Market Share



Plating key issues

- ➢ Copper not directly in contact with silicon!!!!! → Need Barrier Layer
- ➢ Pin-holes and Scratches
- ➢ Adhesion (> 1 N/mm)
- ➢ Speed of Plating → Throughput, Space floor and Chemical quantities
- ➢ Drag-out → Reduce additive consumption

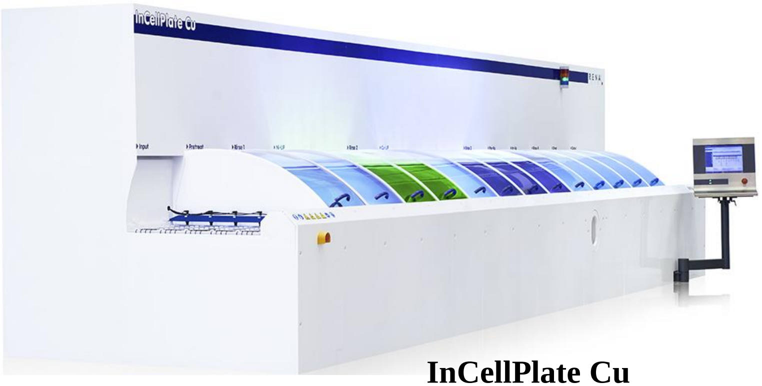


State of the art

- Industrial Plating for Solar Cell
  - LIP or LAP

BE Semiconductor Industries N.V.

Meco Direct Plating Line (DPL)
(www.besi.com/products-technology/productgroup/plating/com)



InCellPlate Cu
www.rena.com

R|E|N|A|

State of the art

- Industrial Plating for Solar Cell
  - Plating seed layer

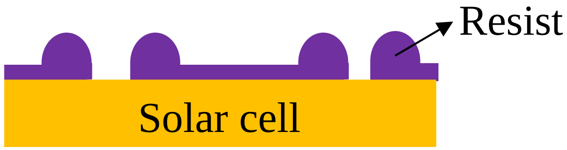
Meco CPL - Plating on seed layer
https://www.besi.com/products-technology/product-details/product/meco-cpl/

Whatever plating industrial technique you use is necessary to use Protective MASK

MEYER BURGER

PiXDRO JETx P
Inkjet printing equipment for solar cell fabrication

Alternative to printing:
Apply a film and open it by laser



State of the art

- Plating Issues
  - Mask + Plating  ≈ Ag
  - Adhesion ….to silicon …..to TCO
  - Speed of plating……..

Industrial line for 100MWp is:

≈ 30 – 45 m long !!! HUGE FLOOR SPACE!!!!!

Solution make-up is >1500 liter

!!!!!

!!!!!

Is there a possible solution that could solve all these plating issues

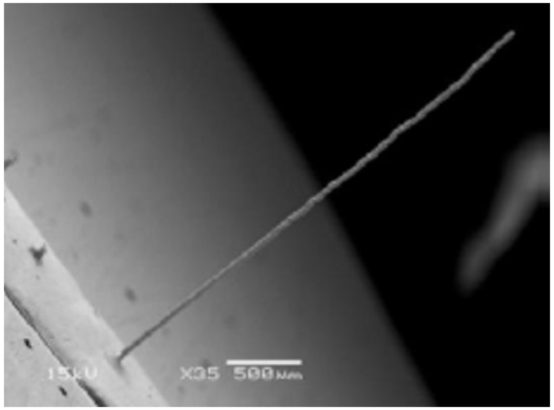
Selective Plating Process and a Fast process

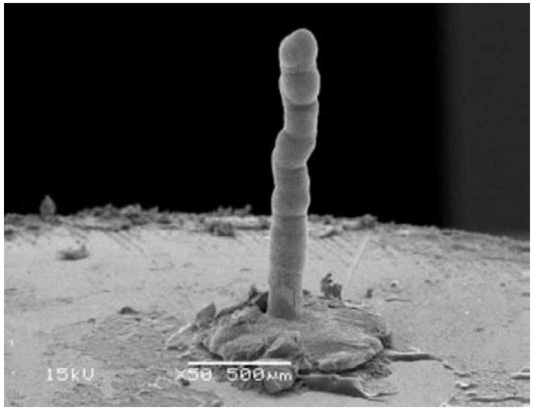
Without using RESIT or PHOTORESIST

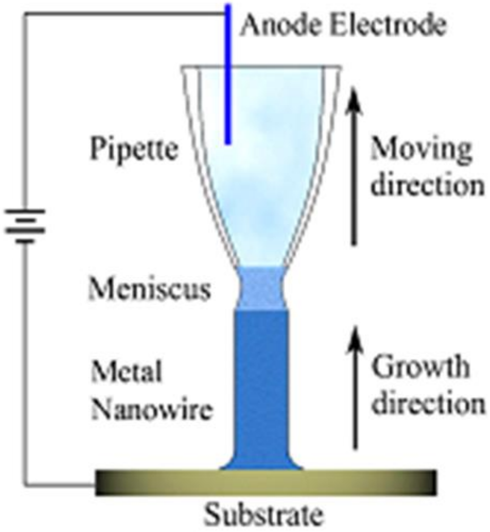
State of the Art: Localized Plating

Localized electrochemical deposition (LECD)

Static Meniscus







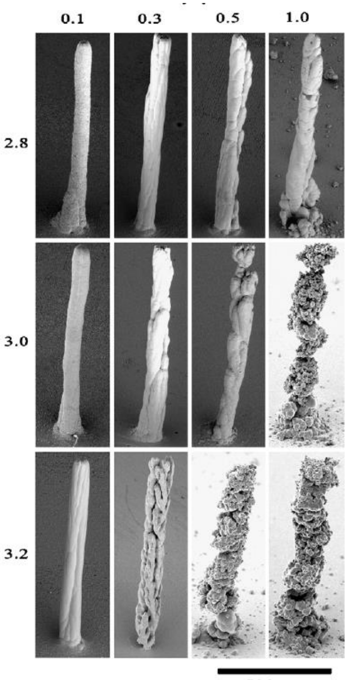
Main Issues:

- ➢ **No Refreshment of solution**
- ➢ **High current density: strong bubbling**
- ➢ **Base footprint dimension**

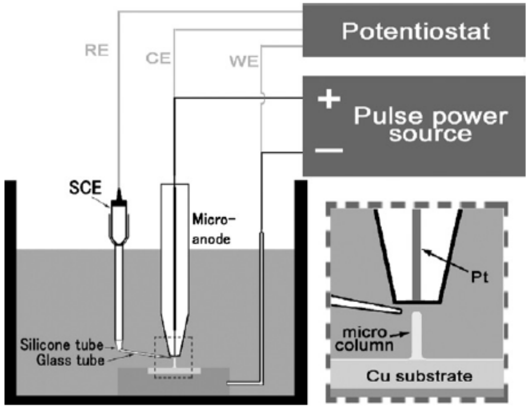
[R. A. Said Nanotechnology 14 (2003) pp. 523–53]

State of the Art: Localized Plating

Localized electrochemical deposition (LECD)



[1,2]Microanode guided Electroplating (MAGE)



Cu deposition rate up to 867 μm/min

<u>Main Issues</u>:

(1) Electrode must be quite close to cathode (i.e. < 50 μm)

(2) Very difficult to keep confined the plated area: reduced only for (1) < 5μm

(3) Necessary to move the micro-anode

(4) Porous structure due to very low convection contribution

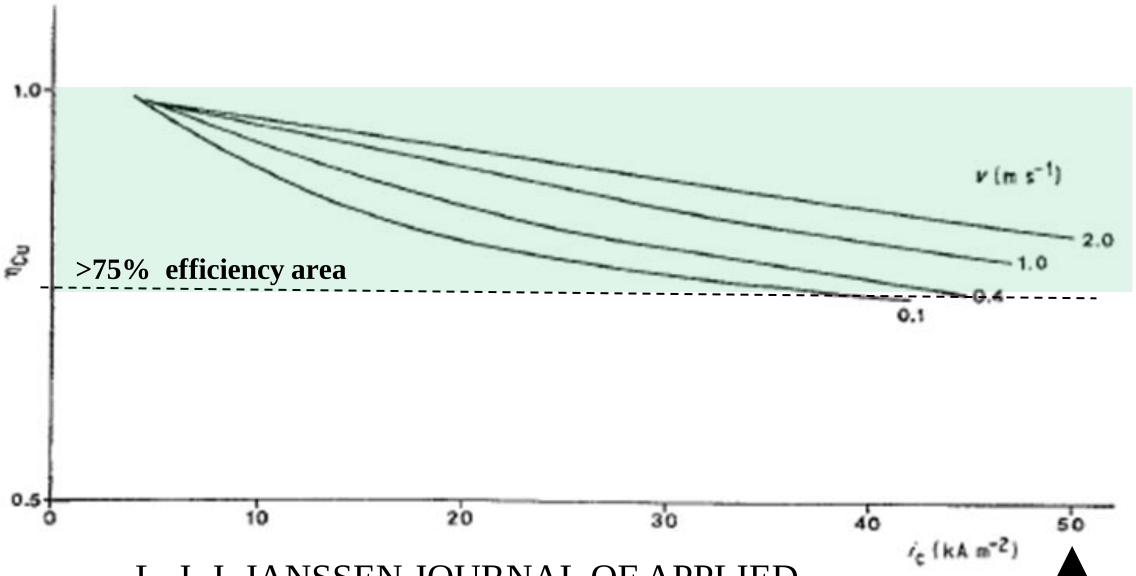
1] E. M. El-Giar et al. Journal of The Electrochemical Society, 147 (2) 586-591 (2000)

2] J.C. Lin et al. Electrochimica Acta 55 (2010) 1888–1894]

State of the Art: Localized Plating

Mass transport of copper ions in the electroplating process is theoretically governed by the Nernst–Planck equation:

$$F_{ion} = -D\nabla c - \frac{nF}{RT} D c \nabla \varphi + c v \qquad [\text{mol s}^{-1}\,\text{m}^{-2}]$$



L. J. J. JANSSEN JOURNAL OF APPLIED ELECTROCHEMISTRY 18 (1988) 339-346

IBM by Jet plating (1)
Record of Cu deposition
50 µm s^{-1}
J=150 A cm^{-2}

Not porous and very nice morphology

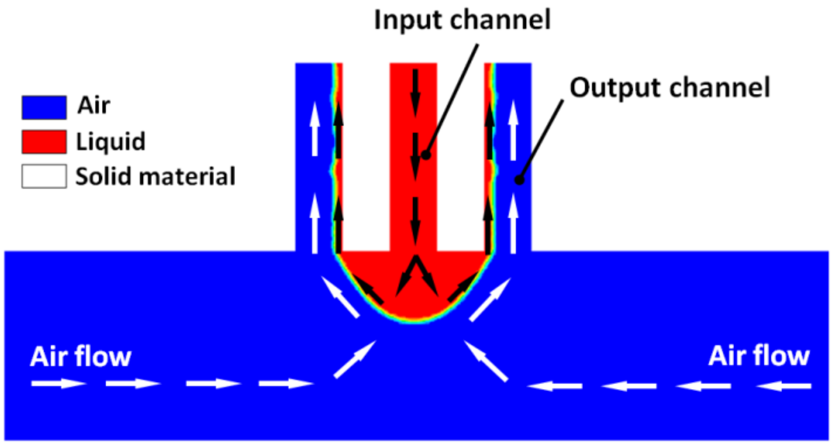
(1) R. J. von Gutfeld and D. R. Vigliotti, High-speed electroplating of copper using the laser-jet technique, Appl. Phys. Lett. 46, (1985), pp. 1003-1005

~2 µm s^{-1} Cu deposition rate

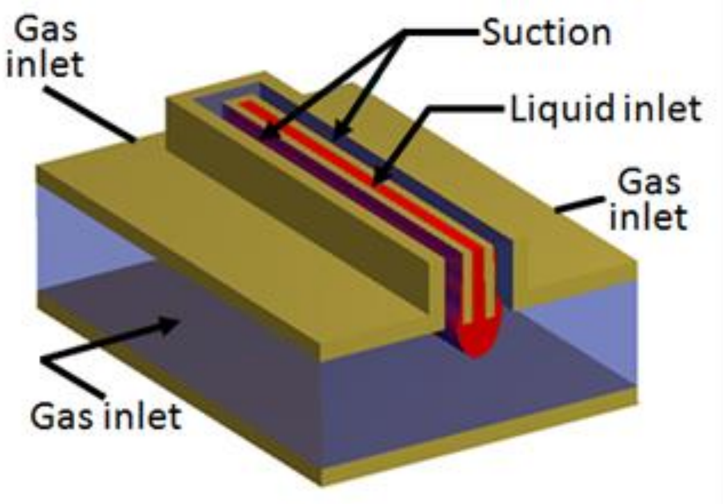
WHAT WE LOOK FOR

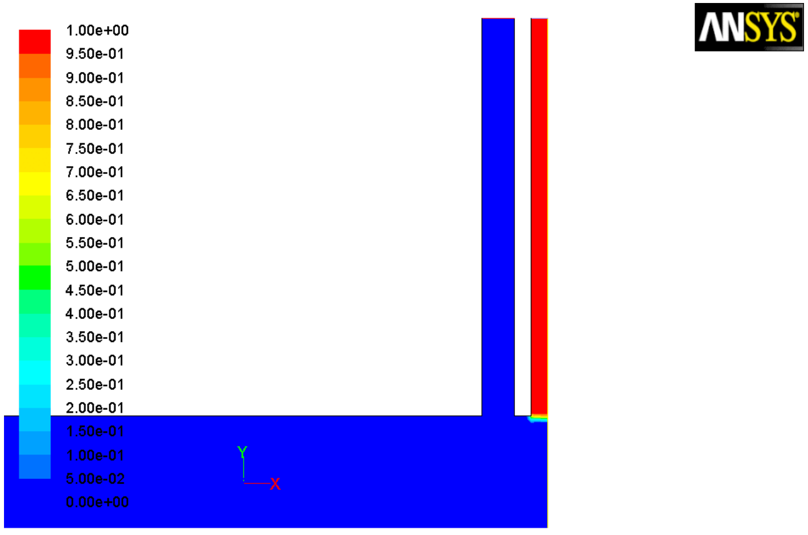
- Don’t want to use resist or photoresist
  - Confined plating
- Want to have fast plating regimes
  - Non-porous structure …as low as possible !!!
  - Low chemical consumption, small footprint and reasonable make-up (<300 litre)
  - Find a process to guarantee adhesion

Our Approach: DLD



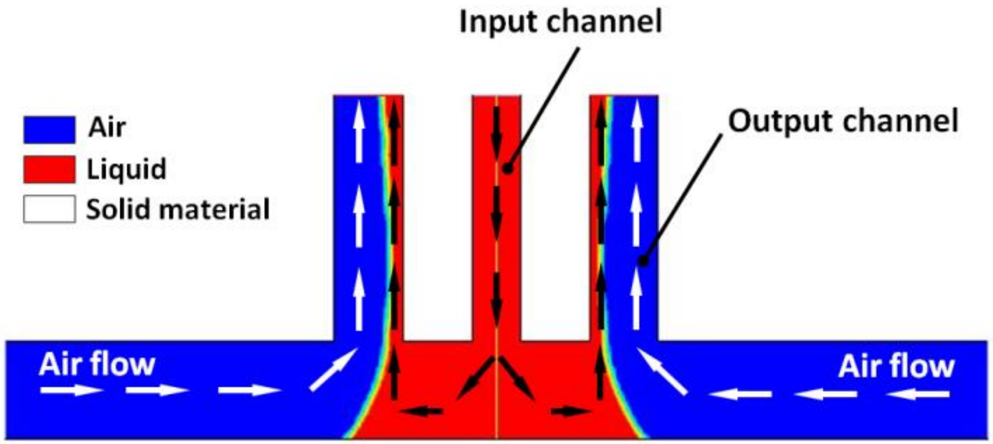
Dynamic Liquid Drop DLD



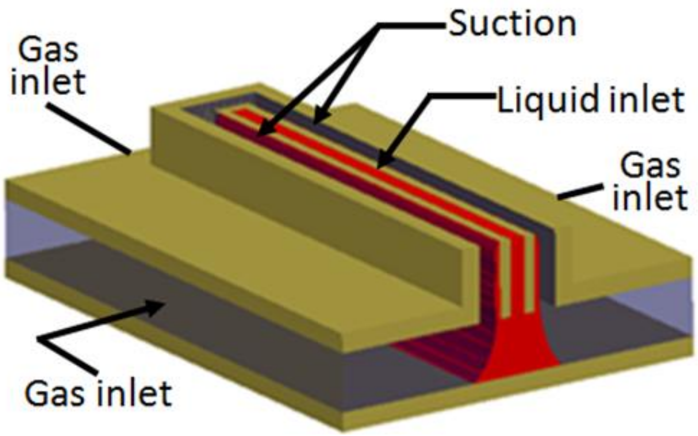


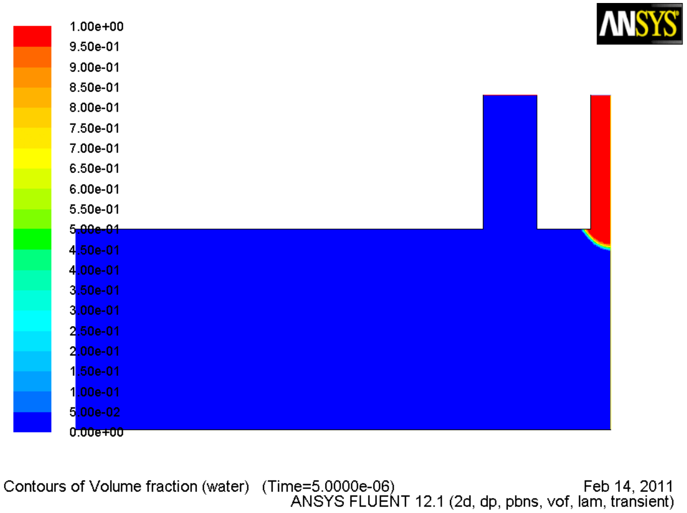
Contours of Volume fraction (water) (Time=5.0000e-04)
ANSYS FLUENT

Our Approach: DLM



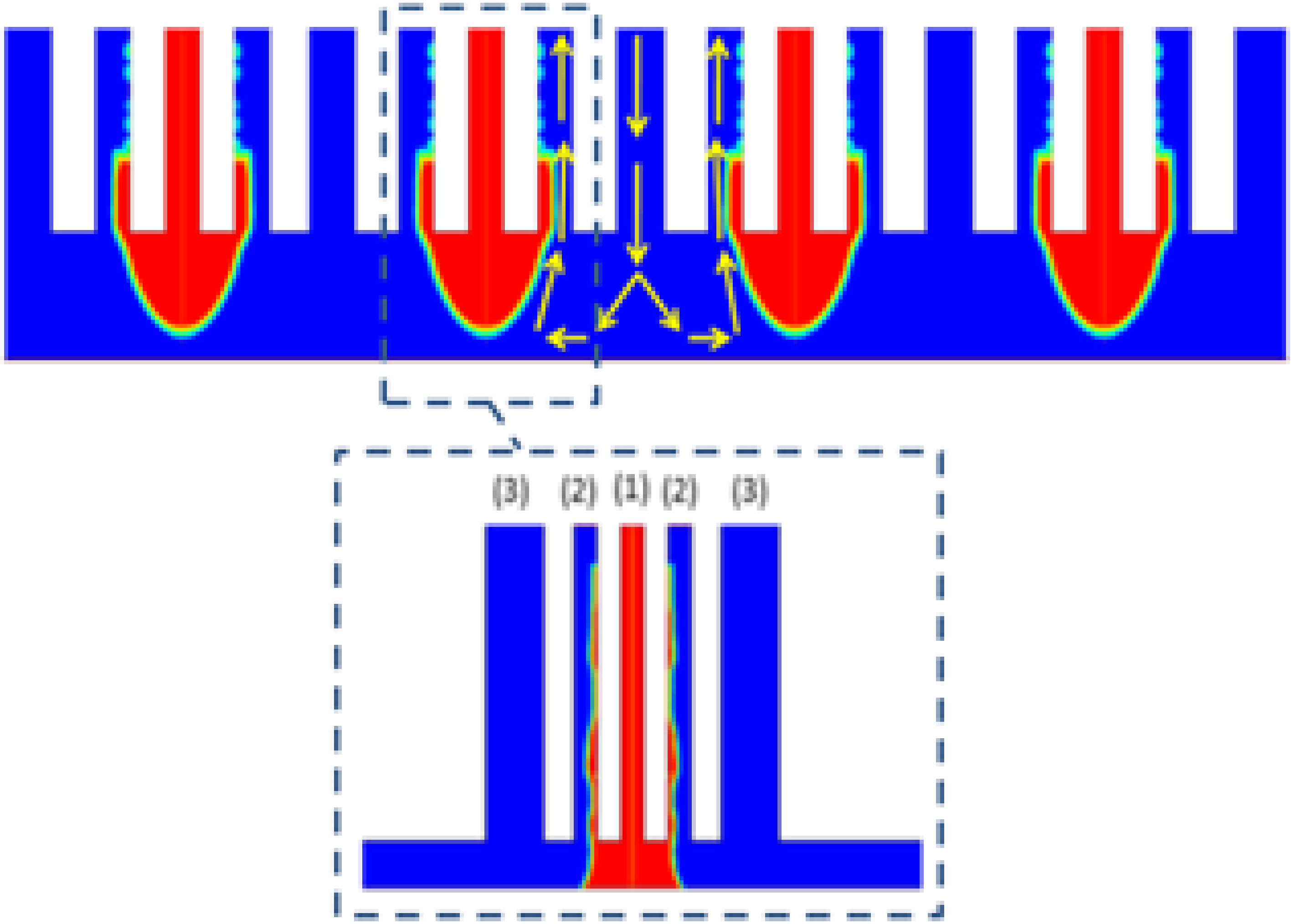
Dynamic Liquid Meniscus DLM





Contours of Volume fraction (water) (Time=5.0000e-06) Feb 14, 2011
ANSYS FLUENT 12.1 (2d, dp, pbns, vof, lam, transient)

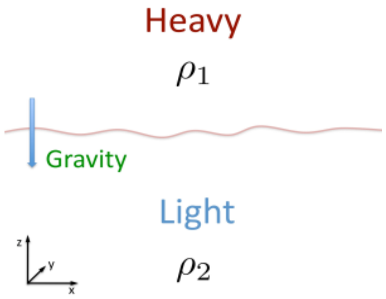
Dynamic Liquid Multi Drop/Meniscus

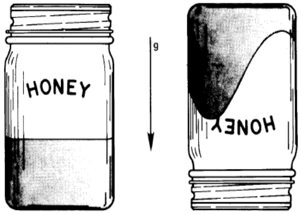


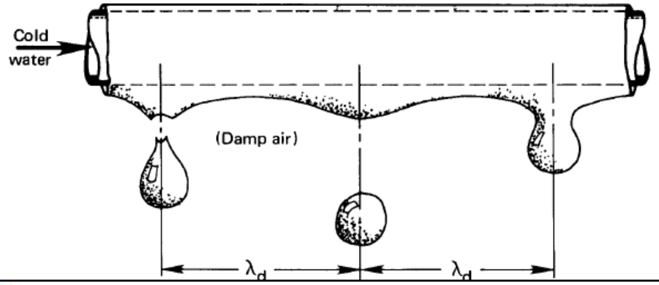
DLD/DLM: Problem to solve

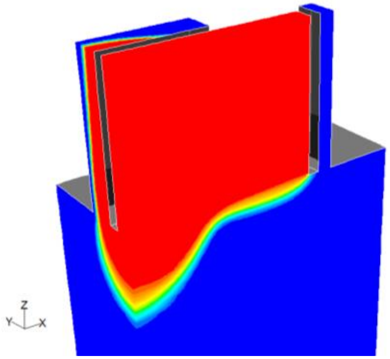
Rayleigh Taylor (RT) instability:

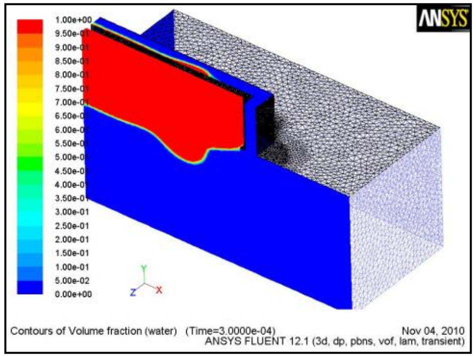
When a heavy fluid is supported by a light fluid, the system is RT unstable



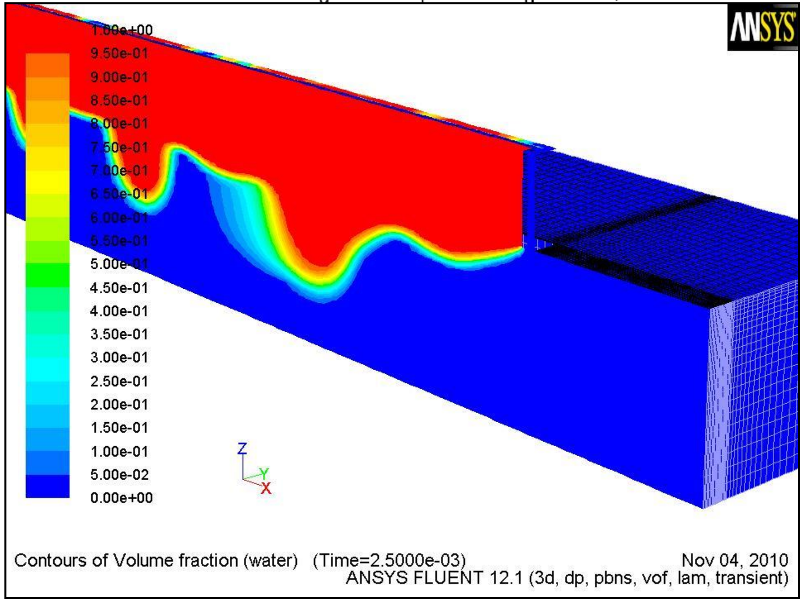






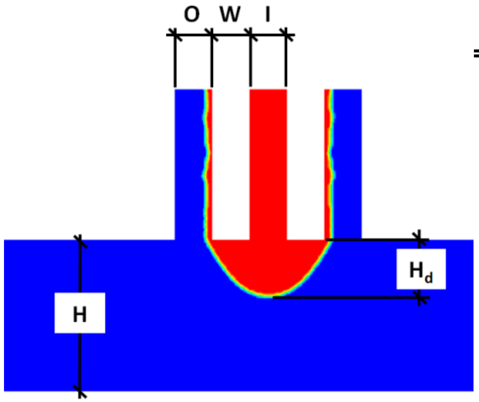


Contours of Volume fraction (water) (Time=3.0000e-04) Nov 04, 2010
ANSYS FLUENT 12.1 (3d, dp, pbns, vof, lam, transient)

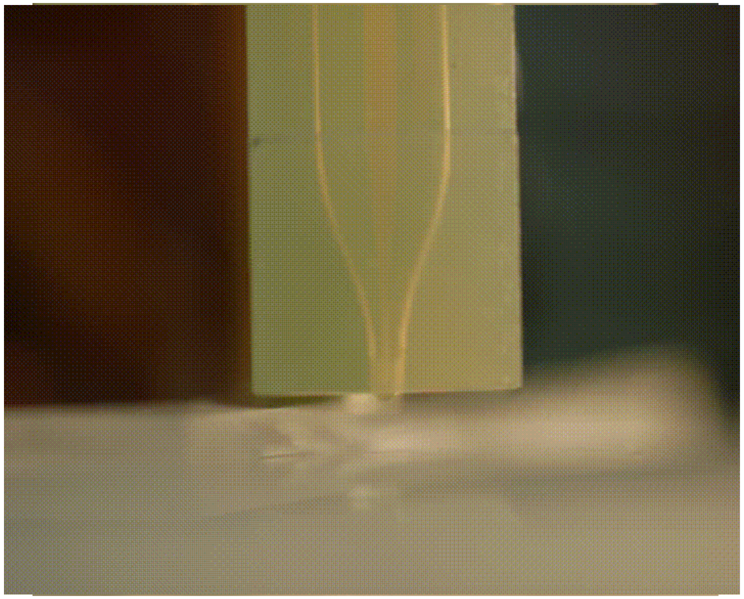


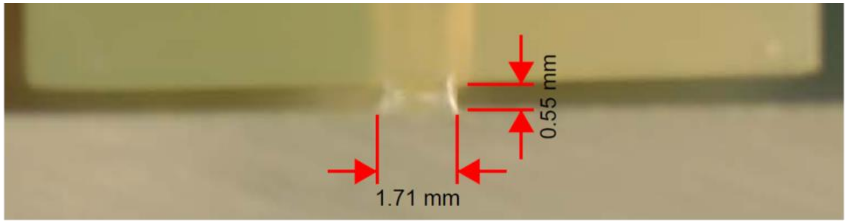
Contours of Volume fraction (water) (Time=2.5000e-03) Nov 04, 2010
ANSYS FLUENT 12.1 (3d, dp, pbns, vof, lam, transient)

Simulation and Experimental Results

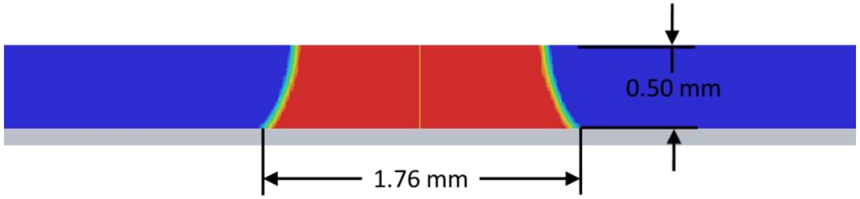


I (μm)	W (μm)	O (μm)	H (μm)	V_{inlet} (ms^{-1})	Δp (Pa)	Re_{Liquid}	H_d (μm)
500	500	500	2000	0,45	1000	437	733
300	300	300	1000	0,5	1500	291	573
100	100	100	600	0,8	2000	155	213
70	70	70	600	0,9	2500	122	187
50	50	50	300	1	3000	97	118
30	30	30	200	1,25	3500	73	73
15	20	20	75	1,5	4000	44	32





Experimental result

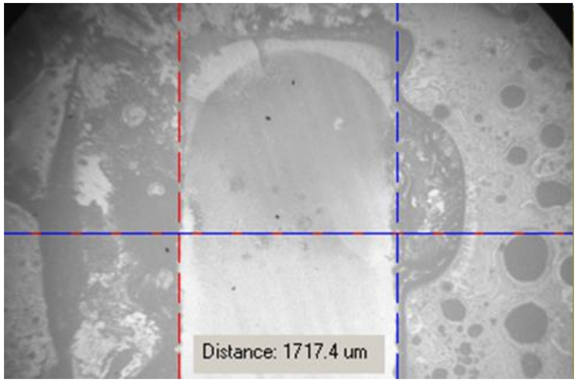


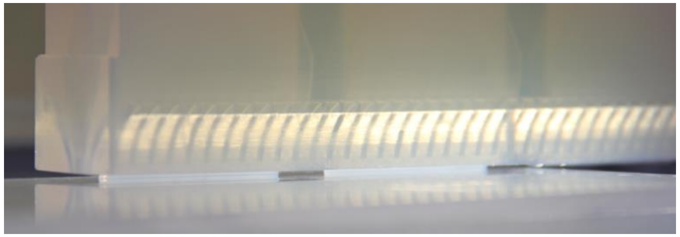
CFD result

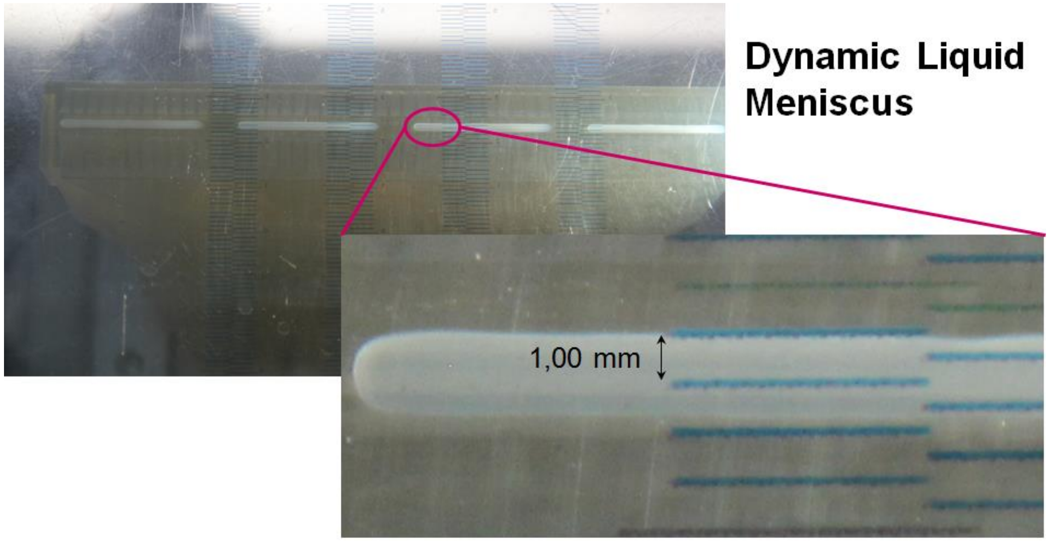
Simulation and Experimental Results

	I (µm)	W (µm)	O (µm)	H (µm)	V_{inlet} (ms^{-1})	Δp (Pa)
Nozzles operating conditions	500	500	500	2000	0,4	2000

	TEST	CFD
Dynamic drop height (µm)	570	590
Dynamic meniscus footprint (µm)	1710	1760
Air volume flow rate (l/min)	60,5	63,9

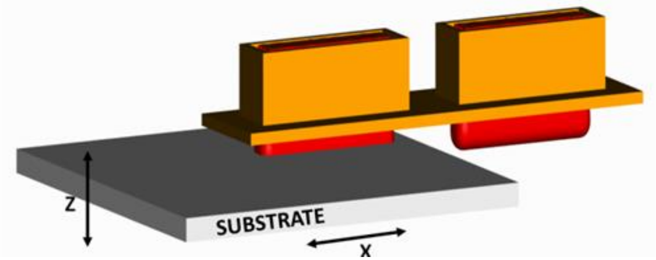






Dynamic Liquid Meniscus

PV and Cu Pillar Application:
Continuous or Stop-Go



M. Balucani et al.

Equipment Evolution in Time

https://www.youtube.com/watch?v=xDIsubIi5EM

Search in you tube "meniscuspad"

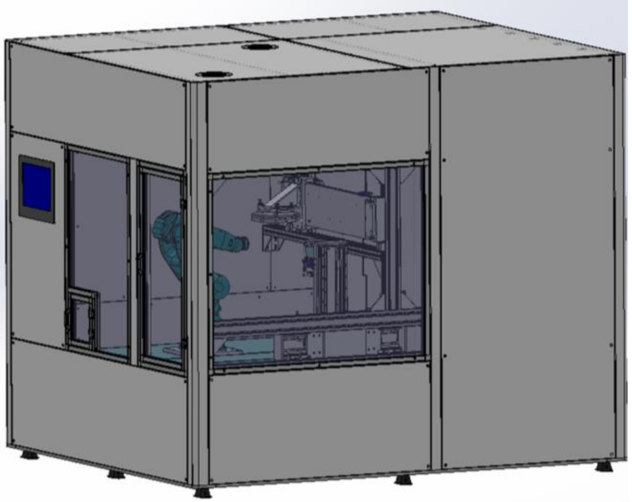
2011

2012

2013

2014

2016



January 2019

Micro Nozzles

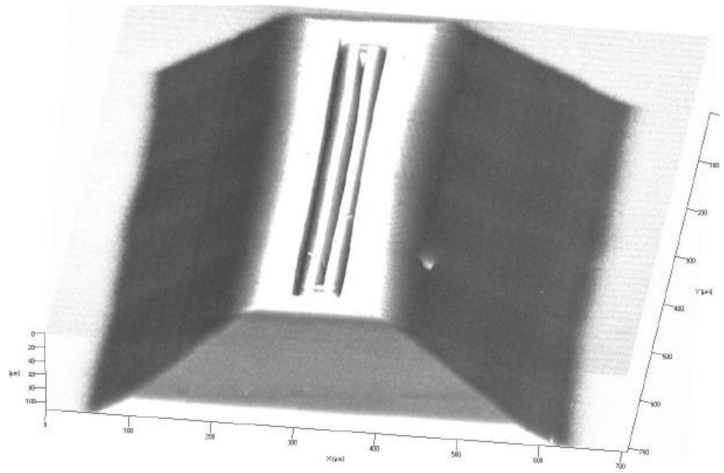
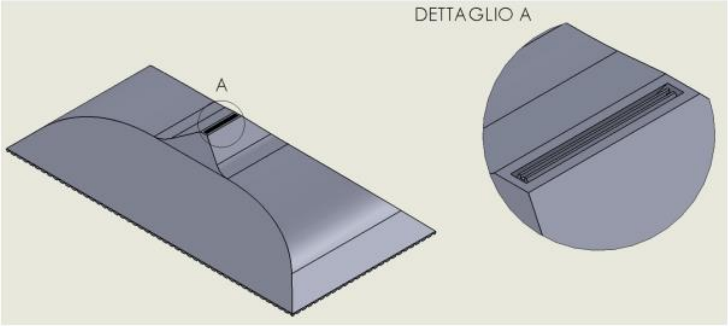
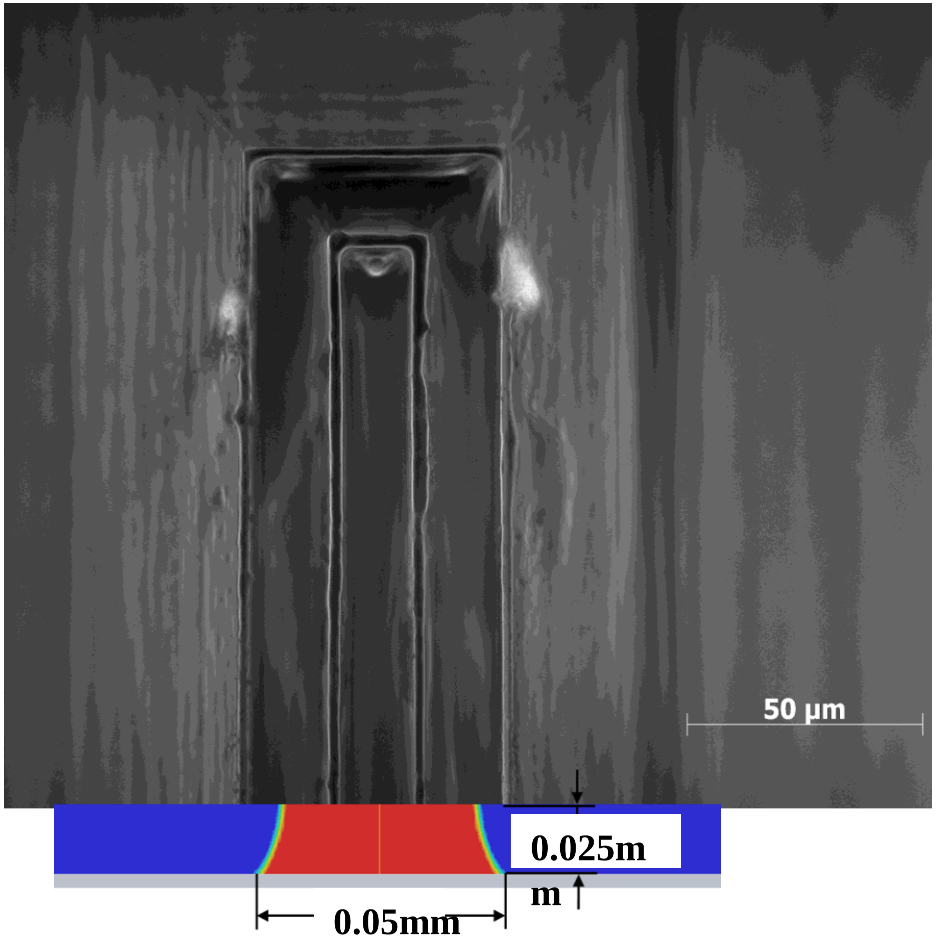


Figura 154: Immagine del micro-ugello finale fatta al microscopio confocale

Microugello MN_12.5_7_15_V02.2

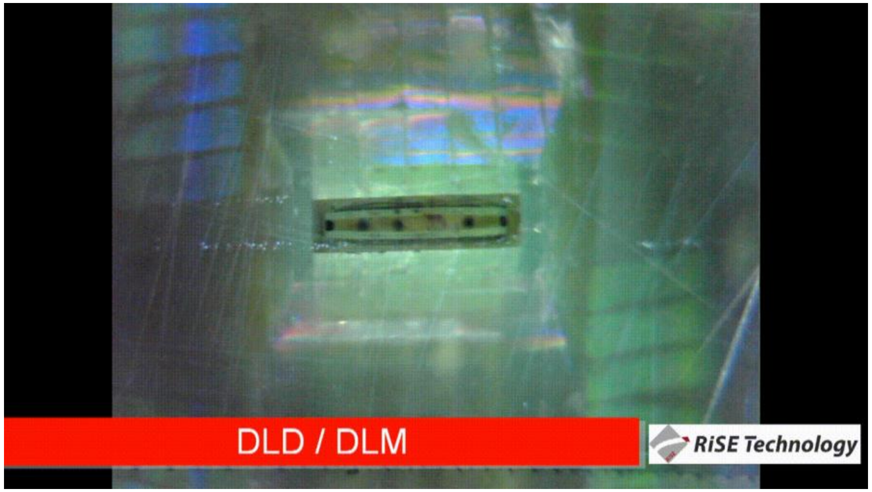


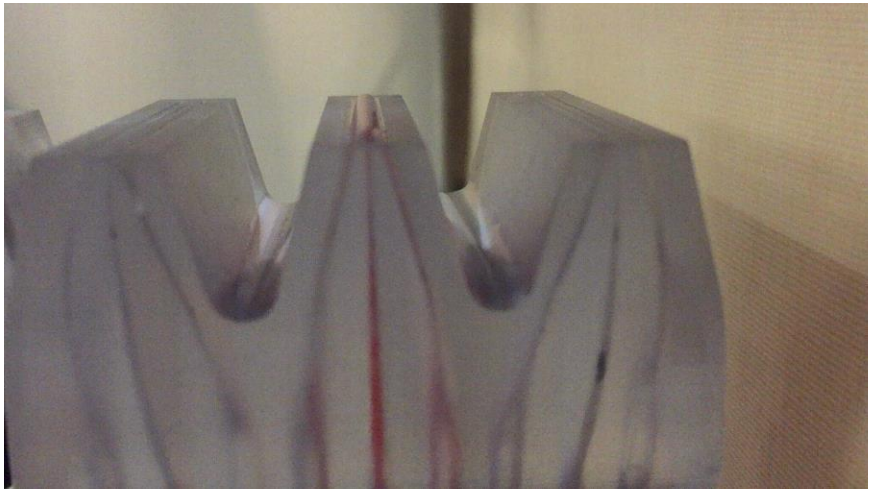


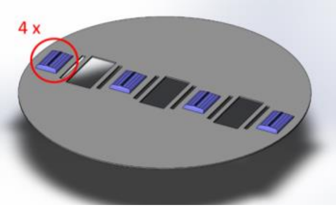
CFD result

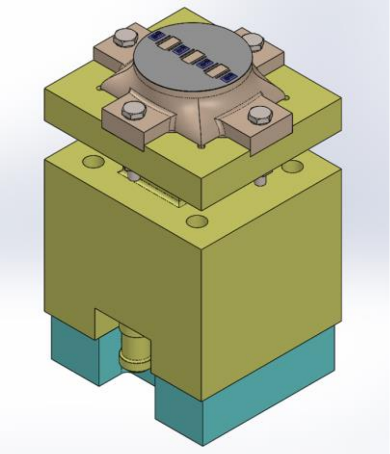
Micro Nozzles

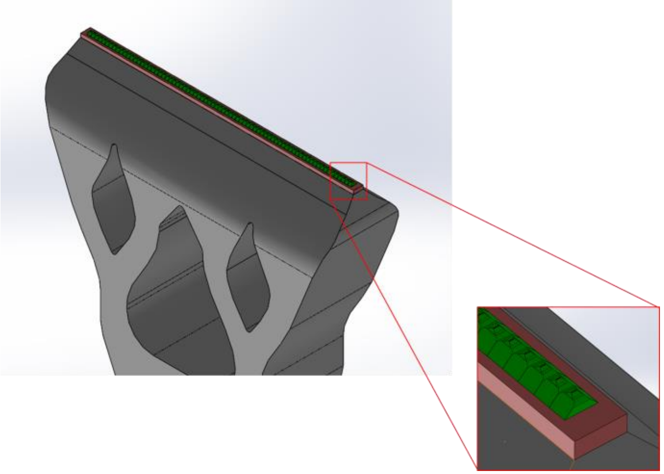
Speed of liquid is in the range of 1m/s





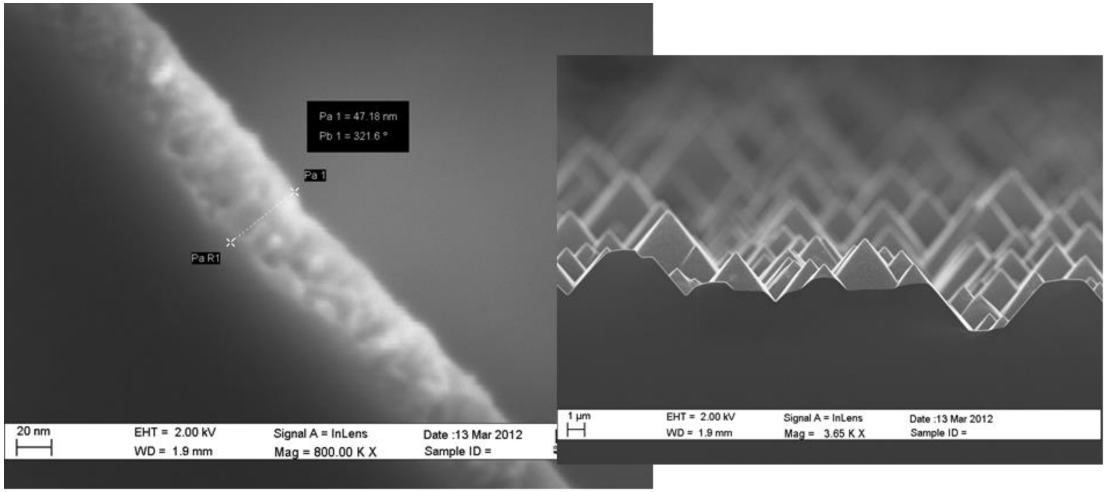


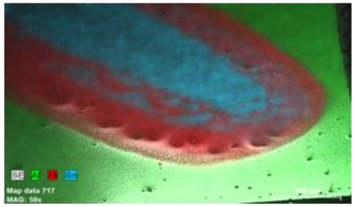


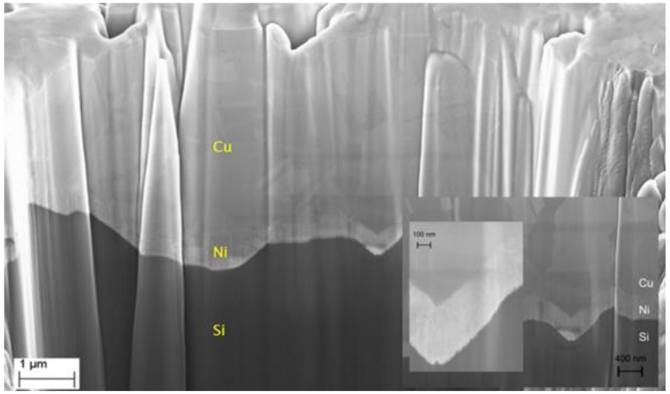


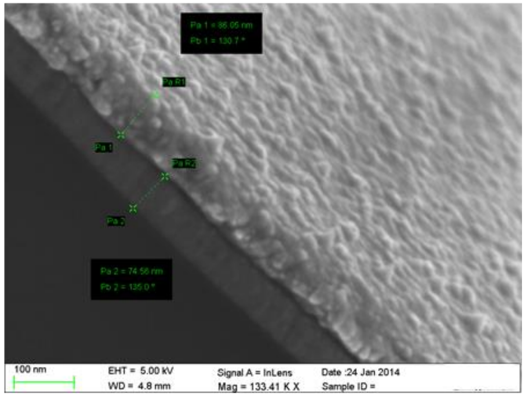
Main results achieved

- Front and back side of c-Si









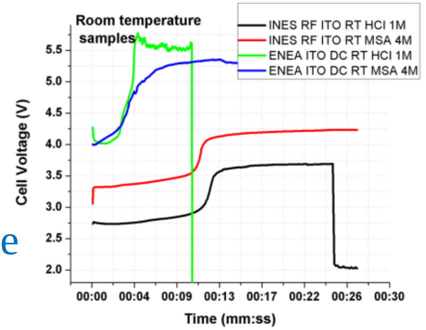
On Going Work – H2020 AMPERE

- Cu on ITO
  - ***Main Tasks:***
    - Adhesion > 1N/mm
    - No damage of SHJ solar cell after ITO processing
    - Quality of metal better than low temp. Ag-paste
    - FF and BB plating without mask
    - Speed of plating → Prove industrial feasibility of technique
      - Productivity > 2500 w/h
      - Make-up solution quantity
      - Floor space

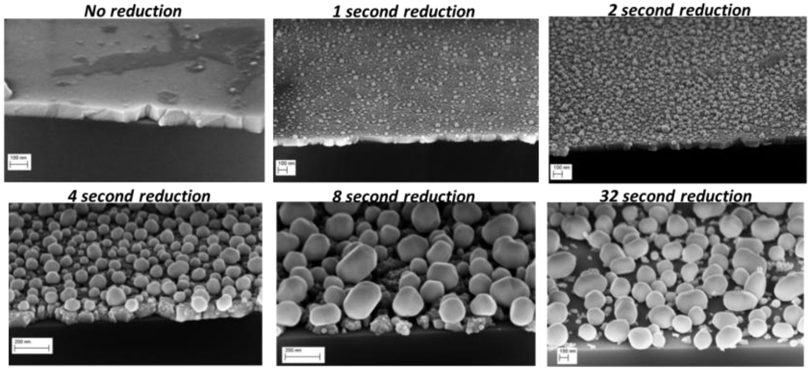
On Going Work – H2020 AMPERE

- Cu on ITO
  - ***Adhesion solved by ITO reduction***

$In_2O_3:Sn + 6HCl \rightarrow 2In:Sn + 3H_2O + 3Cl_2$

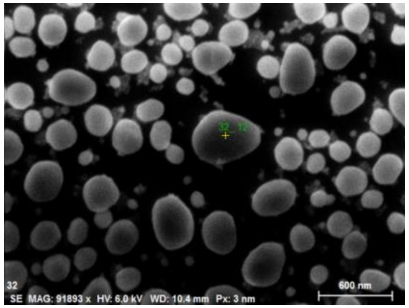


ITO reduction in galvanic regime ($10mA/cm^2 \leq J_0 \leq 320mA/cm2$)

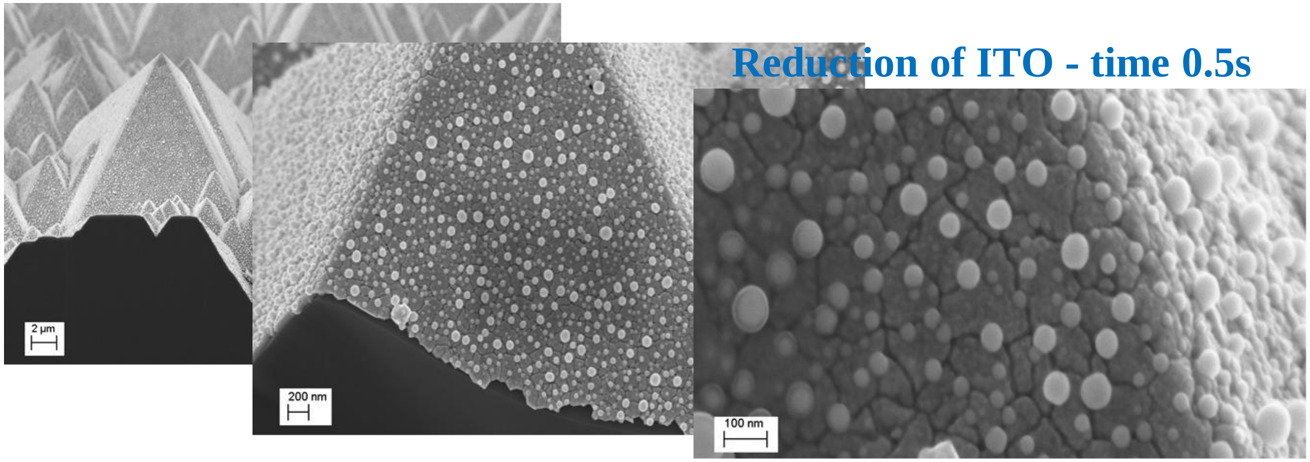


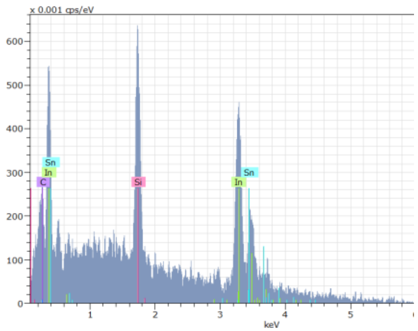
```
Spectrum: 32_ 12

El AN  Series  unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
-----------------------------------------------------
C   6  K-series   1.12    1.22    7.66             0.44
Si 14  K-series  12.44   13.60   36.53             0.74
In 49  L-series  71.30   77.94   51.20             4.33
Sn 50  L-series   6.63    7.24    4.60             0.80
-----------------------------------------------------
        Total:   91.49  100.00  100.00
```



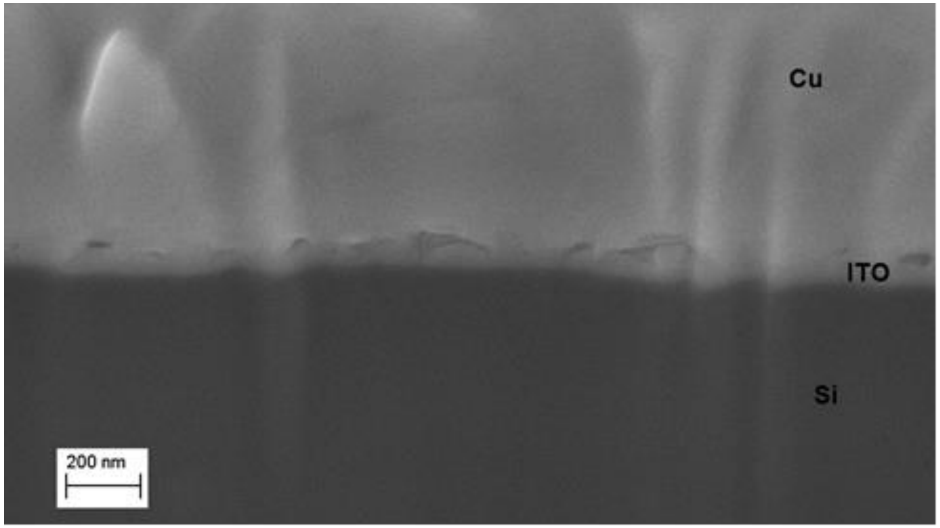
Reduction of ITO - time 0.5s

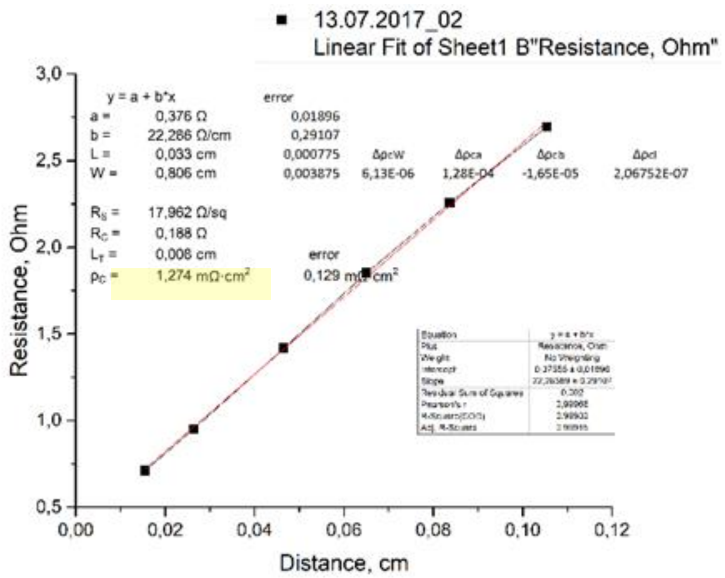




On Going Work – H2020 AMPERE

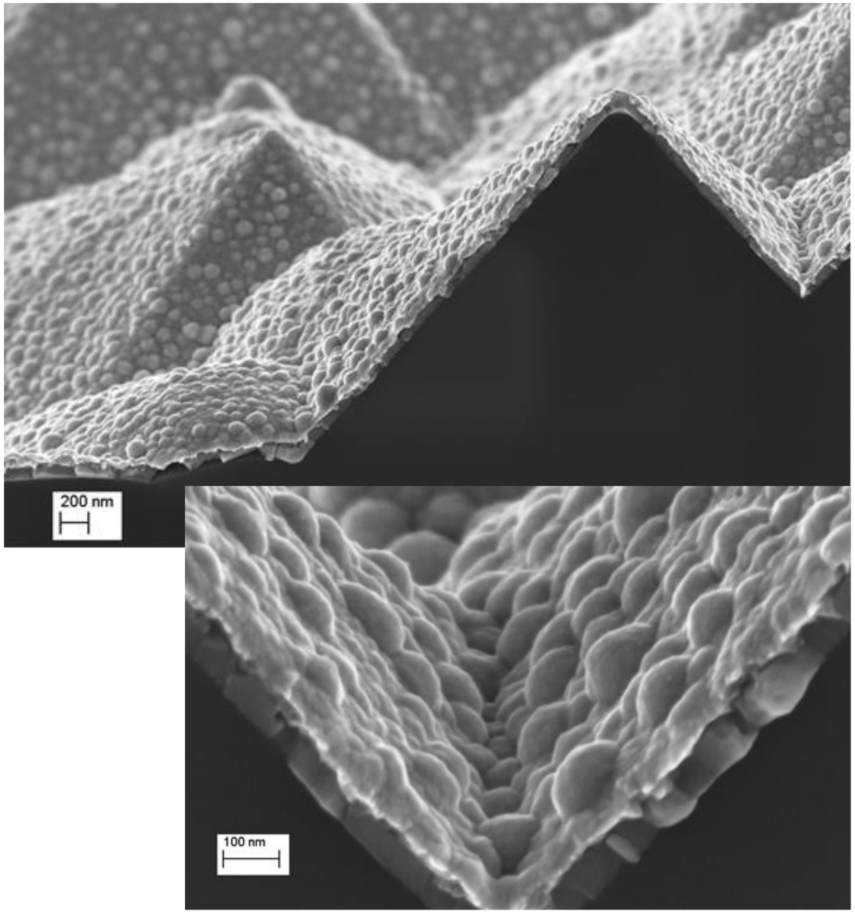
- Cu on ITO directly
  - ***Adhesion Issue***

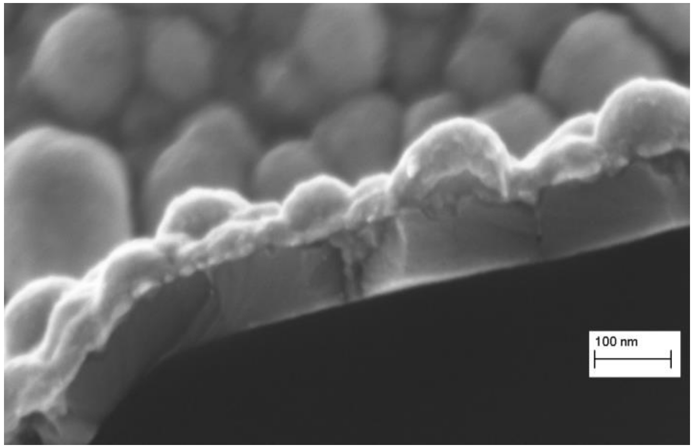


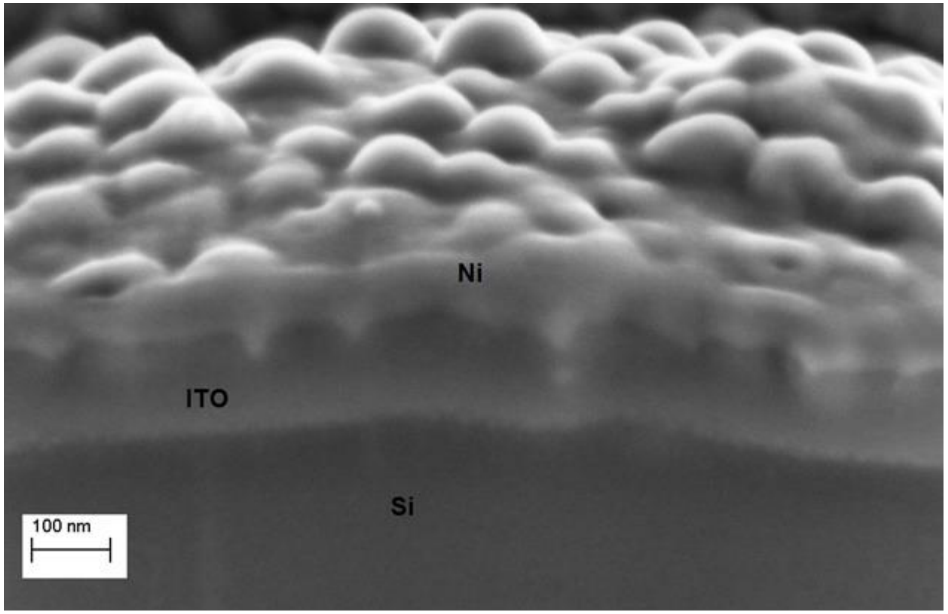


On Going Work – H2020 AMPERE

- Cu on ITO after flash of Ni



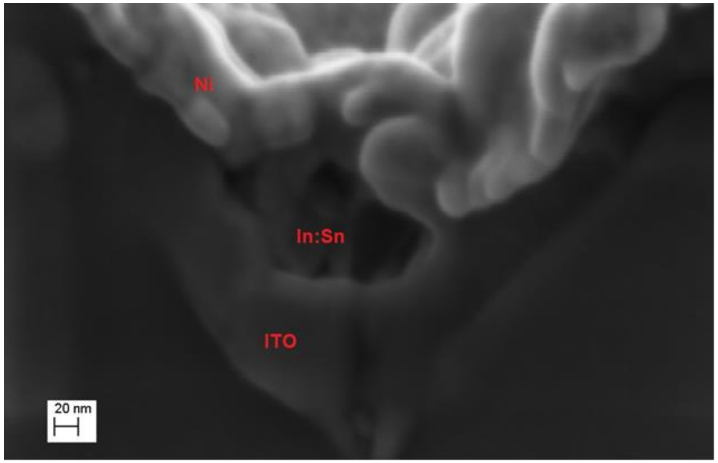




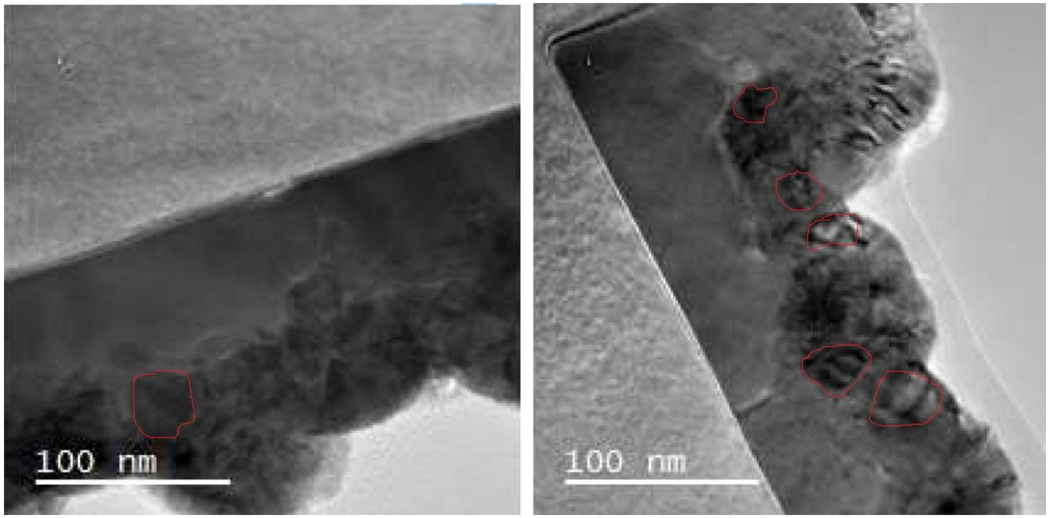
On Going Work – H2020 AMPERE

- Cu on ITO after flash of Ni

After 2 min @ 200° C

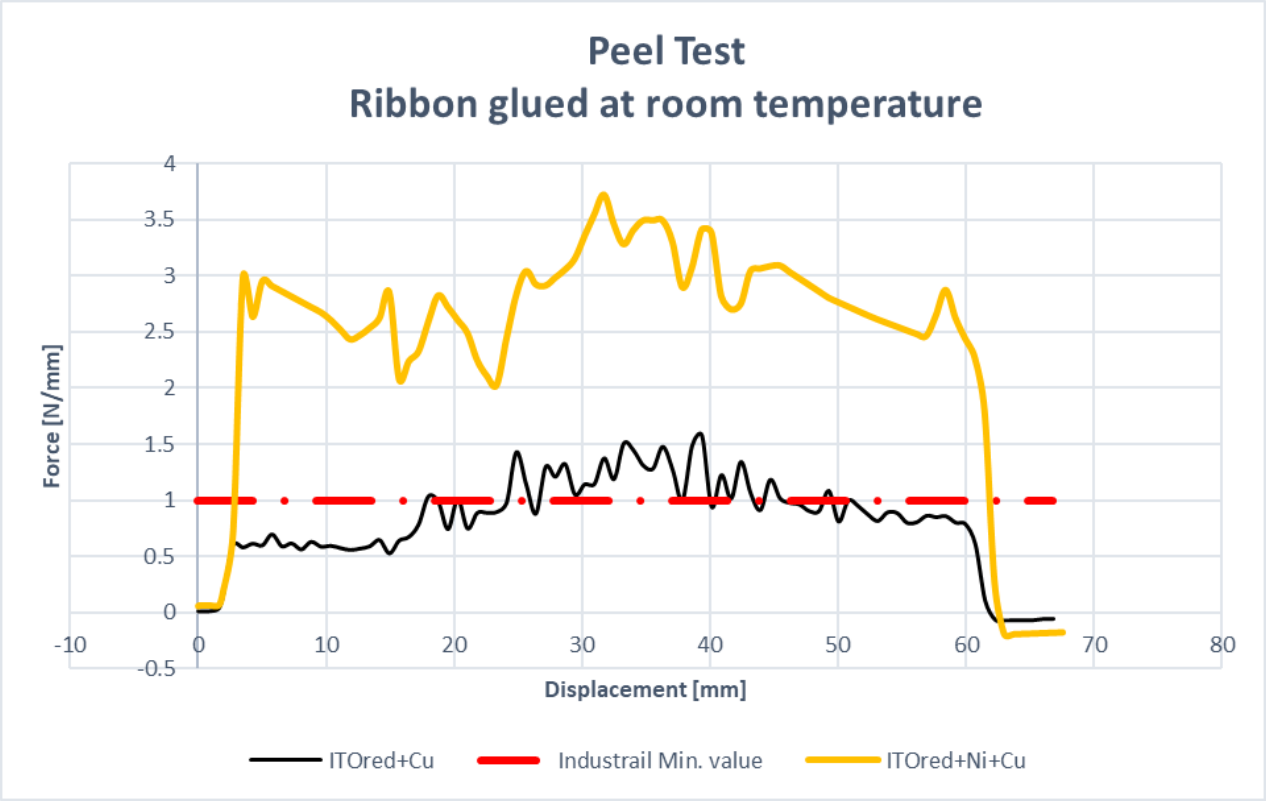


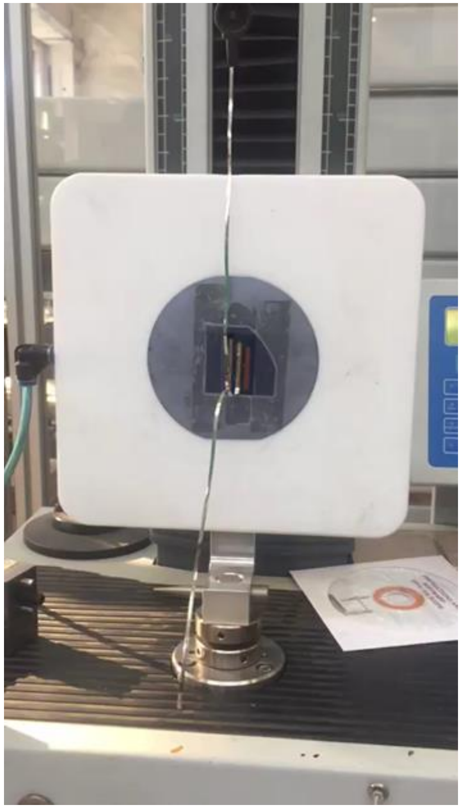
Plating post anneling	Specific contact resistance [mΩcm²]
NO	0.61 ± 0.07
200°C - 120 s	0.58 ± 0.02
150°C - 600 s	0.43 ± 0.1
NO	0.49 ± 0.05
150°C – 600 s	0.3 ± 0.1



On Going Work – H2020 AMPERE

- Cu (10µm) on ITO after flash of Ni





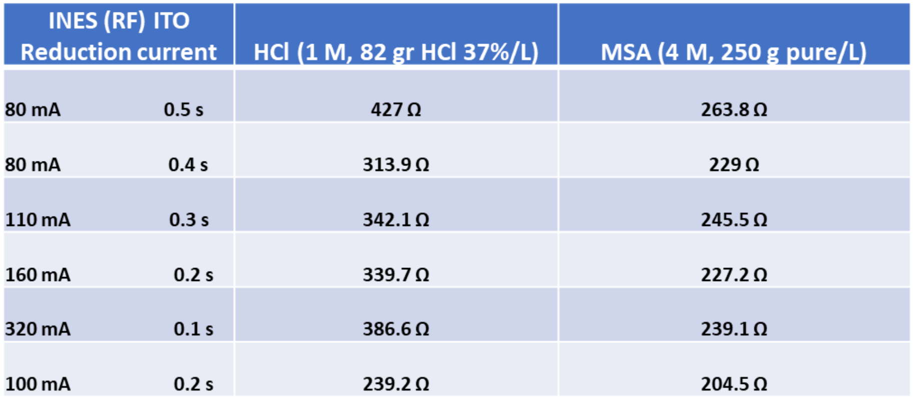
On Going Work – H2020 AMPERE

- Evaluation of ITO damage:

Recombination lifetime

Before ITO reduction	***After ITO reduction***	***Reduction in MSA***
τ =1054 µs	**τ = 1079 µs**	**p-side 320 mA 0.1 sec.**
τ = 749 µs	**τ = 803 µs**	**p-side 200 mA 0.1 sec.**
τ = 1291 µs	**τ =1227 µs**	**p-side 100 mA 0.1 sec.**

ITO reduction in MSA solution doesn't affect recombination lifetime leaving the passivation layer intact.



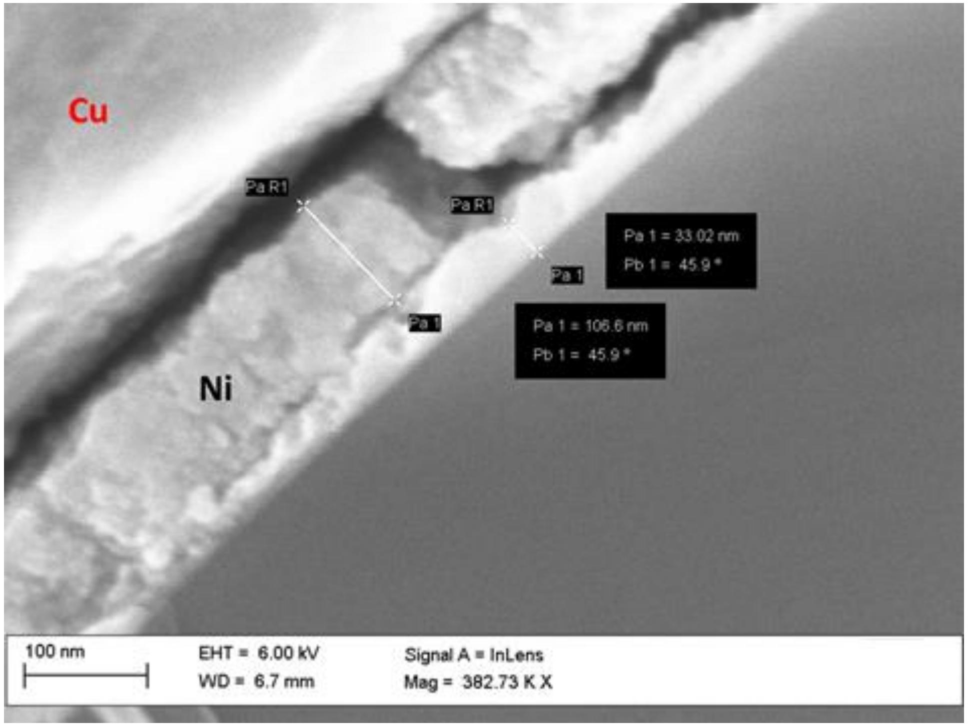
INES (RF) ITO Reduction current	HCl (1 M, 82 gr HCl 37%/L)	MSA (4 M, 250 g pure/L)
80 mA 0.5 s	427 Ω	263.8 Ω
80 mA 0.4 s	313.9 Ω	229 Ω
110 mA 0.3 s	342.1 Ω	245.5 Ω
160 mA 0.2 s	339.7 Ω	227.2 Ω
320 mA 0.1 s	386.6 Ω	239.1 Ω
100 mA 0.2 s	239.2 Ω	204.5 Ω

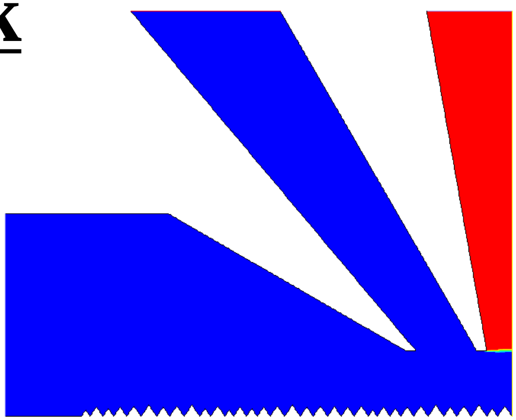
HCl-MSA comparison

MSA is capable of reducing ITO inducing less damage and limiting the corrosion of the formed In-Sn phase

On Going Work – H2020 AMPERE

- FF and BB plating **without mask**

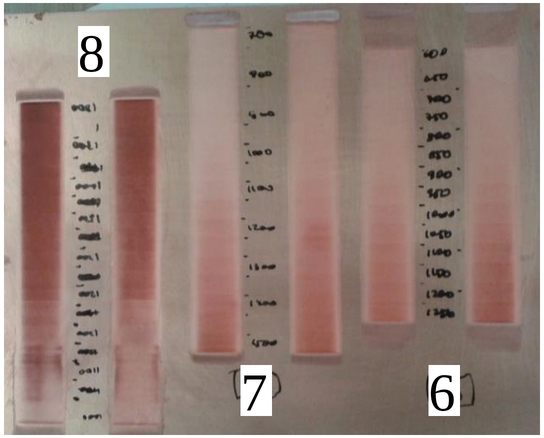


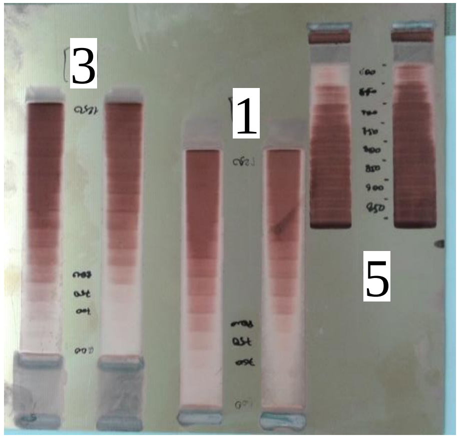


Moving down to 50µm FF

On Going Work – H2020 AMPERE

- Cu Speed of plating

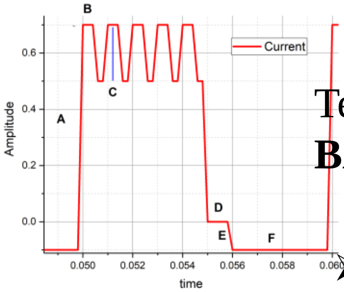




N.	I_{min} [ASD] DR [µm/s]	I_{max} [ASD] DR [µm/s]	Fluid Velocity [m/s]	Optimal I [ASD] DR [µm/s]	Cu [g/l]
5	200 0.74	300 1.10	0.17	-	17
3	200 0.74	413 1.53	0.87	200 0.74	17
1	166 0.61	433 1.59	1.04	233 0.86	17
6	200 0.74	300 1.10	1.04	300 1.10	38
7	233 0.86	500 1.84	1.04	366 1.35	45
8	333 1.23	600 2.21	1.04	366 1.35	45

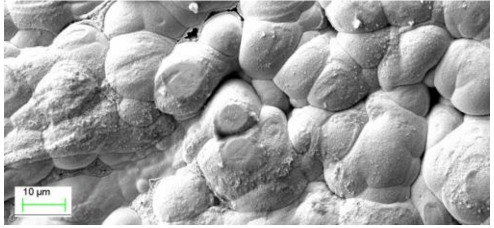
$\rho_{Cu} \leq 3.0\ \mu\Omega\cdot cm$

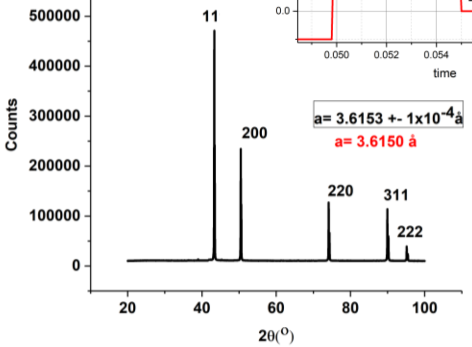
6



Testing PRP average **J** up to **1500ASD**

BASF additive for dendrite suppression



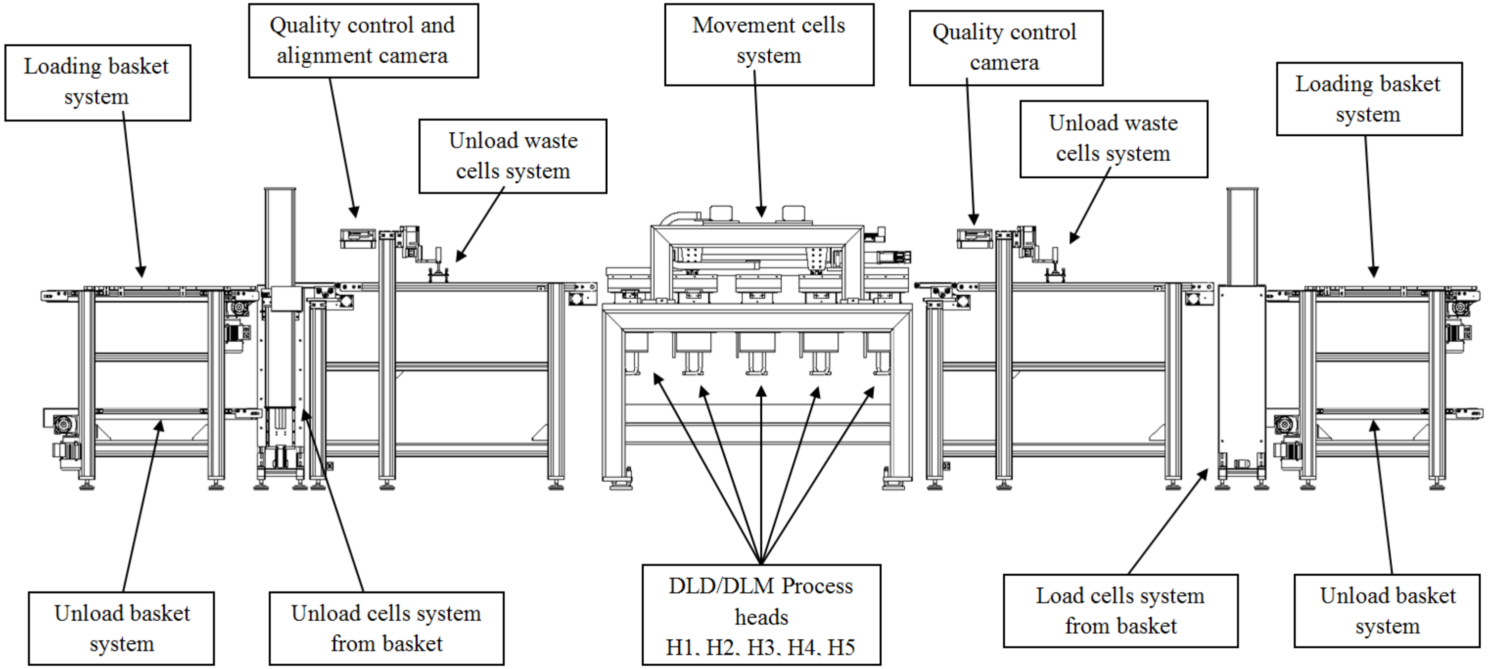


- ➢ **High crystallinity (low background, sharp and intense peaks, $k_{\alpha 2}$ visible even at high ϑ).**
- ➢ **High purity (no detectable Cu_2O, $Cu(OH)_2$, CuO or $CuCO_3$ phases).**
- ➢ **Large crystallites (over the instrumental resolution ≈ 150 nm)**
- ➢ **High density (8.93 g/cm³), substrate (brass) contribution is immaterial.**
- ➢ **Williamson-Hall Plots and Warren-Averbach shows strain in the range 100-200MPa**

Industrial Feasibility

- DLD/DLM INDUSTRIAL PILOT LINE

PIPELINE CONFIGURATION



Loading basket system

Quality control and alignment camera

Unload waste cells system

Movement cells system

Quality control camera

Unload waste cells system

Loading basket system

Unload basket system

Unload cells system from basket

DLD/DLM Process heads H1, H2, H3, H4, H5

Load cells system from basket

Unload basket system

Speed of Plating	1um/s	2um/s	5um/s
Length of Equipment for 100MW @20um Cu [liter make-up]	12 m x 1 m= 12 m^2 [300]	6 m x 1 m= 6 m^2 [200]	2.4 m x 1 m= 2.4 m^2 [150]

M. Balucani et al.

Acknowledgement

ENEA
Italian National Agency for New Technologies,
Energy and Sustainable Economic Development

Dr. Mario Tucci and Dr. Massimo Izzi

samples, measurement and discussion

liten
cea tech

Dr. Jean-François Lerat and Dr. Delfina Munoz

ITO samples and discussion

ines

3SUN

AMPERE
AUTOMATED PHOTOVOLTAIC CELL AND MODULE INDUSTRIAL PRODUCTION
TO REGAIN AND SECURE EUROPEAN RENEWABLE ENERGY MARKET

H2020 Project Coordinator

IMM Institute for Microelectronics and Microsystems

Dr. Salvatore Lombardo

TEM and discussion

Conclusion

- Adhesion > 1N/mm
- No damage of SHJ solar cell after ITO processing
- Quality of Cu better than low temp. Ag-paste
- ITO red., Ni and Cu plating - NO MASK
- Speed of plating → 1µm/s→2µm/s→10 µm/s
  - Productivity > 2500 w/h
  - Make-up solution ≤ 300 liter
  - Floor space at least 5 times less than state of the art

Breakthrough in Plating for
Solar Cell Metallization