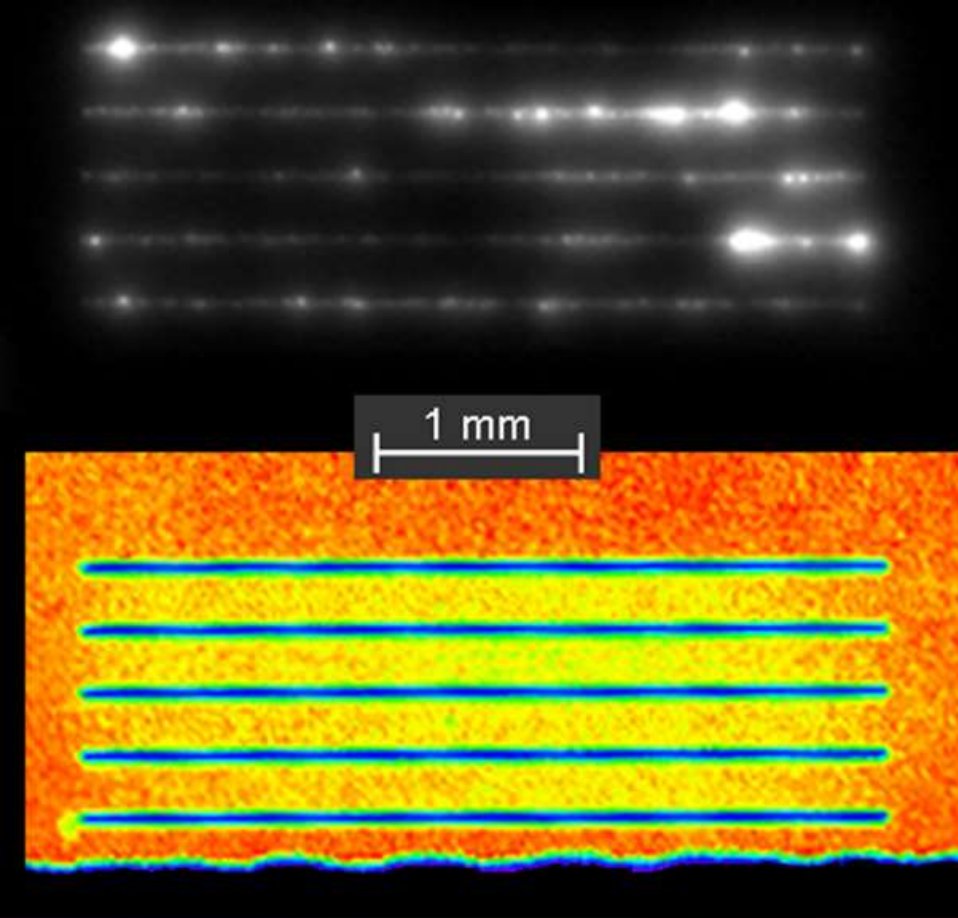
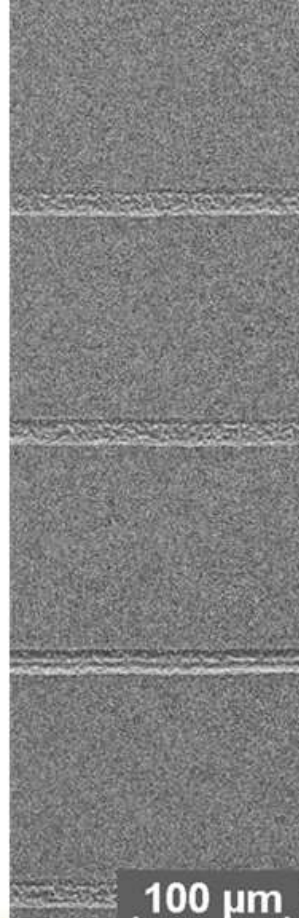
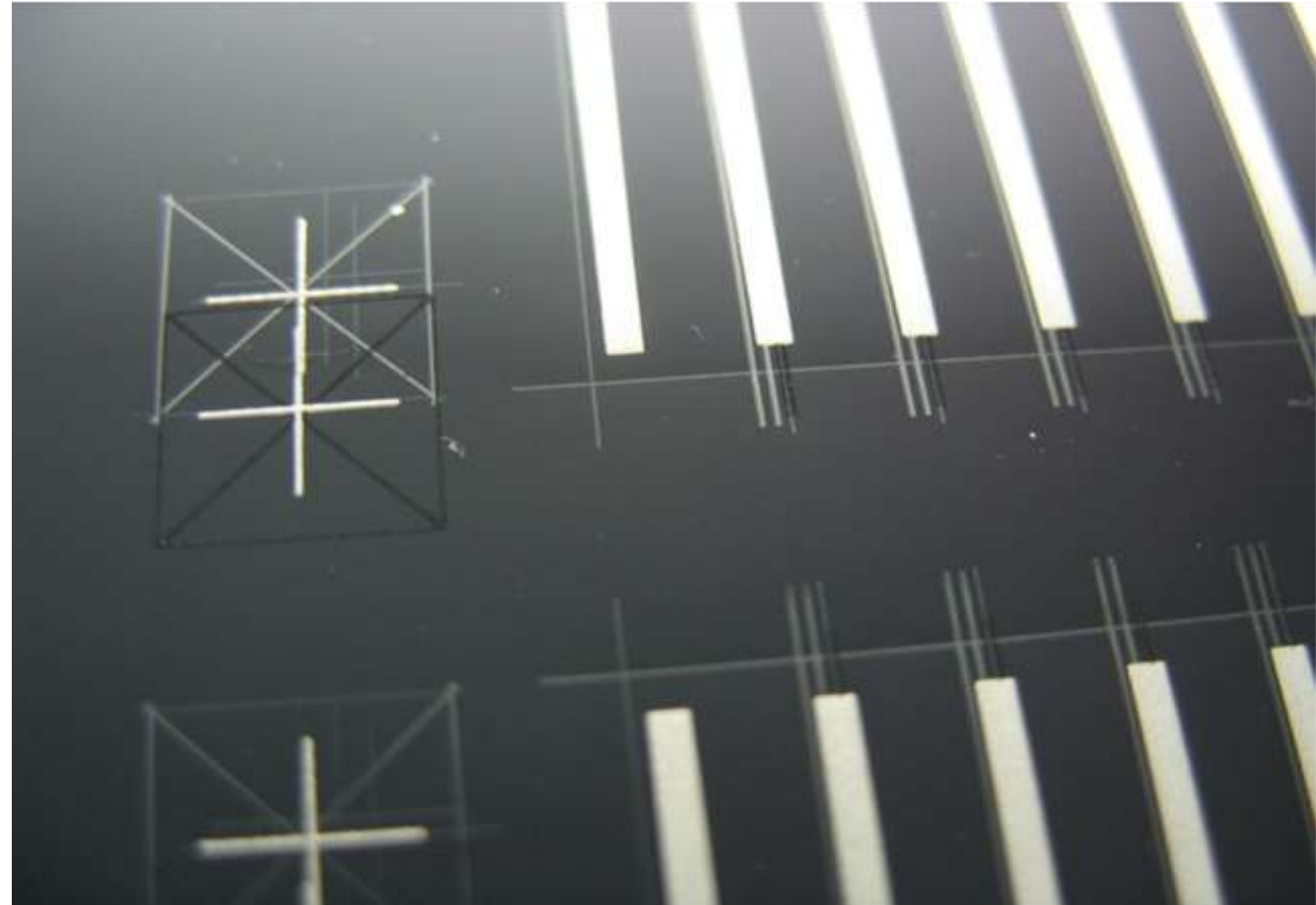




LASER PATTERNING OF THIN FILMS FOR APPLICATIONS IN PHOTOVOLTAIC



ABENGOA SOLAR



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Symp. X: "New frontiers in laser interaction: from hard coatings to smart materials"

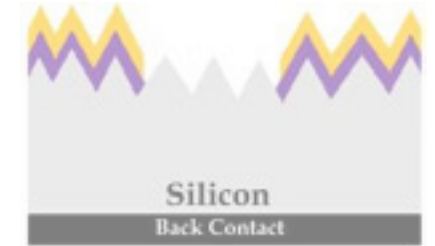
EMRS 2017: May 22 to 26, 2017 Strasbourg (France)



klaus.zimmer@iom-leipzig.de

■ Silicon solar cells

- local emitter (PERC)
- edge isolation
- laser fired contacts
- laser drilled holes (ETM cell)



■ Thin film solar cells

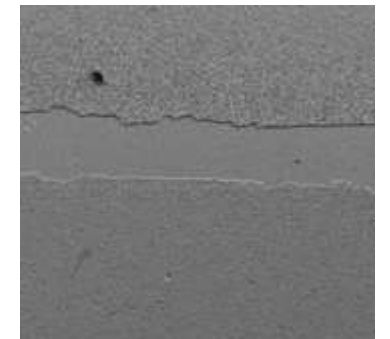
- laser scribing
- laser soldering
- laser printing conductive pasts

Laser scribing for

➤ **CIGS**

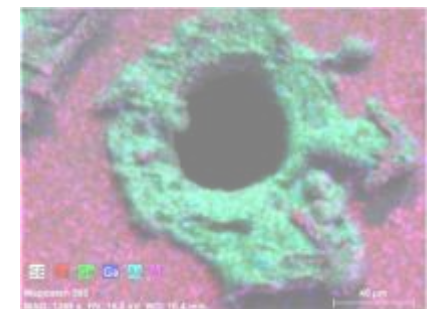
➤ **Perovskite**

photovoltaic



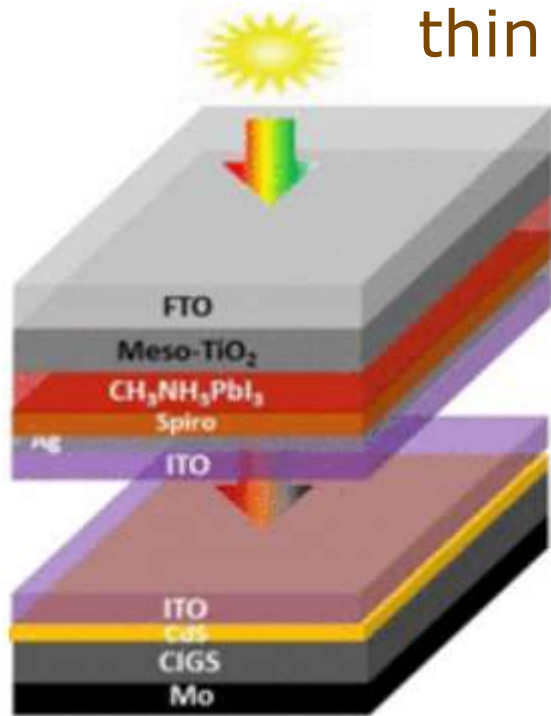
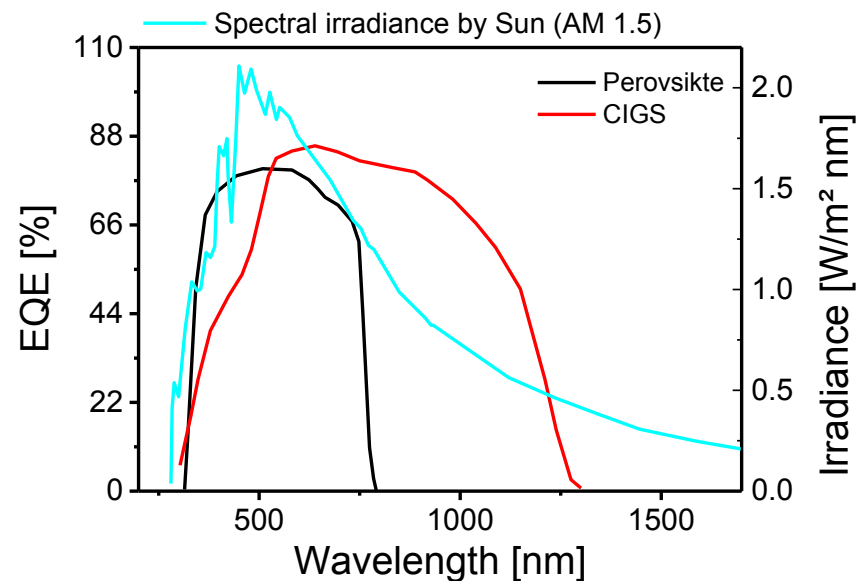
■ Module fabrication

- welding of strings
- welding/soldering of backplanes
- texturing of surfaces



Lasers enable key processes for efficient industrial PV production!

Opportunities and Challenges of tandem thin film CIGS perovskite modules on flexible substrates



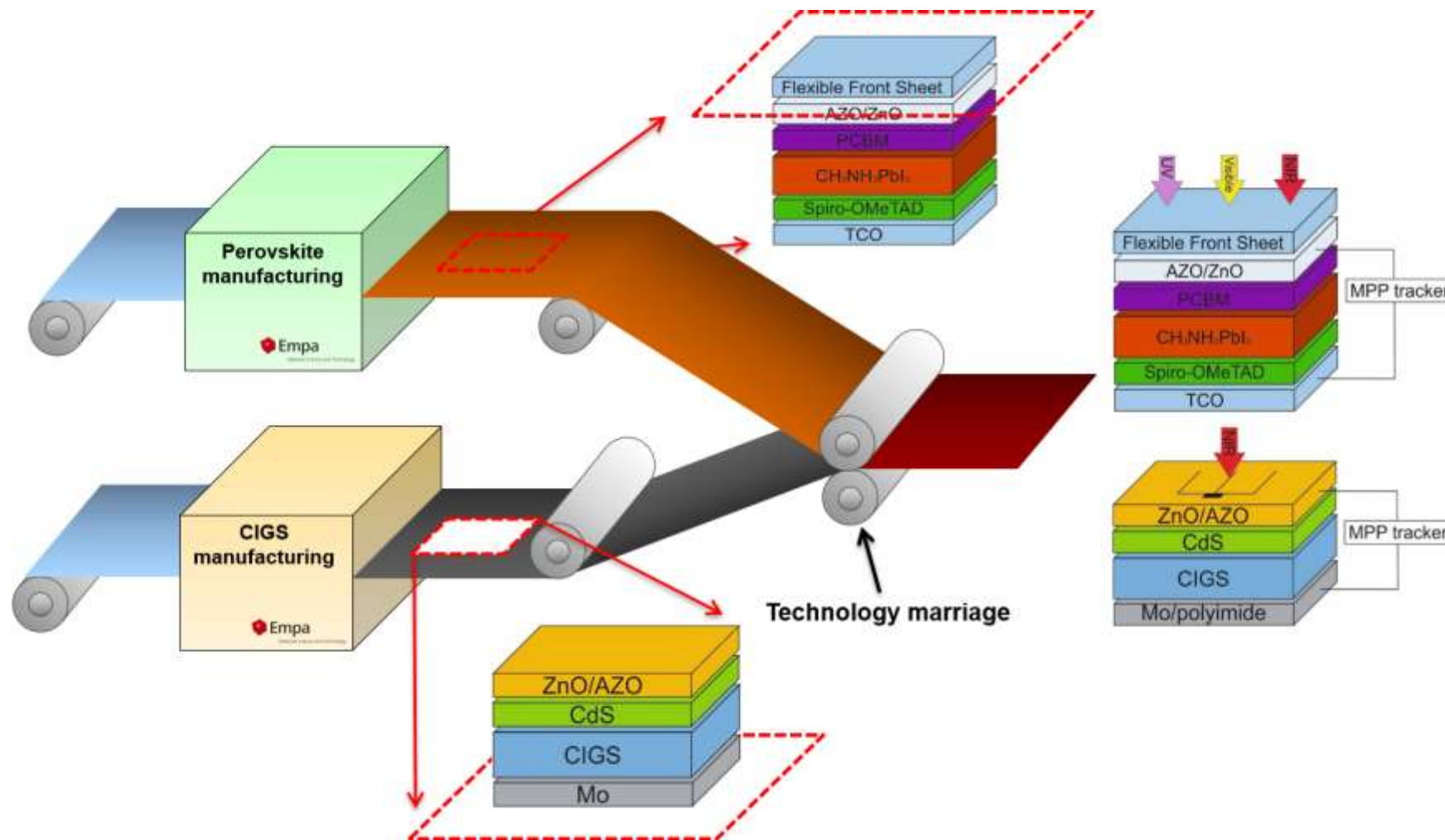
Opportunities

- Efficiency increase (>20% for tandem cells shown)
- maintaining flexibility (thin foils for substrate and sealing)
- independent fabrication processes of CIGS and perovskite

Challenges

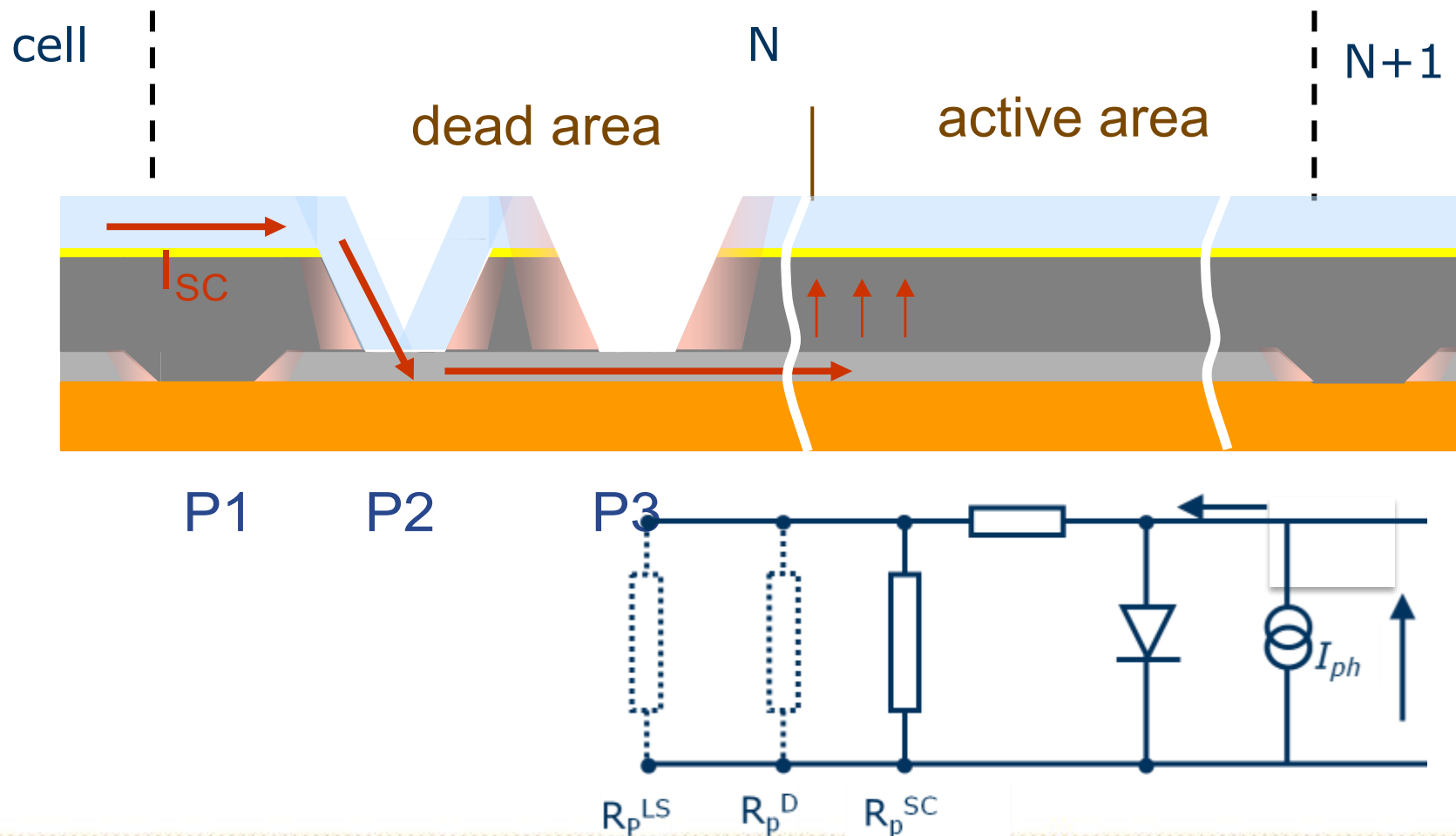
- effective area / overlay
- stability / encapsulation
- matching (electrical / optically) of submodules

A. Guchhait et al., Acs Energy Letters 2(2017)807.

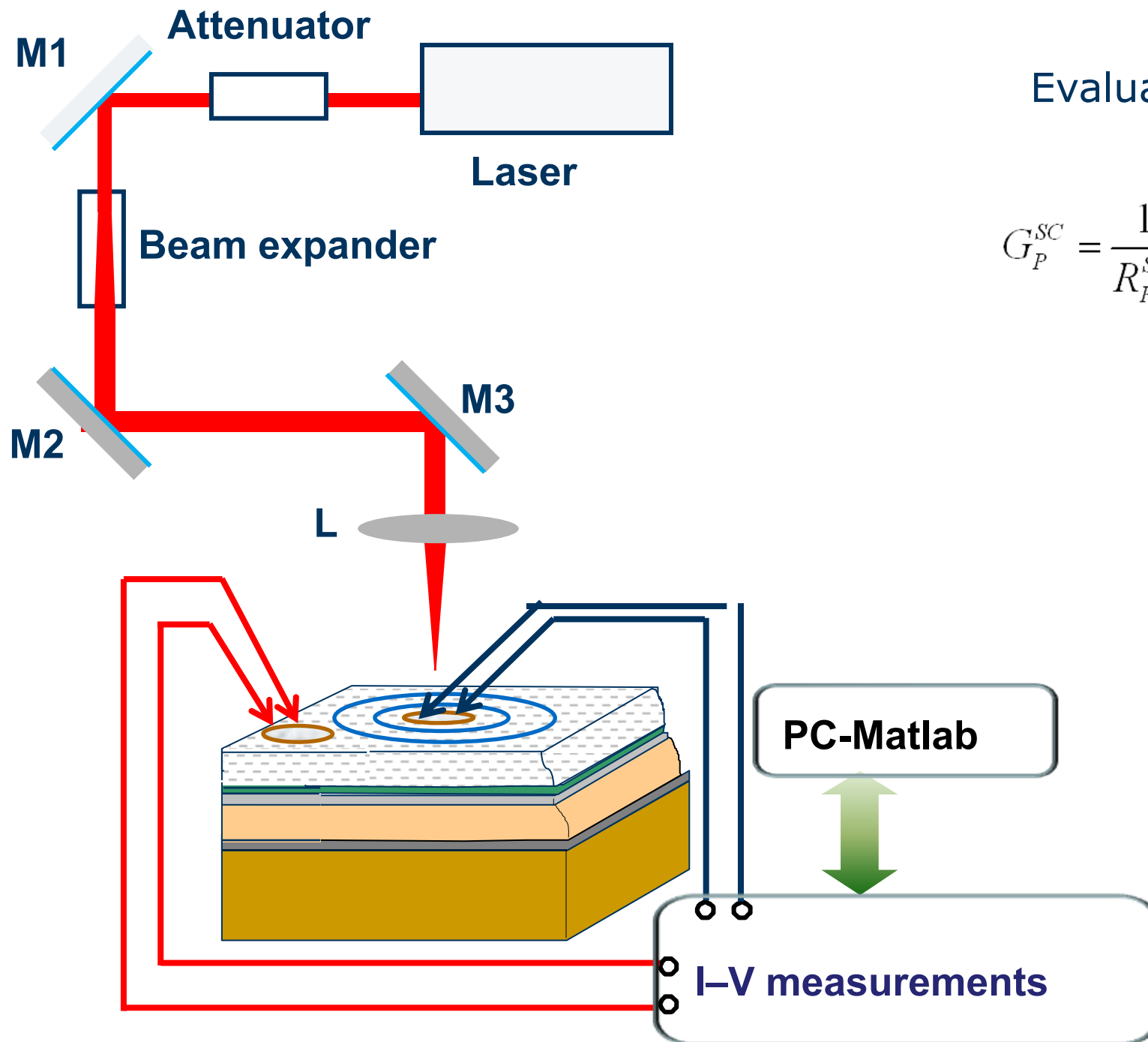


- scribing speed → productivity
- scribe width → dead area → cell efficiency
- distance of the scribes → reduction of dead area
- selective scribing → electrical properties of interconnection
- large process window → reliability for industrial applications

Usually geometry-related characteristics of laser scribing are studied!

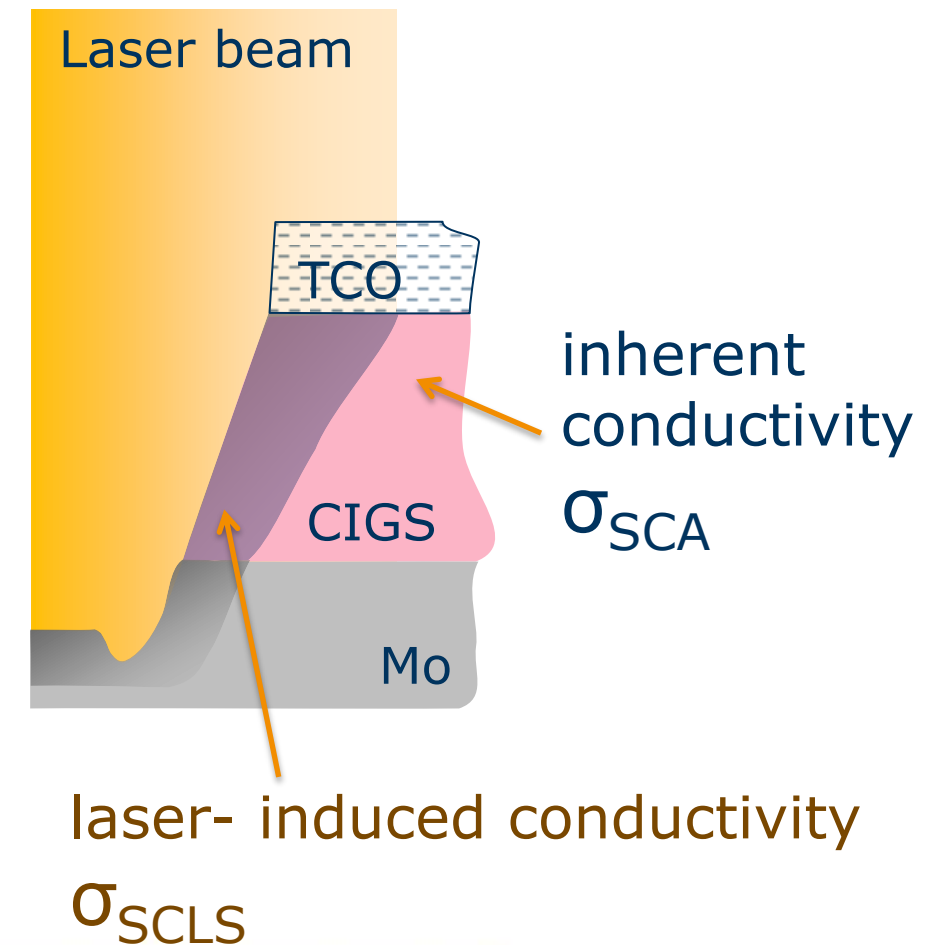


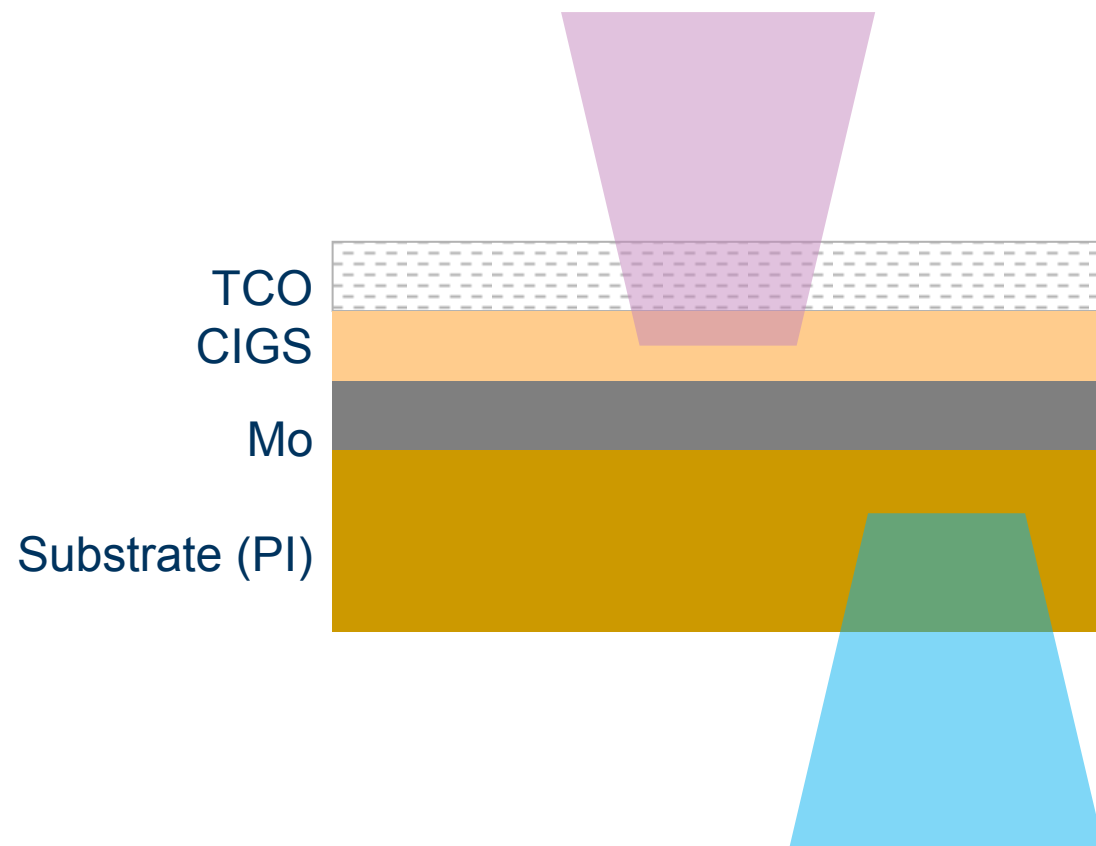
Studying the correlations of LASER SCRIBING and ELECTRICAL PROPERTIES of scribed SOLAR CELLS are needed in addition!



Evaluation of the parallel resistance

$$G_P^{SC} = \frac{1}{R_P^{SC}} = G_P^{SCA} + G_P^{LS} + G_P^{SCD} = \sigma_{SCA}^{**} \cdot r^2 + \sigma_{SCM}^* \cdot r$$

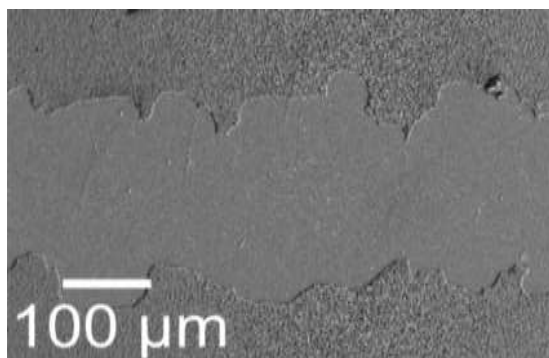
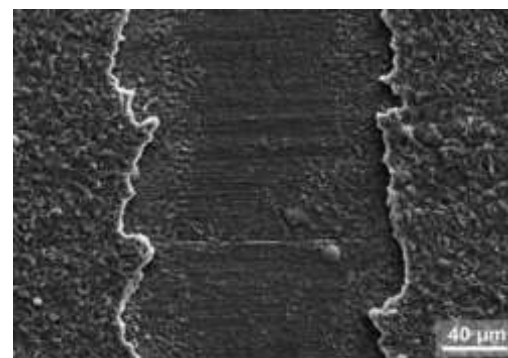




What are the reasons for the different patterning results?

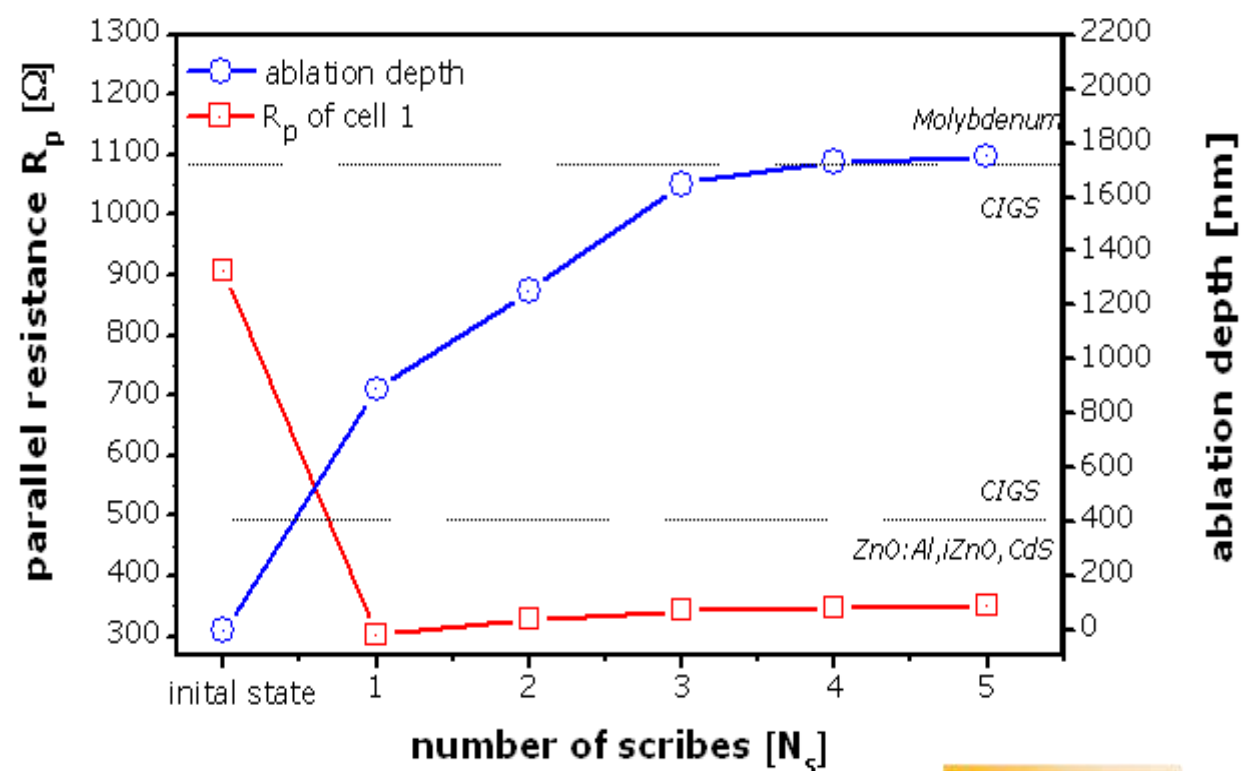
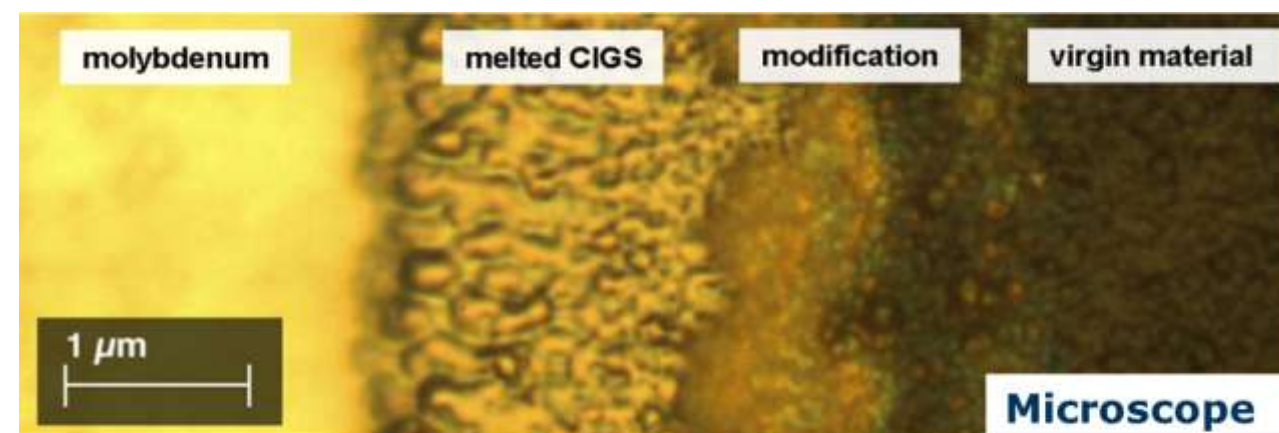
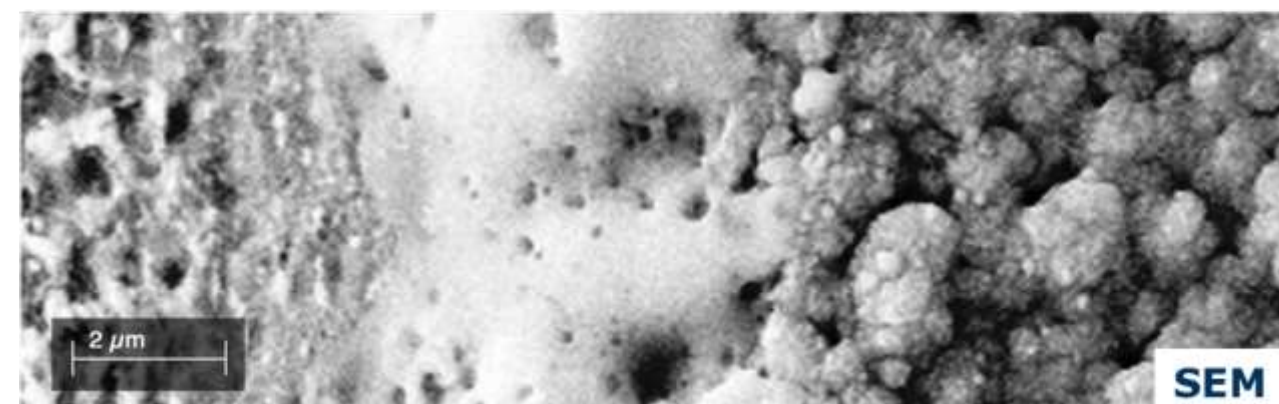
Which give the best performance?

Different scribe morphologies can be found!



λ : 755 nm, t_p : ~120 fs, f : 1 kHz, r_g : 15 μ m Solarion-Material

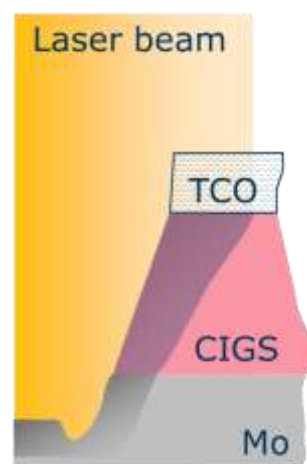
Parallel resistance of the solar cell.



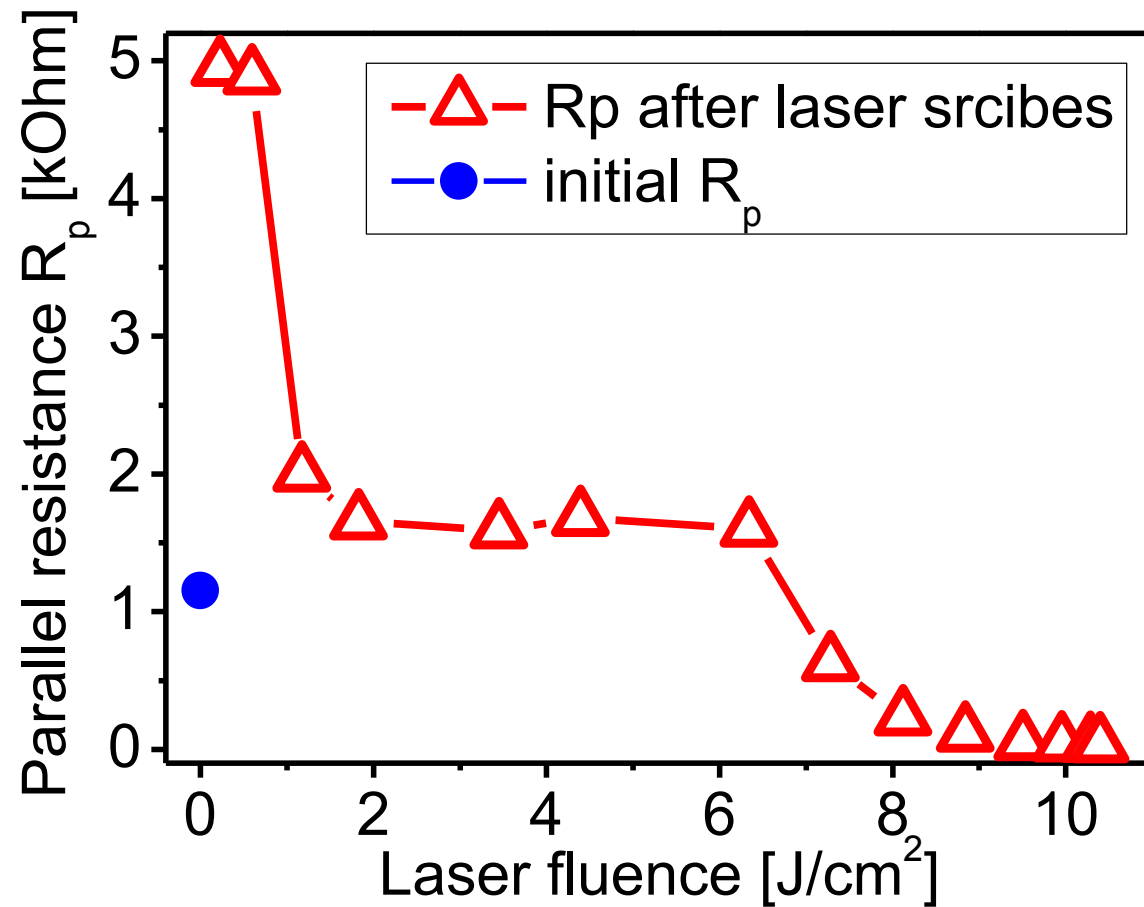
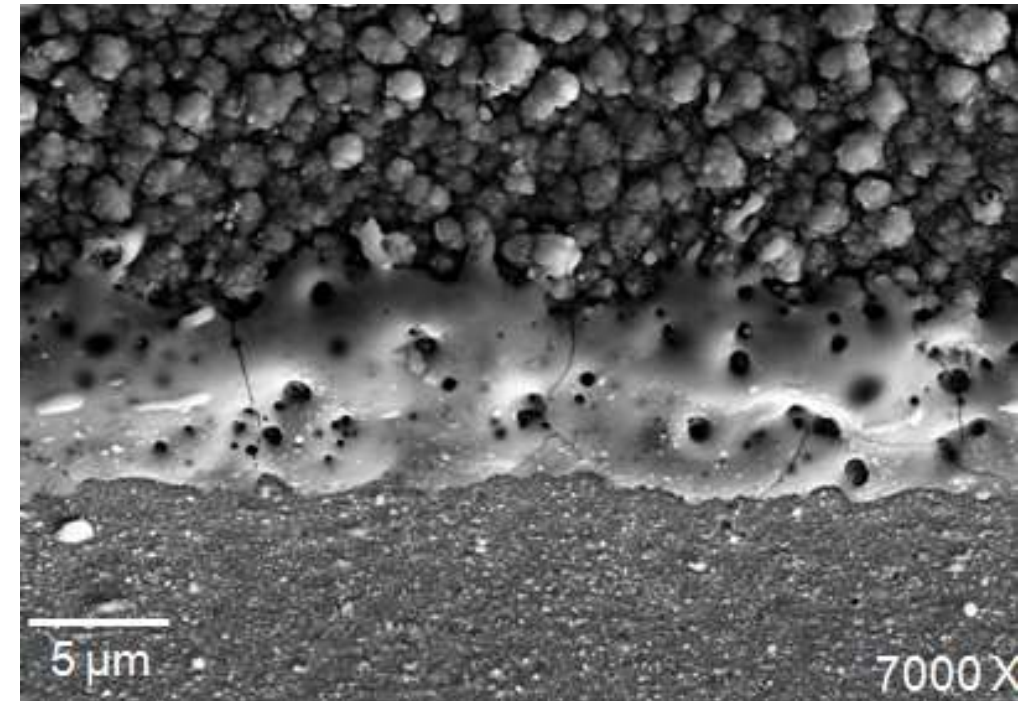
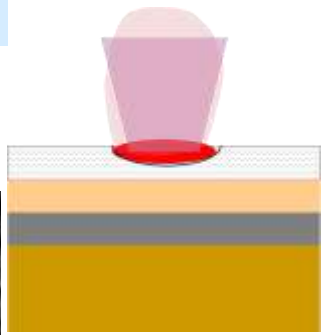
Laser scribe in full CIGS solar cell

Laser pulse energy induce defects in areas of high electrical functionality.

A. Wehrmann, SPIE 20111

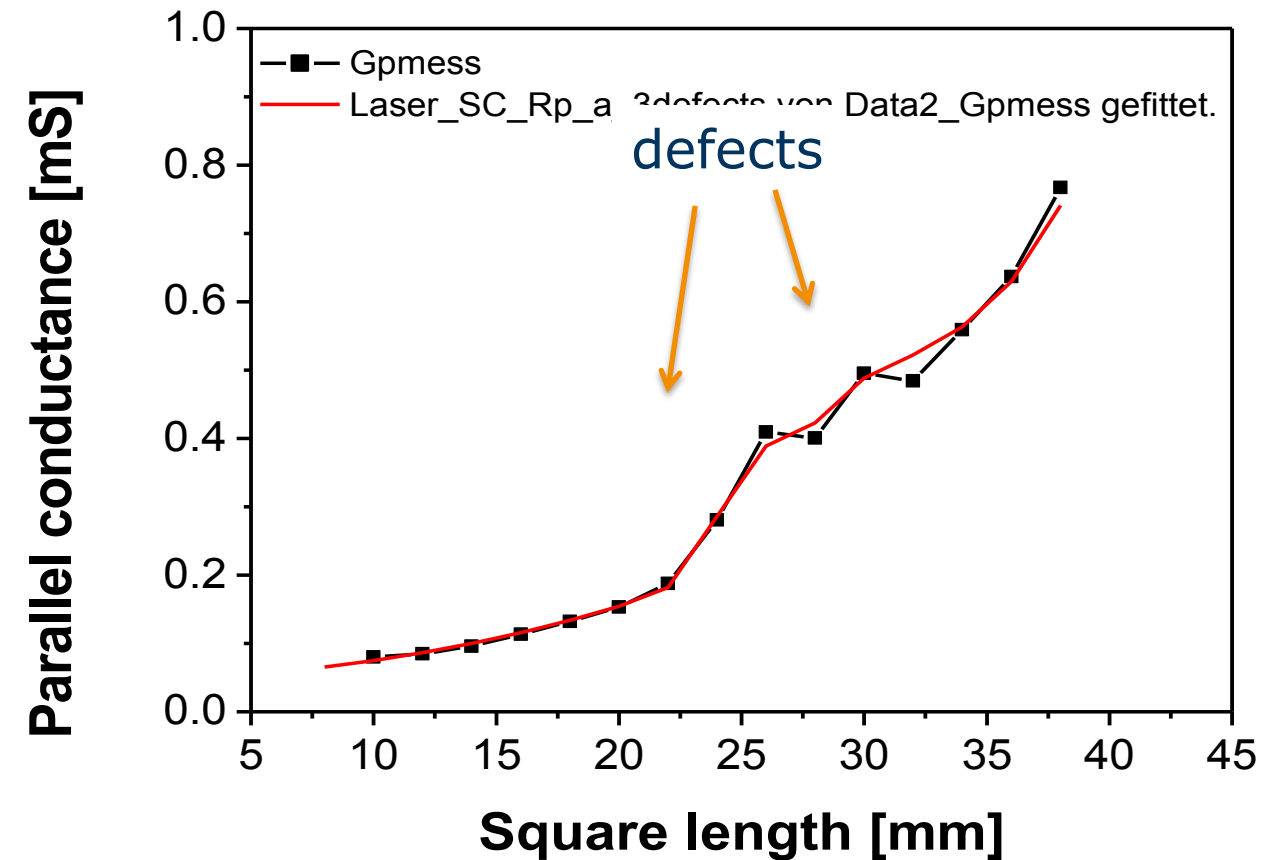
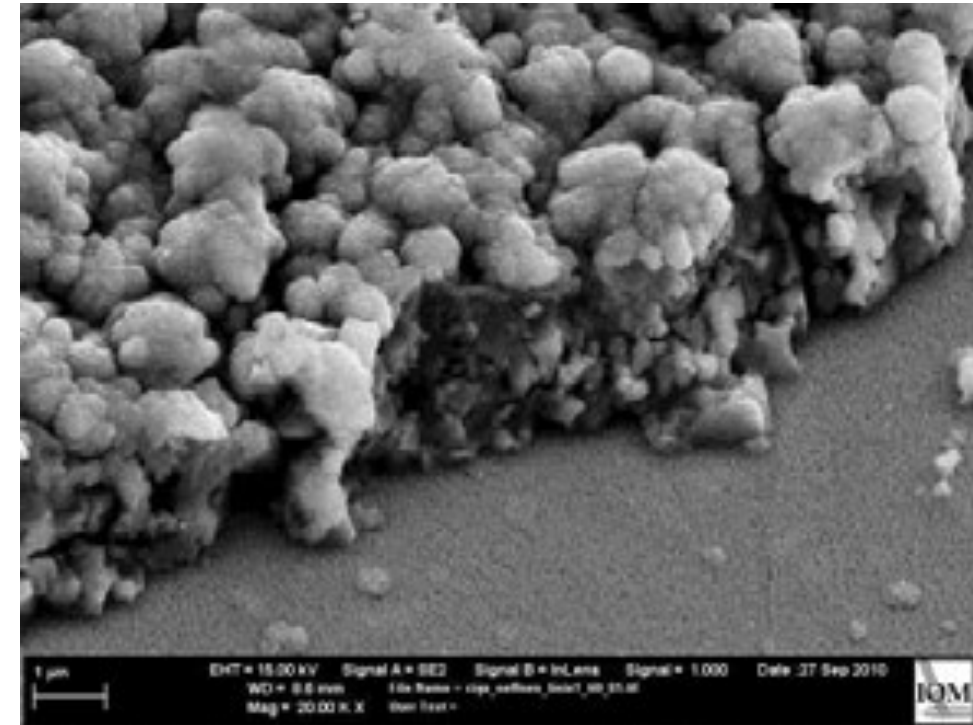
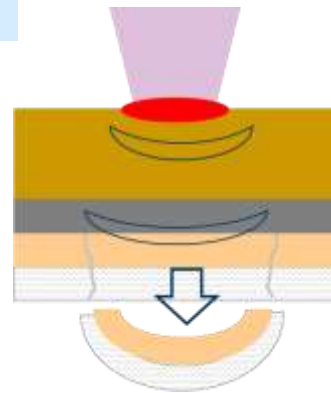


λ : 1064 nm, t_p : ~12 ps, f : 150 kHz, r_g : 17 μ m Solarion-Material



Laser power and pulse overlap are important to limit the number of laser-induced defects!

λ : 248 nm, t_p : ~20 ns, f : 100 Hz, D : 100 μ m Solarion-Material

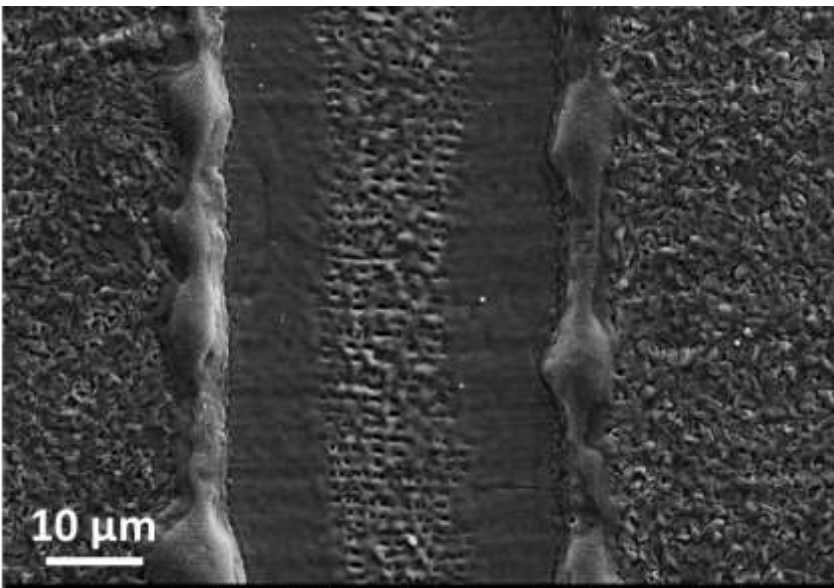


Melt-free delamination lift-off enables a defect free laser scribing process. However, this backside ablation patterning has limitation in precision, scribe width and speed.

Defect insulation was demonstrated!

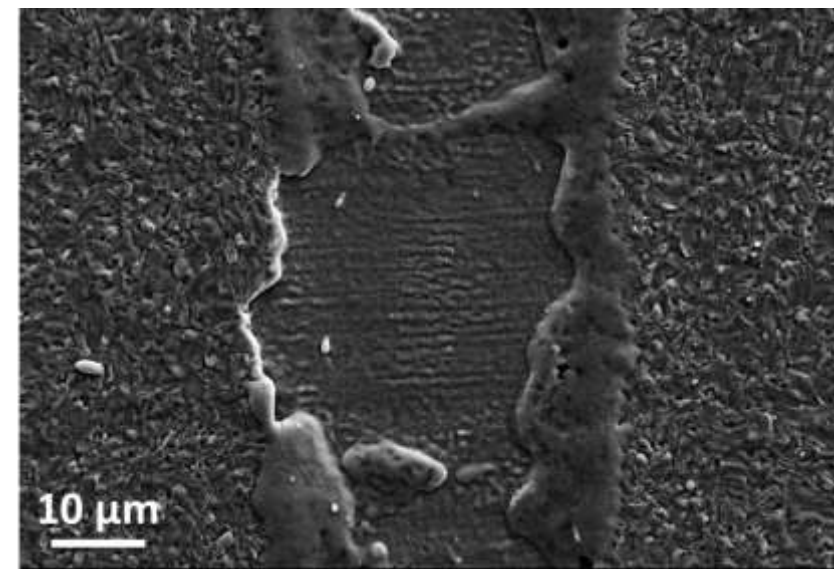
λ : 1550 nm, t_p : ~ 6 ns, f : 100 kHz, r_g : 21 μm

Abengoa Solar NT-Material

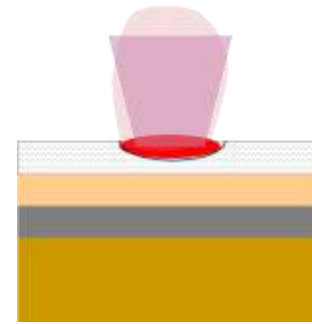
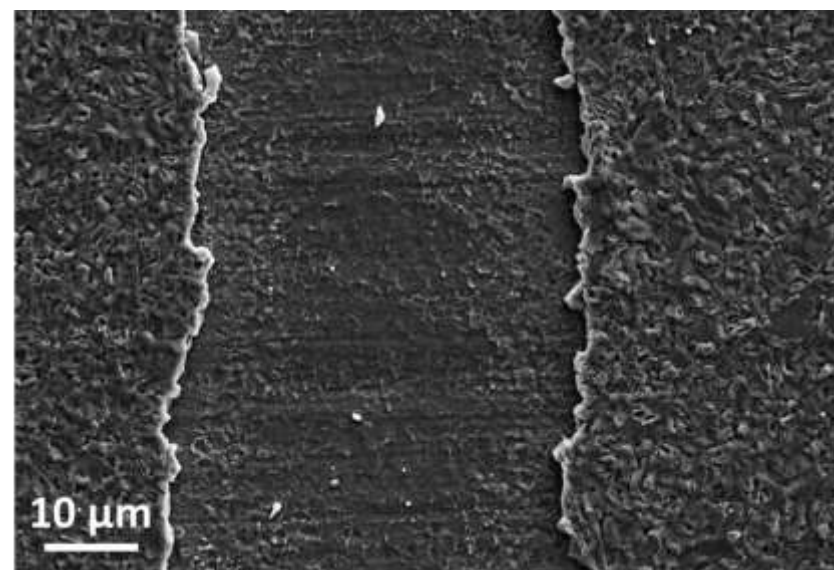


$v_s = 0.05$ m/s

melting
&
ablation

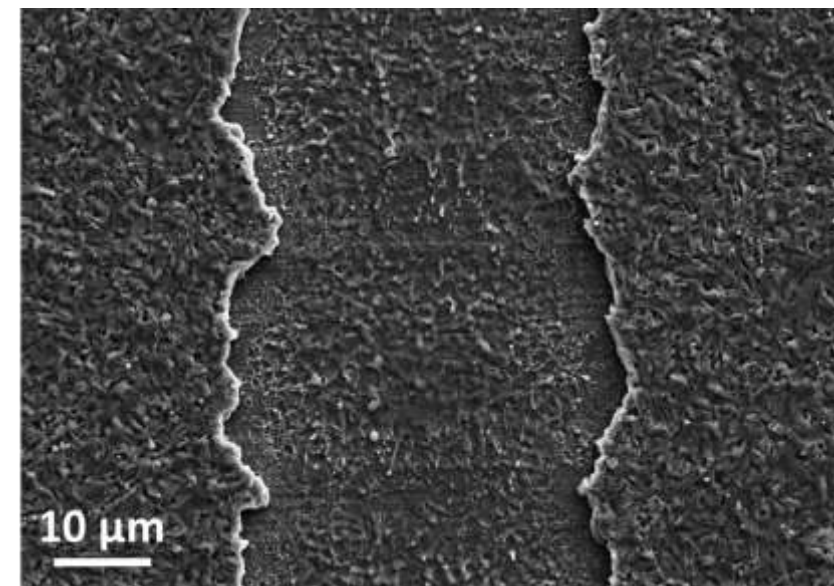


$v_s = 0.15$ m/s

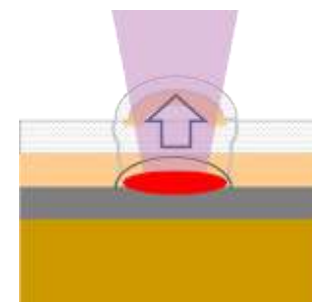


$v_s = 1.5$ m/s

film cracking
&
delamination
lift-off



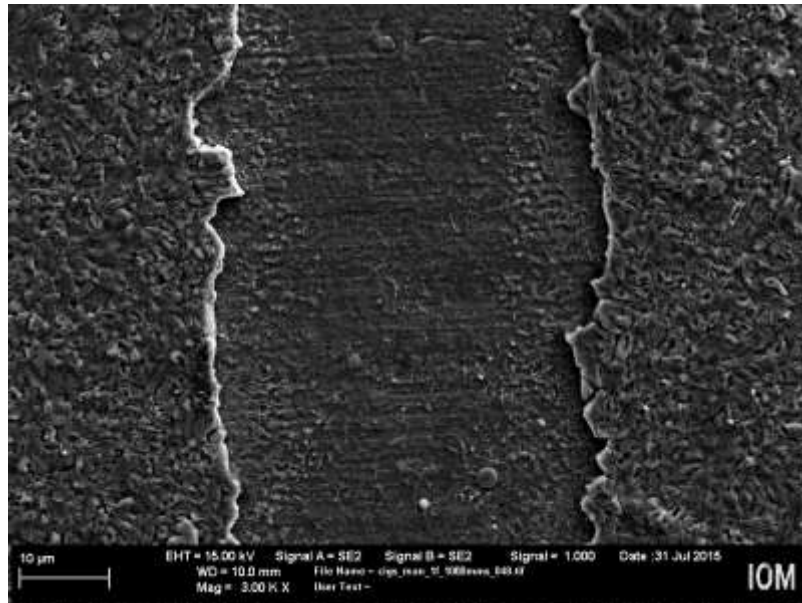
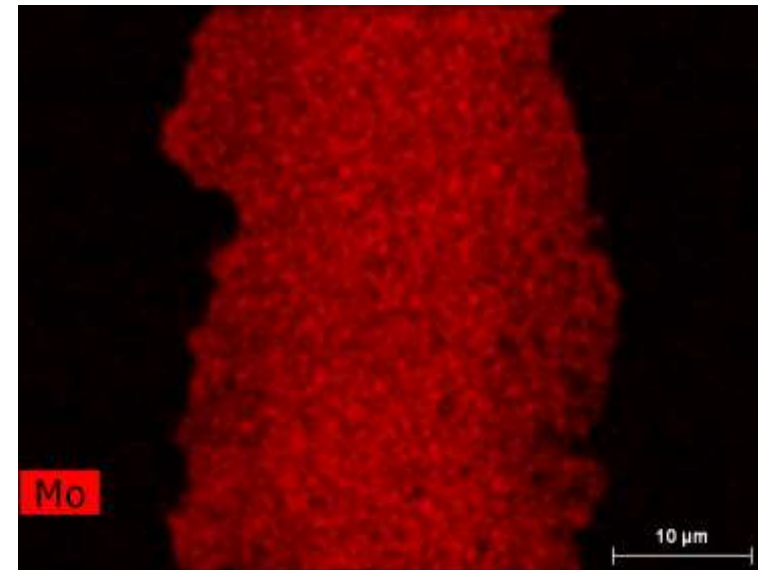
$v_s = 3$ m/s



Composition of CIGS scribe at laser lift-off delamination

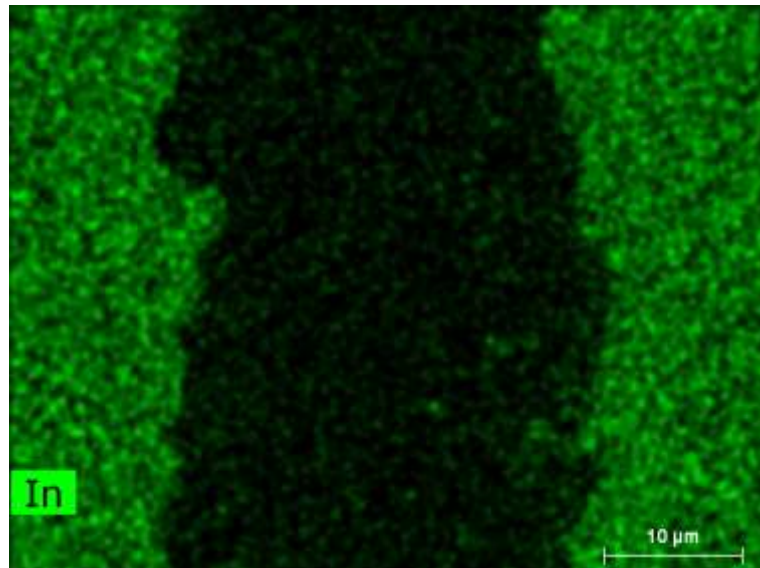
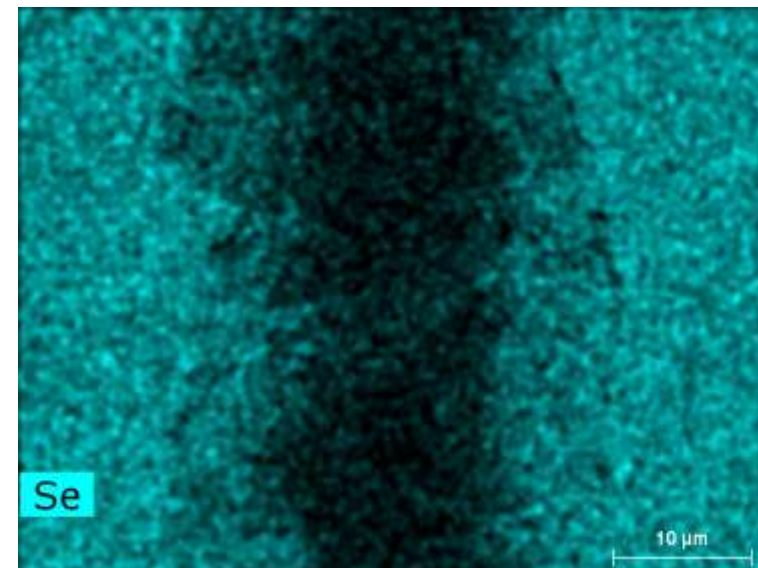
SEM

EDX: Mo



EDX: In

EDX: Se

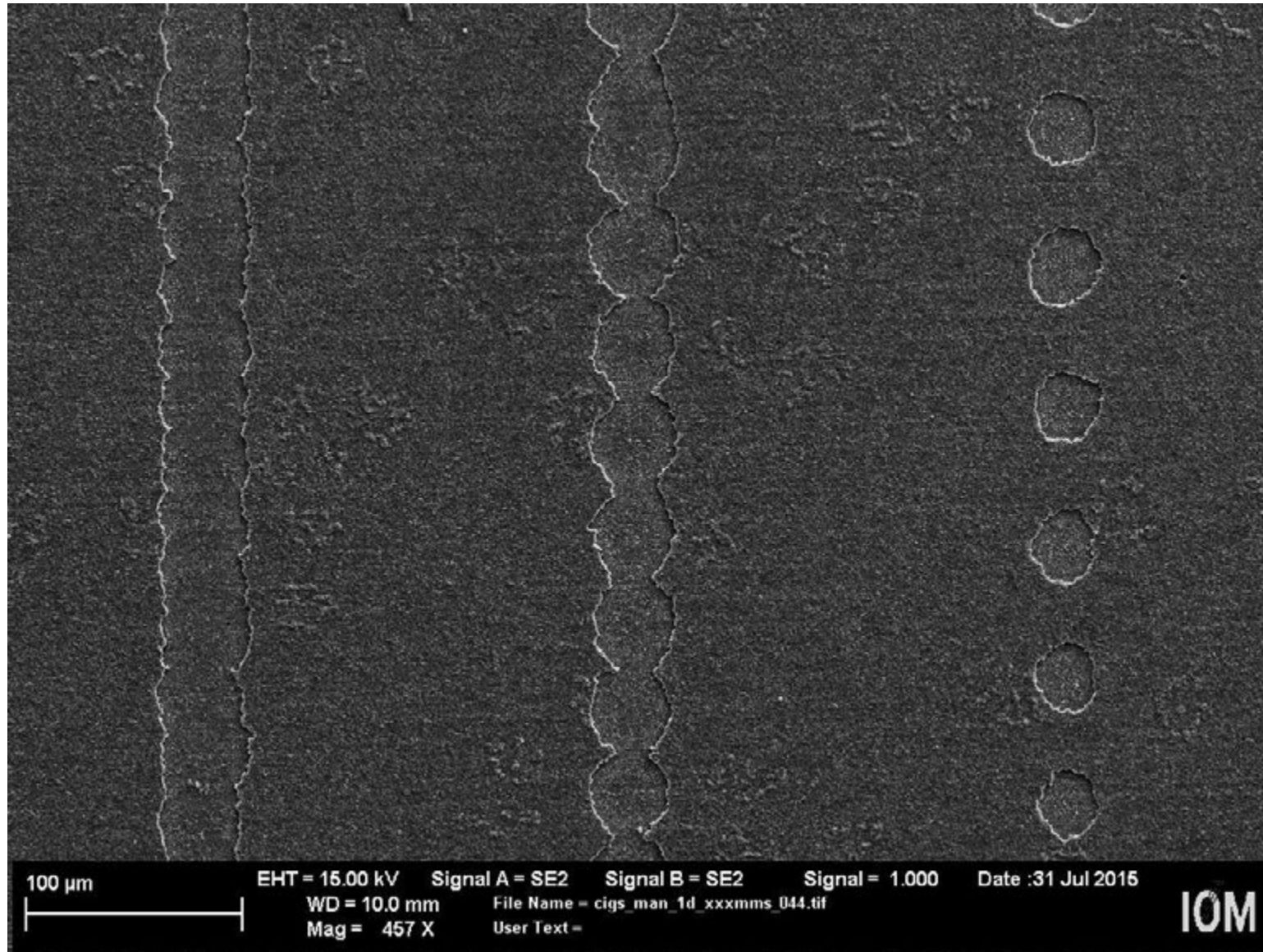


λ : 1550 nm, t_p : ~6 ns, f: 100 kHz, r_g : 21 μ m

Abengoa Solar NT-Material

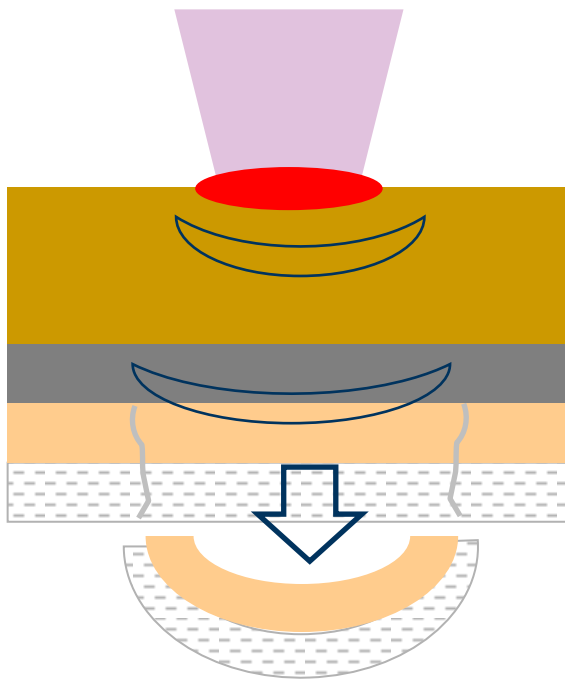
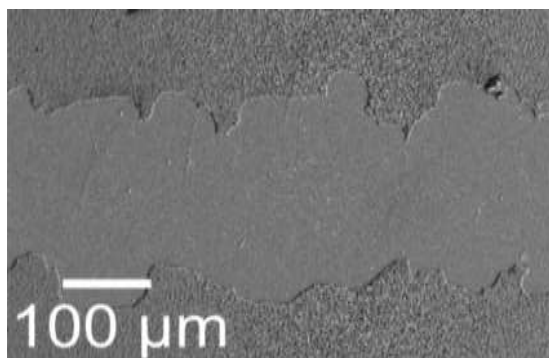
λ : 1550 nm, t_p : ~6 ns, f: 100 kHz, rg: 21 μ m

Abengoa Solar NT-Material

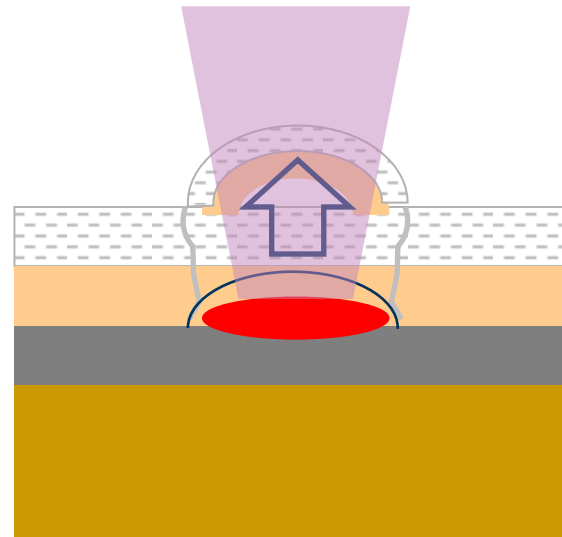
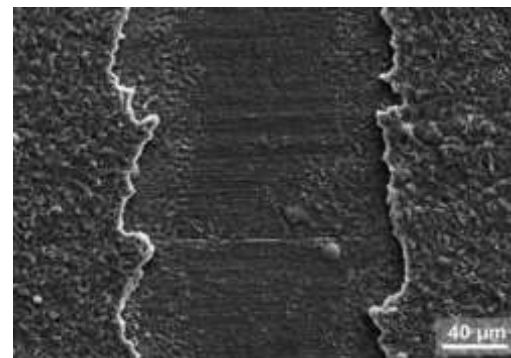


SEM image of CIGS scribes with different scribing speeds (3, 5, and 10 m/s)

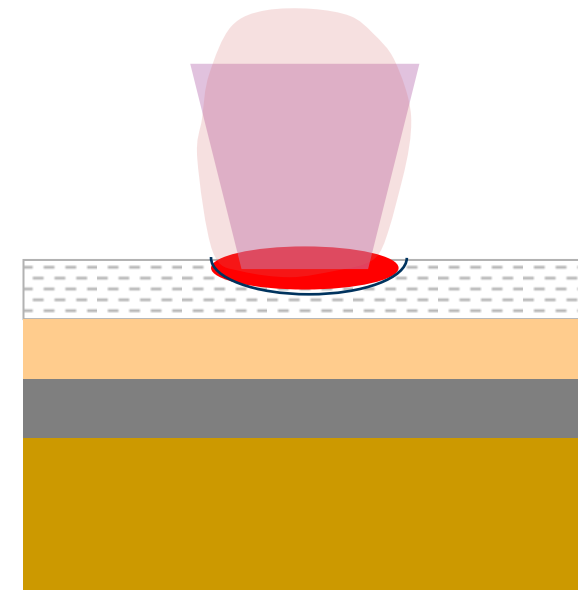
shock wave induced
thin film
delamination



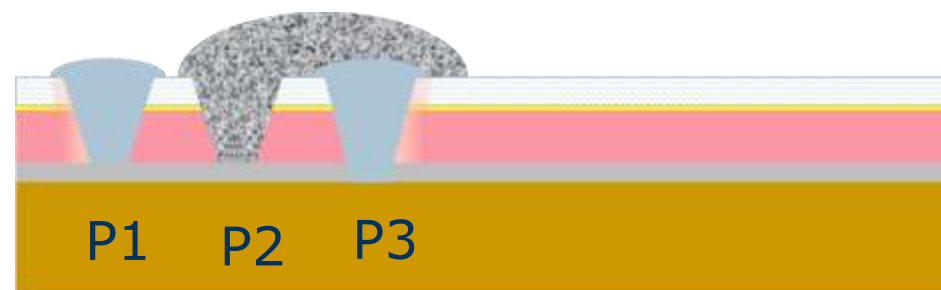
confined ablation
induced thin film
delamination



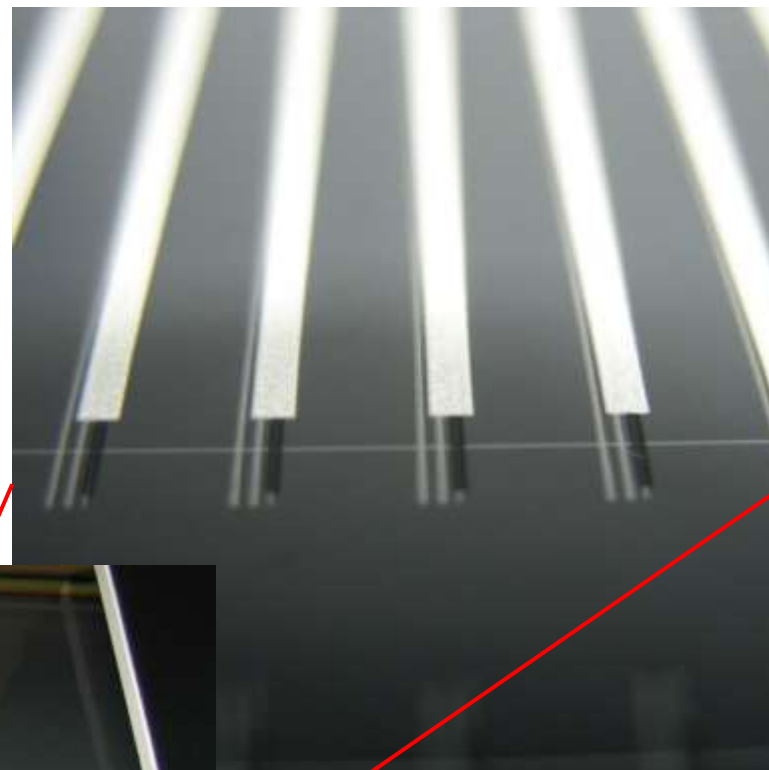
laser ablation



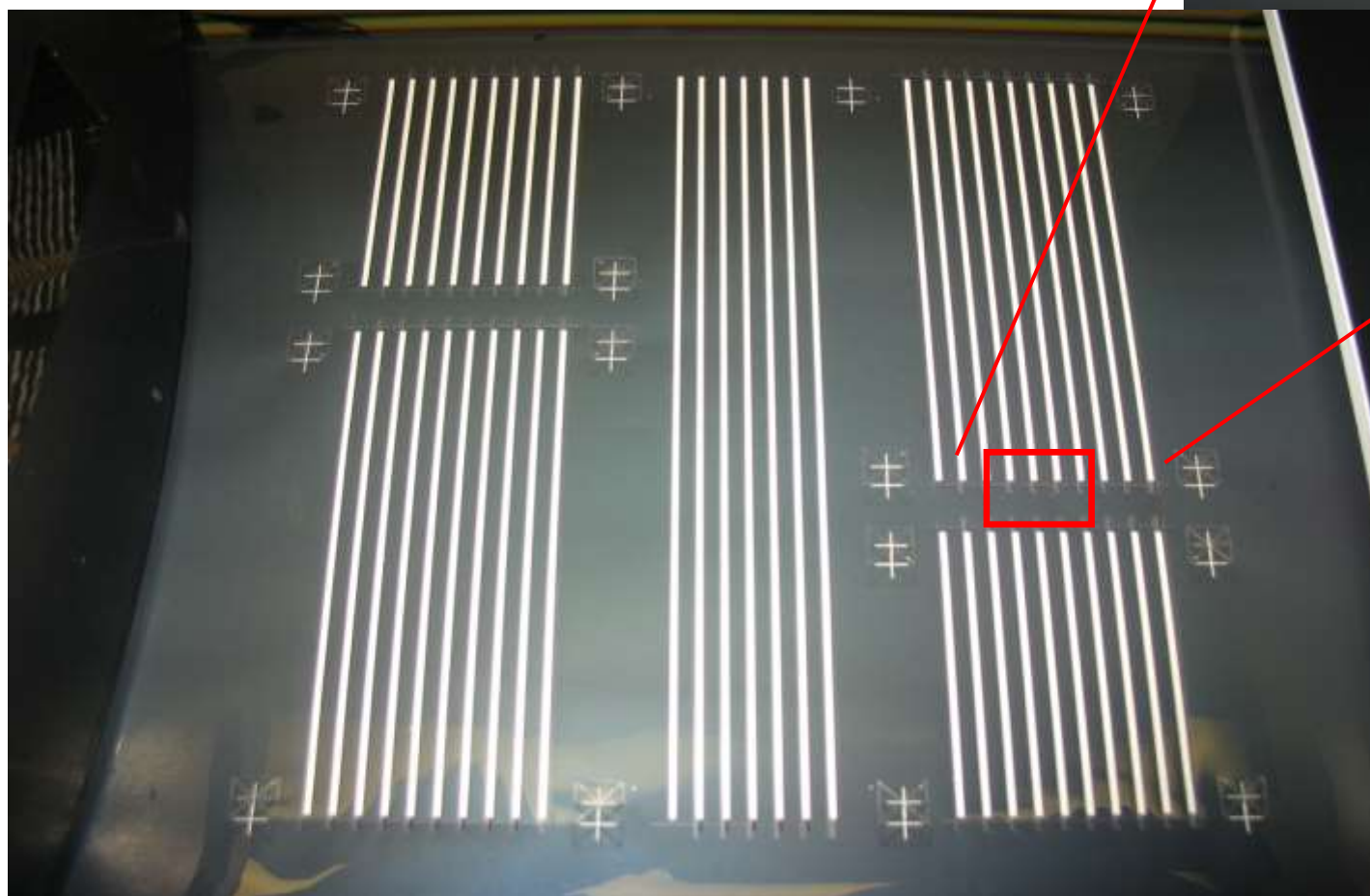
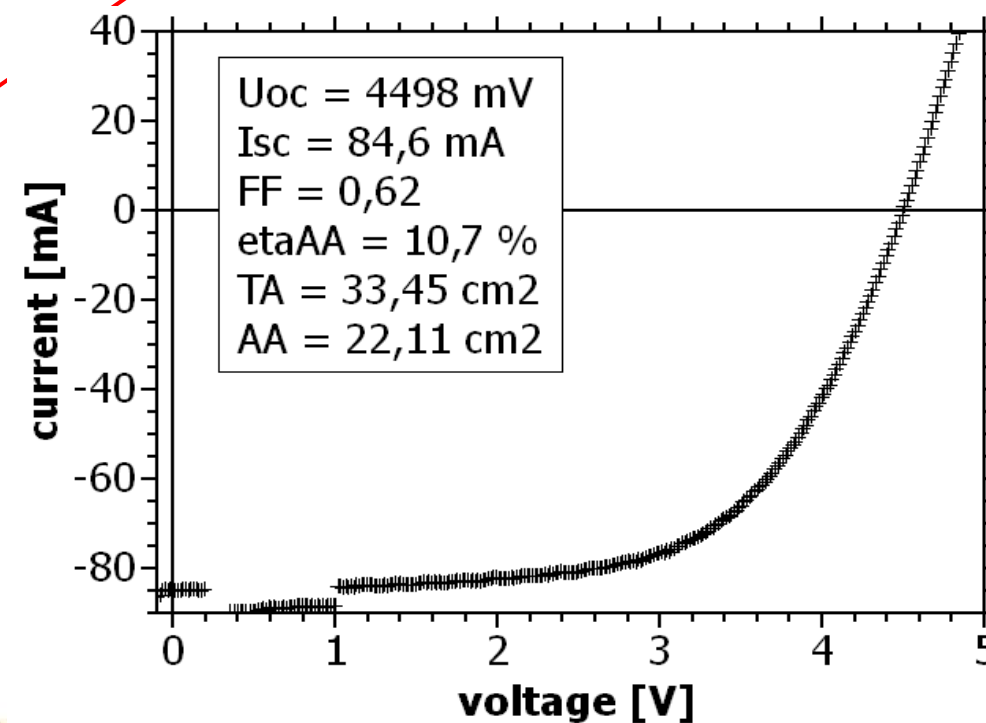
TCO
CIGS
Mo
Substrate (PI)



PI CIGS CA
 Mo TCO IA



Mini module by:
vaccum deposition
ps-laser scribing
screen printing



Selected materials for perovskite solar cells

**PCBM,
Phenyl-C61-
butyric acid
methyl ester**

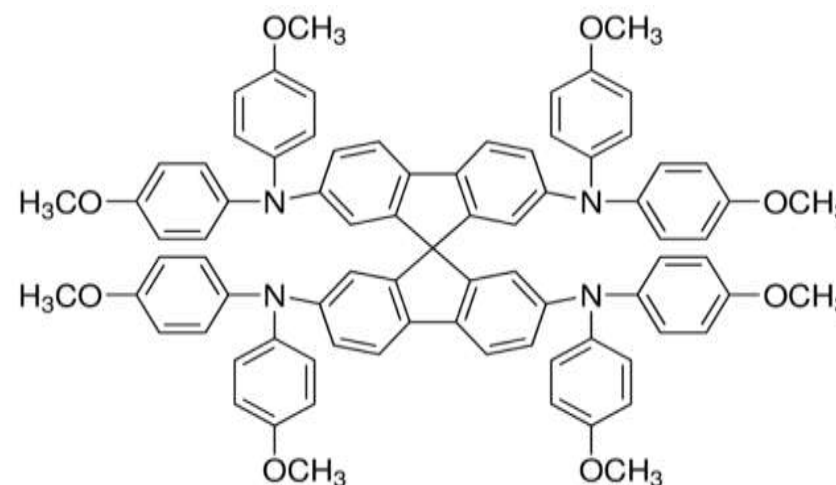
ETL

**perovskite
methyammonium
-lead triiodide,
 $\text{CH}_3\text{NH}_3\text{PbI}_3$
(MAPI_3)**

absorber

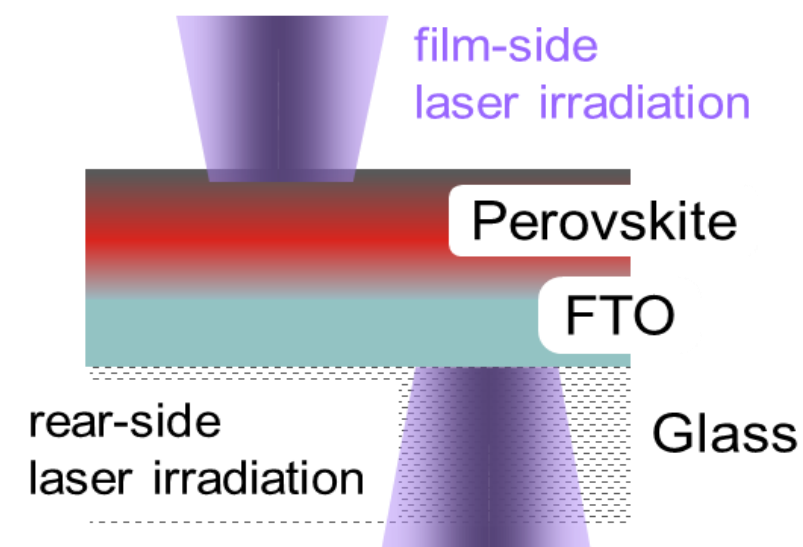
Spiro-MeOTAD

HTL



- Materials Perovskite PV are very different in chemical composition and structure
- Sensitive to UV-light and moisture
- Laser-induced decomposition must be considered
- Specific interface for PV required

Pulse-length	Wavelength	Active medium
7 ns	2500 nm	crystal laser (OPO)*
1 - 300 ns	1064 nm	fiber laser
25 ns	248 nm	KrF Excimer laser
10 ps	355 nm (3 rd)	Nd:YVO ₄
10 ps	532 nm (2 nd)	Nd:YVO ₄
10 ps	1064 nm	Nd:YVO ₄
150 fs	775 nm	Ti:Al ₂ O ₃
230 fs	515 nm (2 nd)	Yb:KGW



Aim: addressing different processes in the perovskite and the substrate.

*laser source: Ekspla and FTMC

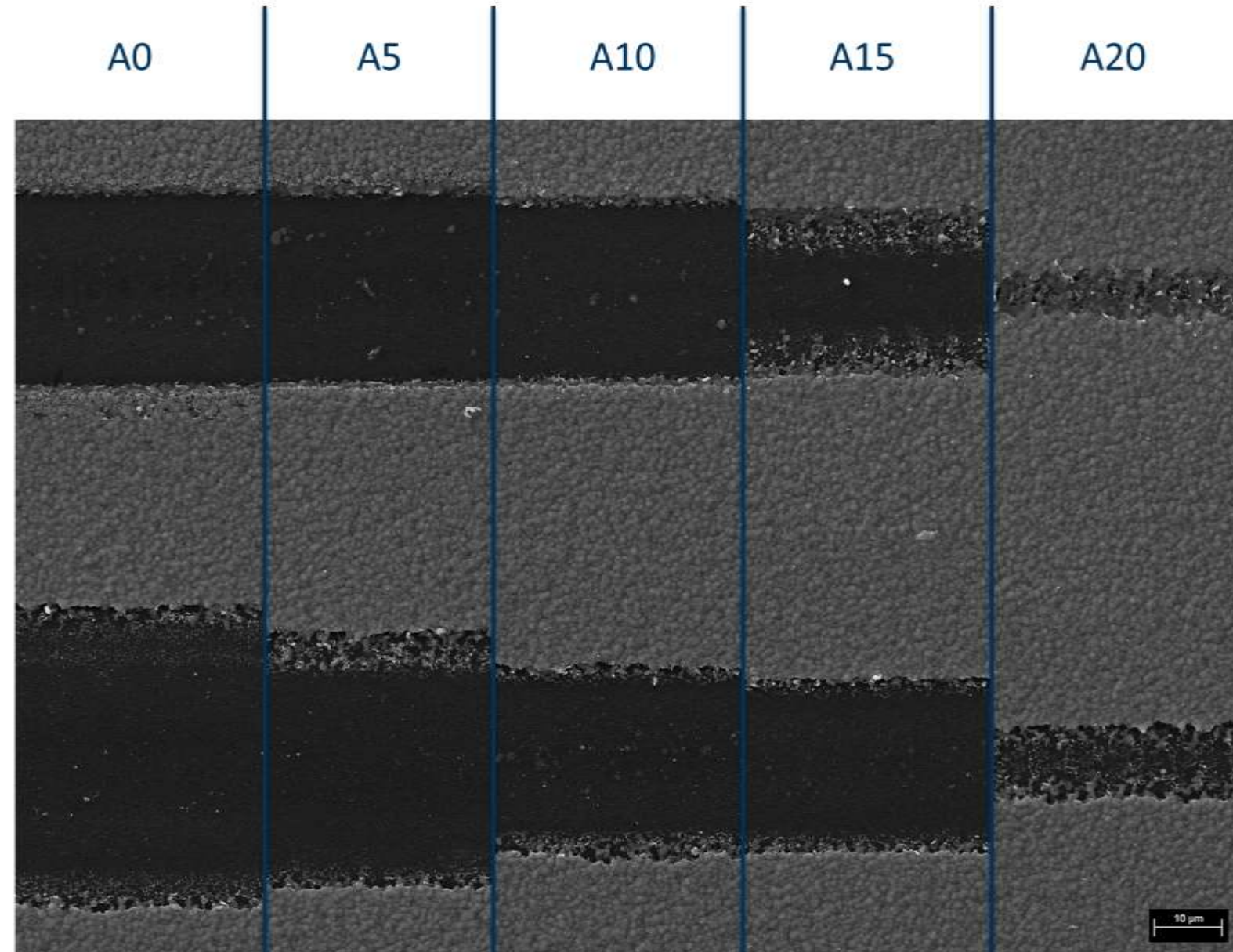
Pulse-/wavelength	Single pulse on perovskite layer	
	Front side [mJ/cm ²]	Rear side [mJ/cm ²]
ns, 2500 nm	-	-
ns, 1064 nm	8500	5700
ns, 248 nm	<100	-
ps, 355 nm	40	10
ps, 532 nm	45	18
ps, 1064 nm	133	154
fs, 780 nm	98	60
fs, 515 nm	30	10

Perovskites
band gap: $\sim 830\text{nm}$

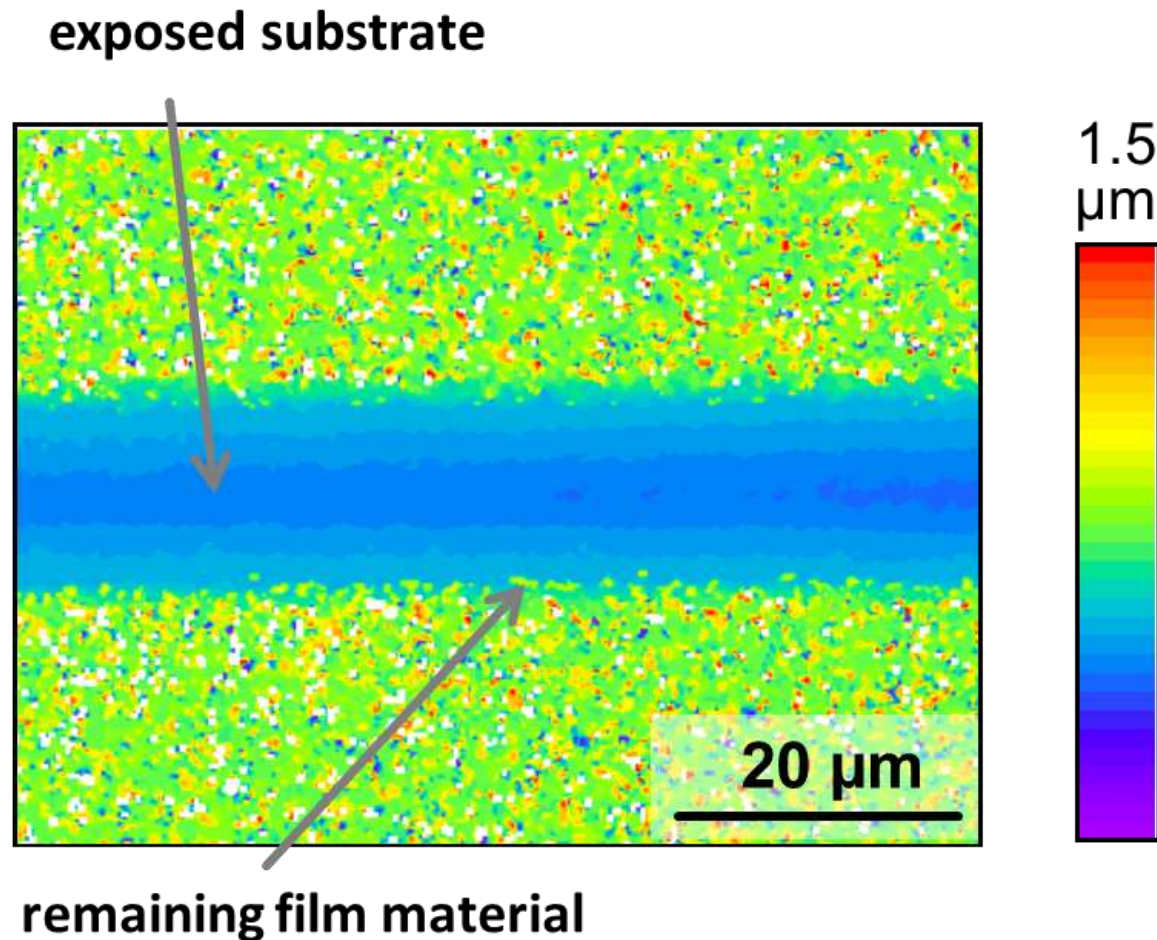
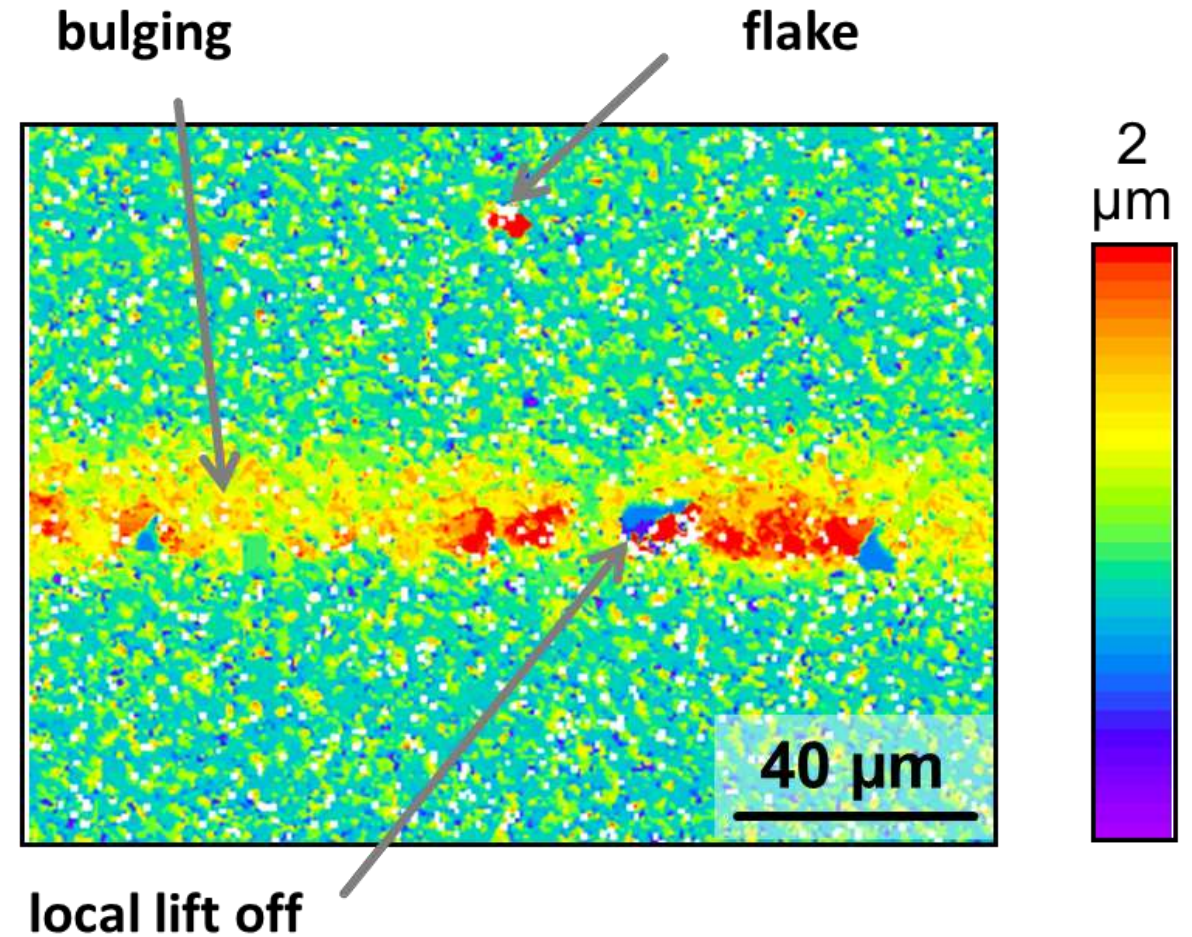
λ : 755 nm, t_p : ~120 fs, f : 1 kHz, r_g : 15 μm EMPA-Material

Front
side

Rear
side

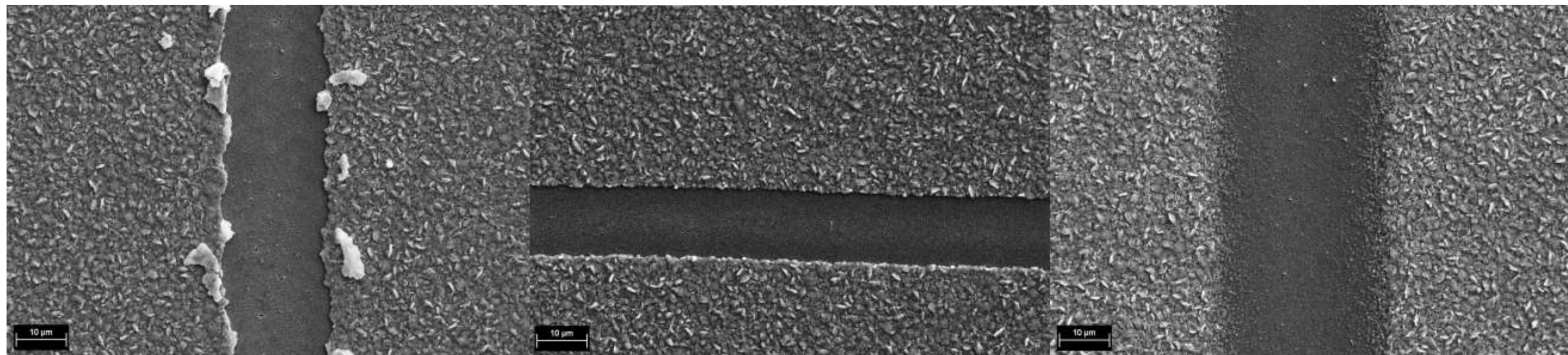


λ : 355 nm, t_p : ~12 ps, f: 100 kHz, r_g : 12 μ m EMPA-Material



WLIM images of front side irradiated sample

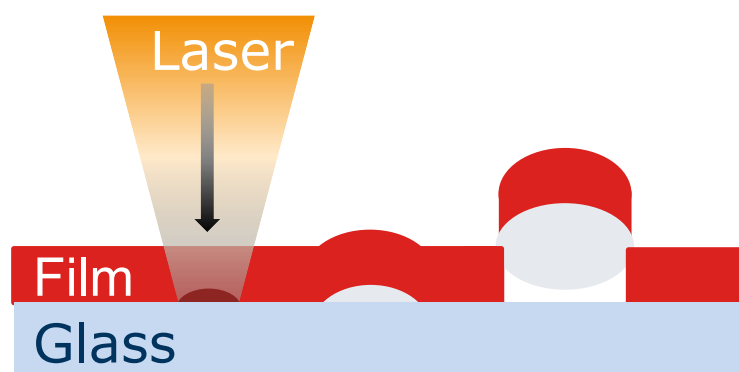
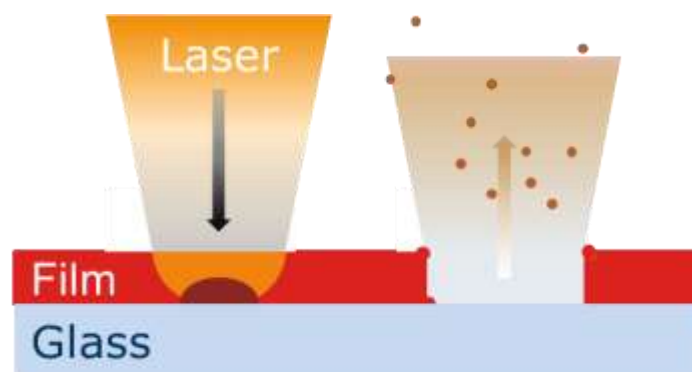
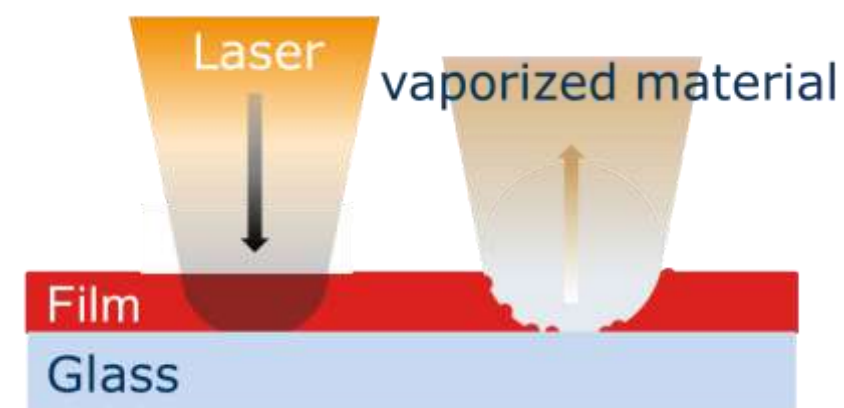
WLIM images of rear side irradiated sample with low fluence



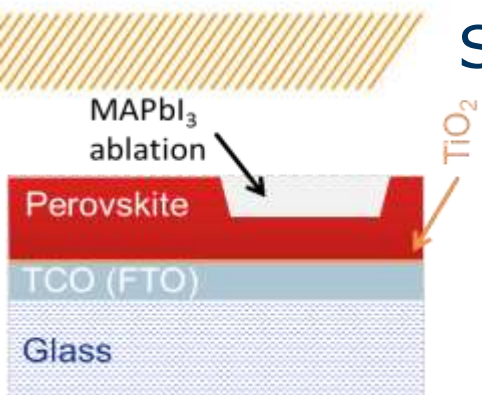
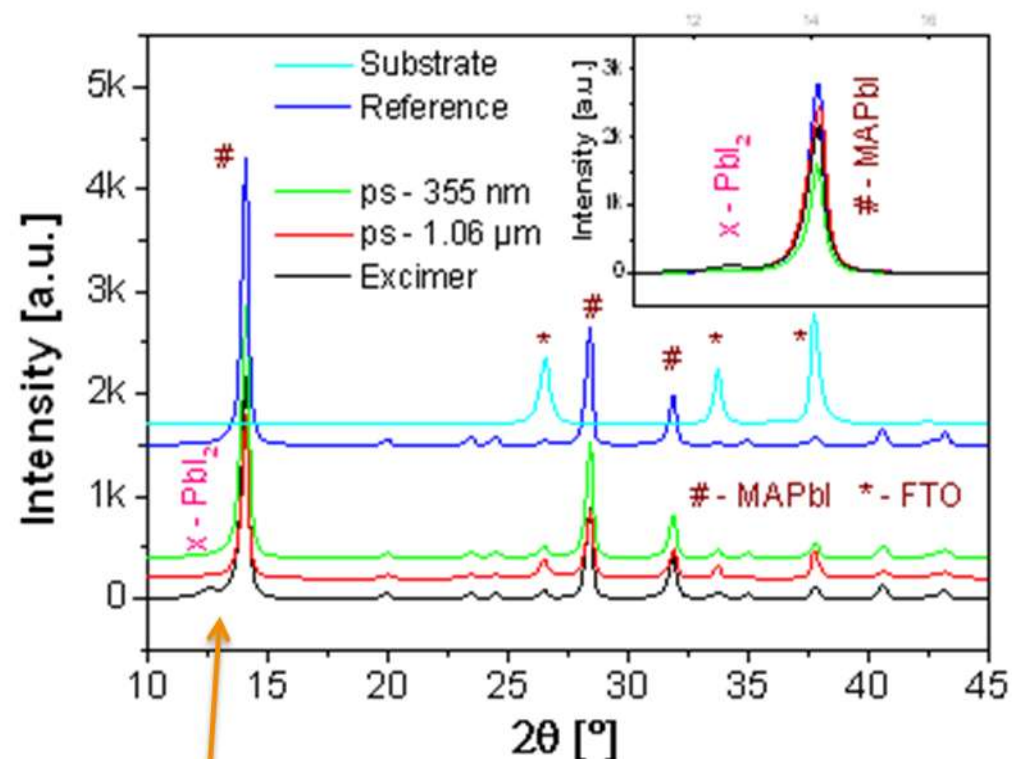
Lift-off (with flaks)
e.g. (1064 nm, ns)

Ablation + Lift-off
e.g. (532 nm, ps)

Ablation
e.g. (1064 nm, ps)



	P2 Solar cell scribe		Single pulse	
Pulse- /wavelength	Front side	Rear side	Front side	Rear side
ns, 2500 nm	lift-off (with flaks)	-	-	-
ns, 1064 nm	lift-off (with flaks)	lift-off (with flaks)	ablation, grain lift-off	ablation, grain lift- off
ns, 248 nm	-	-	ablation	-
ps, 355 nm	ablation	lift-off (with flaks)	ablation	ablation - lift-off
ps, 532 nm	ablation - lift-off	ablation - lift-off	ablation	ablation - lift-off
ps, 1064 nm	ablation	ablation	ablation, grain lift-off	ablation, grain lift-off
fs, 780 nm	ablation	ablation - lift-off	ablation	ablation - lift-off
fs, 515 nm	ablation	ablation - lift-off	ablation	ablation - lift-off



additional PbI_2 in the case of UV ns laser irradiation

MEASUREMENT OF THE PHASE COMPOSITION AFTER LASER ABLATION

Laser irradiated areas ($1.5 \times 1.5 \text{ cm}^2$):

- Excimer
- 355 ps laser
- 1064 ps laser

Analyses of a reference and the laser processed areas with

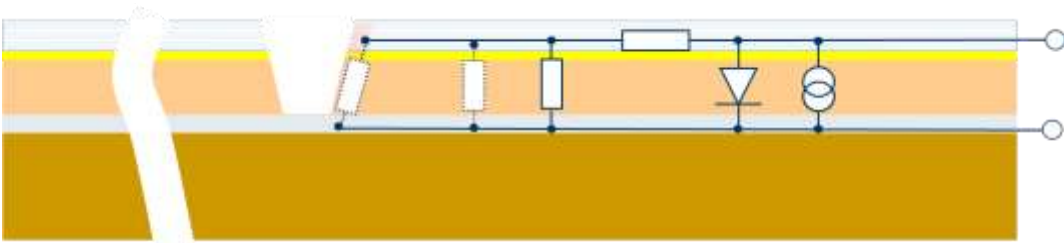
- Raman measurement
- XRD
- UV-VIS transmission measurements

Average thickness of the remaining Perovskite film original appr. 240nm:

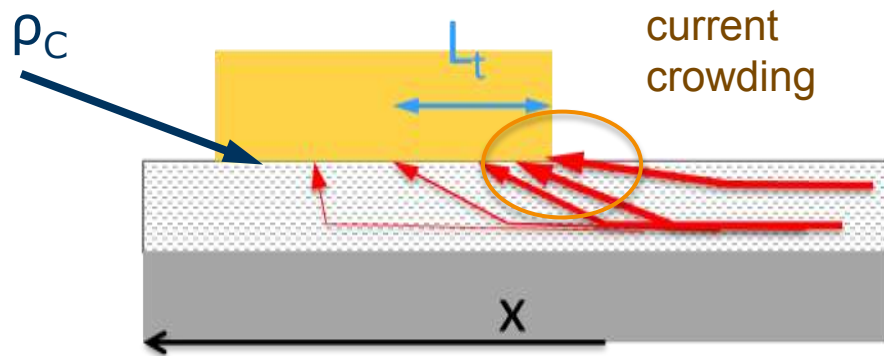
- 355 ps laser 180 nm
- 1064 ps laser 60 nm
- Excimer 160 nm

Study of laser scribing impact to electrical cell and module characteristics

Geometrical efficiency losses the reduction of the effective area have to be considered too.



- Focus on 355 nm ps laser scribing
- specific film resistance
- insulation resistance
- **P2: contact resistance**
- P3: defect/shunt generation and insulation resistance

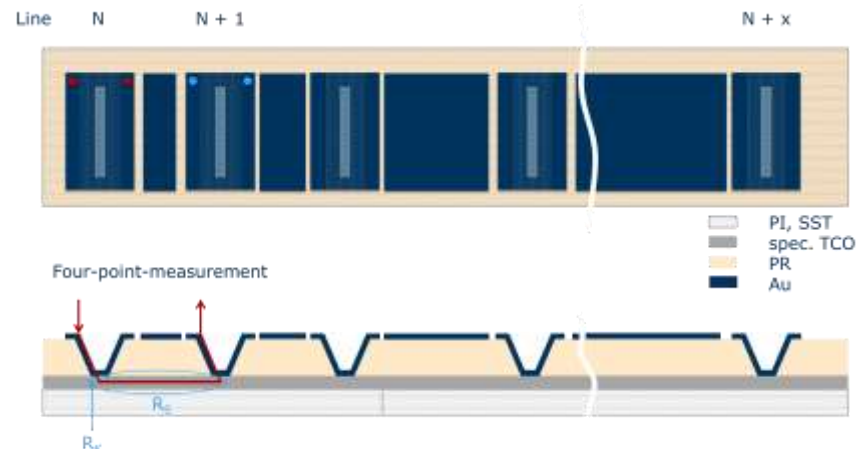


Current density at the contact interface.

$$I(x) \propto \exp\left(-\frac{x}{L_T}\right)$$

W_C - width of the contact
 L_C - length of the contact
 L_T - transfer length
 ρ_C - specific contact resistance

Transfer length measurements



$$R_{mes} = 2 * R_C + R_S(d_{n, n+1})$$

Specific contact resistivity due to the current crowding problem:

- 1) The current is constant over the contact area; this can be assumed for $L_C \ll L_T$
- 2) The current is zero at the trailing edge this can be assumed for $L_C \gg L_T$

$$\rho_C = R_C / L_C \times W_C$$

$$\rho_C = R_S \times L_T^2$$

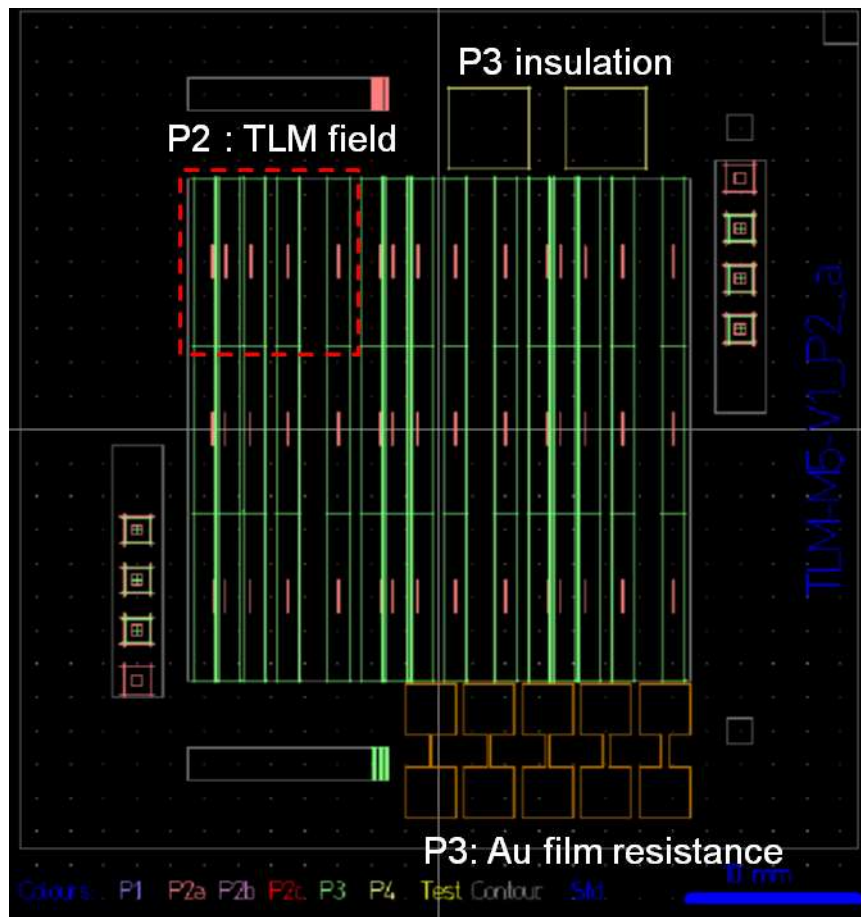
In the design currently tree test are implemented:

parallel resistance of P3:

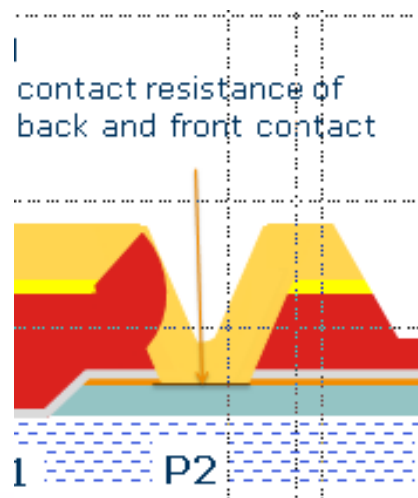
- insulation between cells
 $R_{iso} \sim \infty$
- enabling the P2 contact resistance measurements

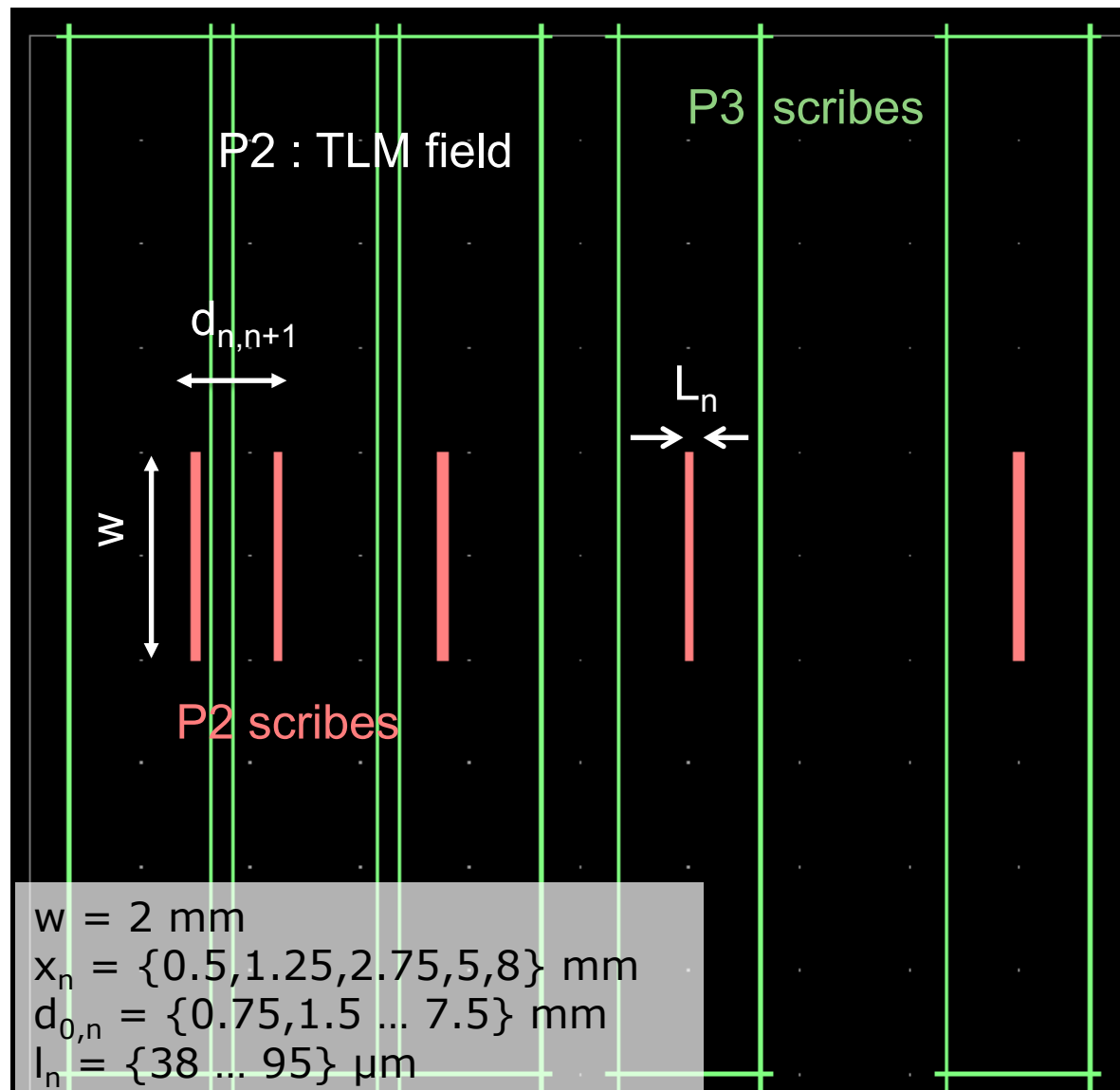
Serial resistance of the module:

- 1) Au thin film sheet resistivity
 $\sim 4 \times$ the bulk resistivity
- 2) TLM-test fields for P2 contact resistance



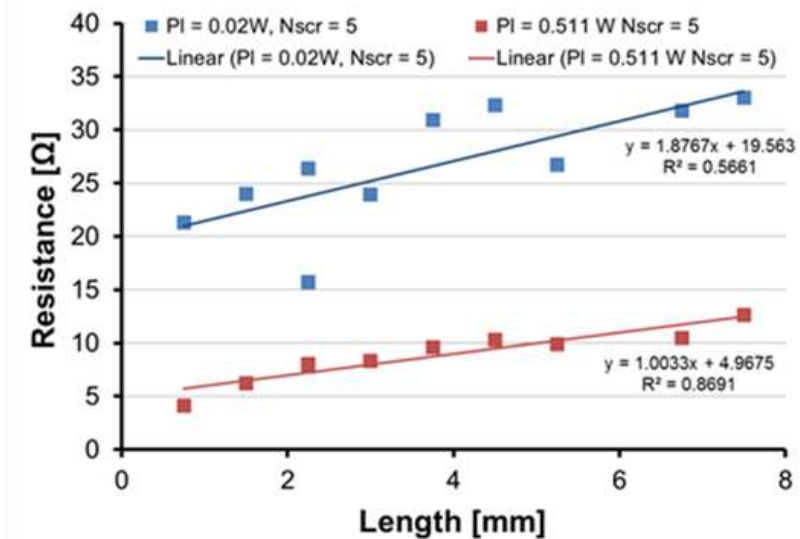
Layout for testing electrical properties of P2





TLM field design with five P2 scribes of different distance

The TLM-fields comprises of 5 P2 contacts performed with the same laser settings (P_L , v_s ...):

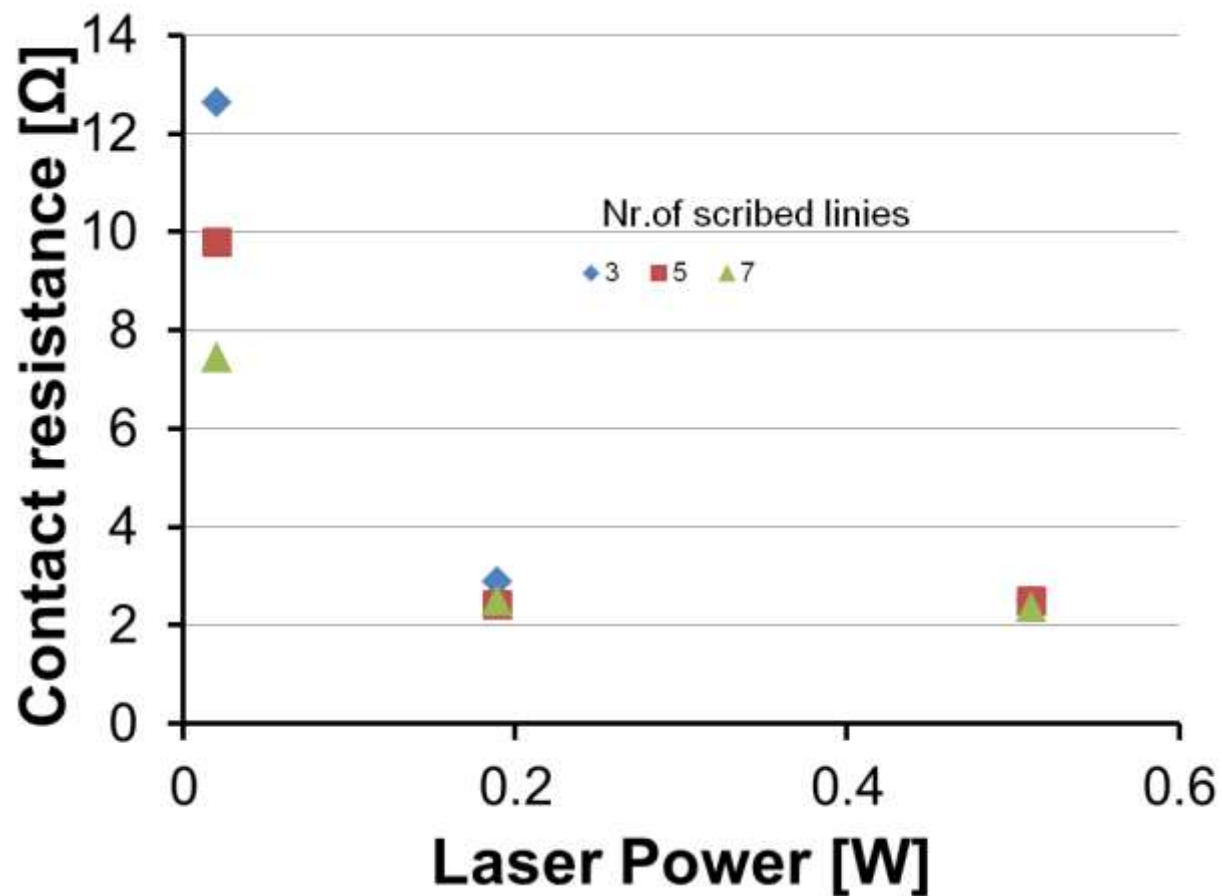


For each TLM-field the

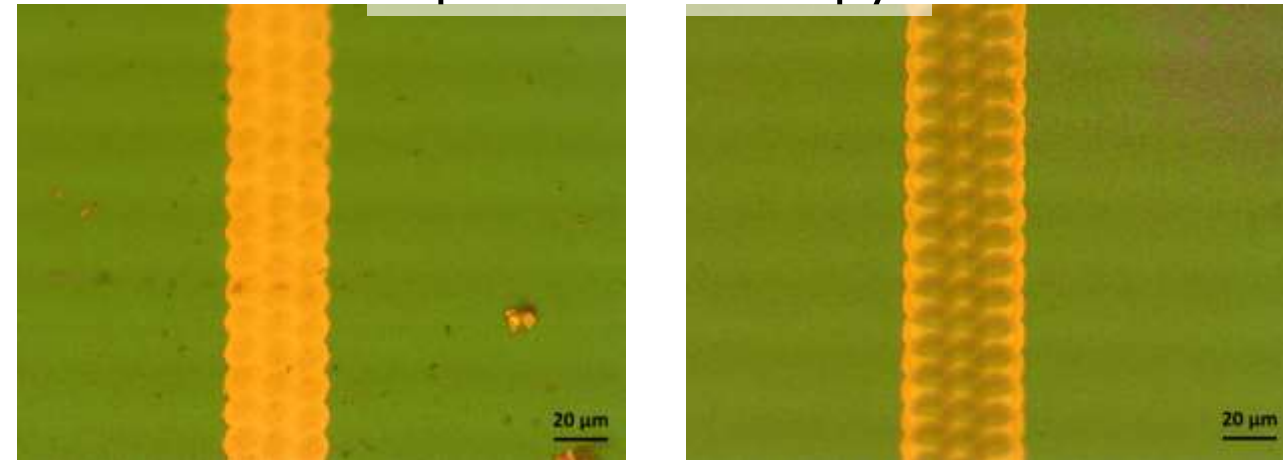
- L_T - transfer length
- R_c - contact resistance
- ρ_c - specific contact resistivity

can be determined.

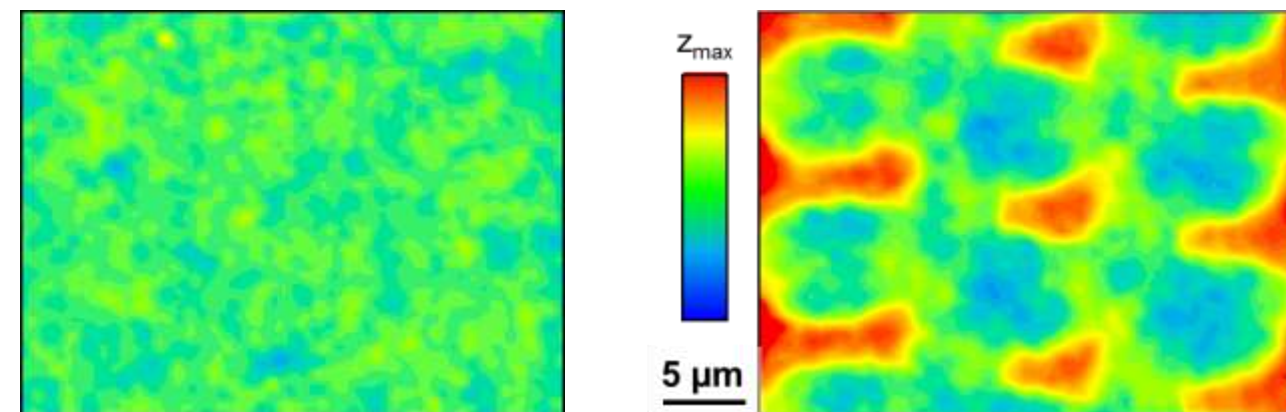
➡ **laser processing dependence of the contact properties**



optical microscopy

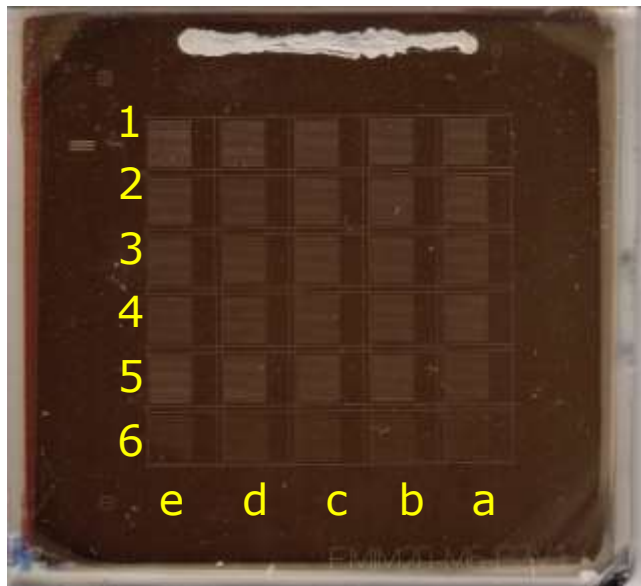
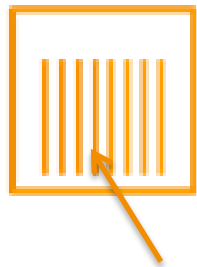


topography

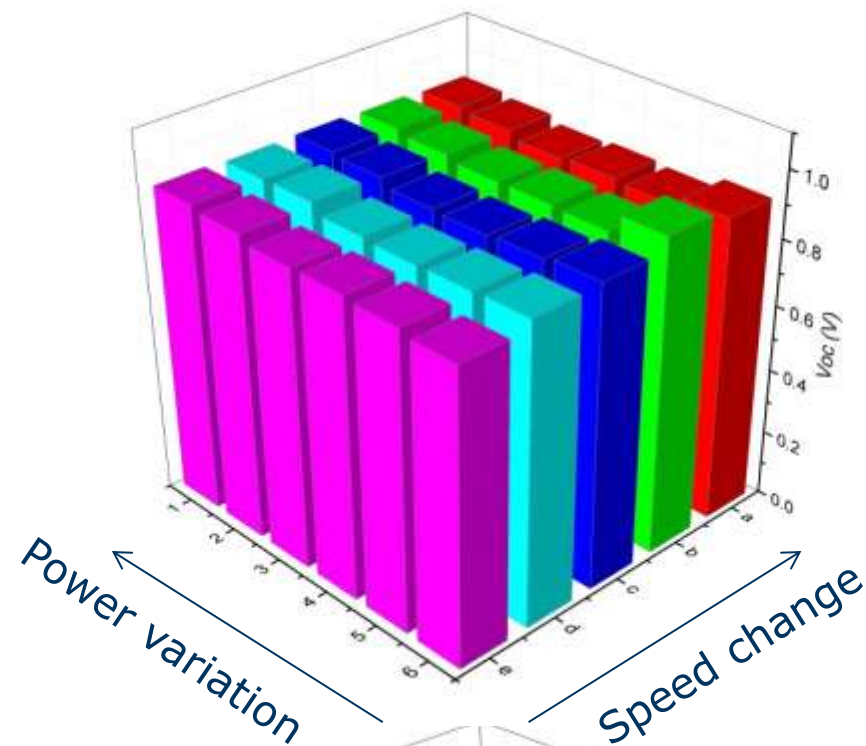
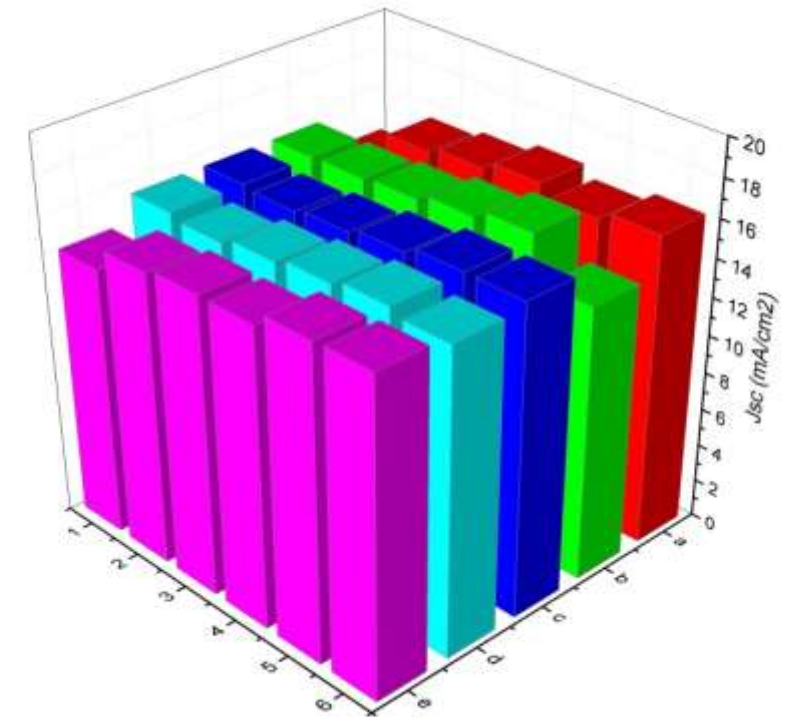
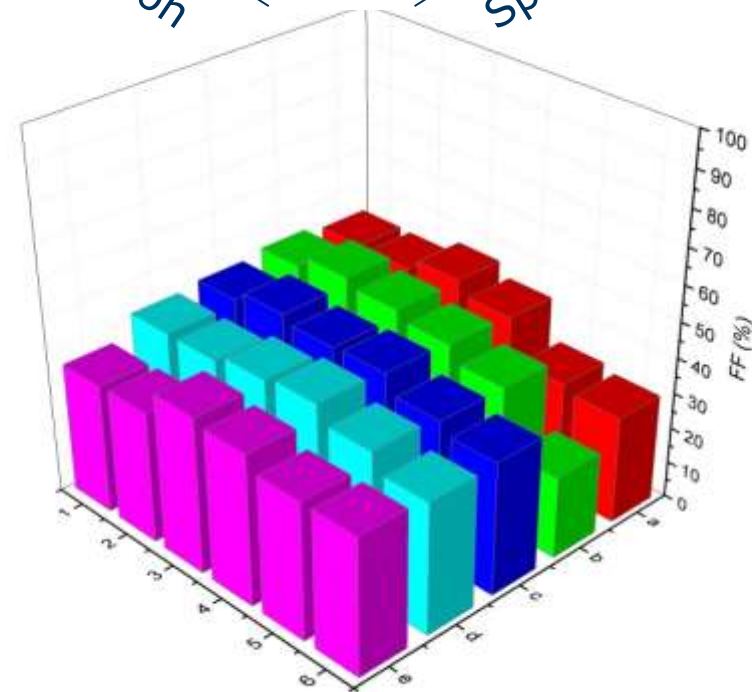
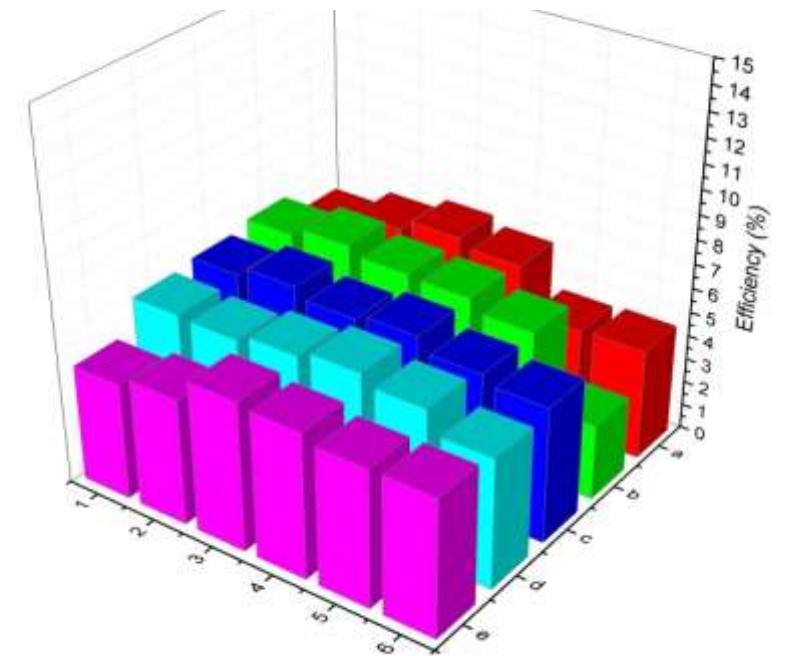


- selective ablation of the perovskite film can be achieved
- cleaning the scribe by partial removal of the next film can be helpful

PL	rms	PV
[W]	[nm]	[nm]
0.05	1.8	20
0.189	10.1	56
0.511	18	82

**M2**

P3 test scribes
(varying parameters)



P3 scribing of perovskite solar cells seems to be a robust process.

For study of the monolithic integrated interconnection all processes for thin film deposition and laser scribing have to be developed/adapted. Handling of perovskite samples must be well defined.

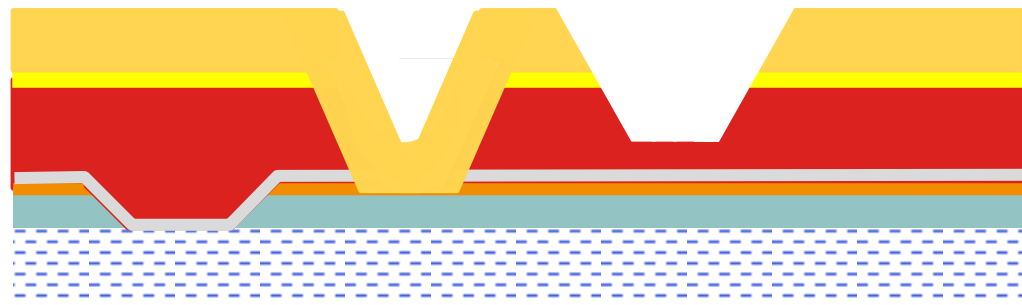


- | | |
|----|--|
| P1 | • Adaption of TCO laser scribing to the specific thin film system used for the front contact |
| P2 | • Selective scribing of Perovskite films |
| P3 | • Selective opening of the back contact (Au) |
| D1 | • Vacuum deposition of thin films for front contact |
| D2 | • Vacuum/liquid fabrication of absorber stack |
| D3 | • Vacuum deposition of back contact |

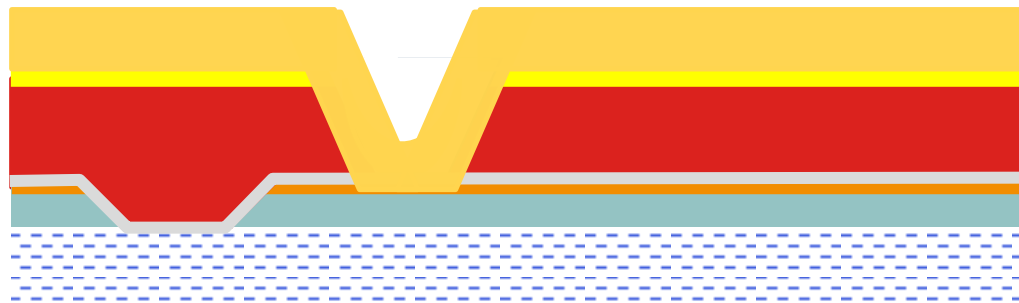
Fabrication sequence for the Perovskite modules on FTO substrates

IOM

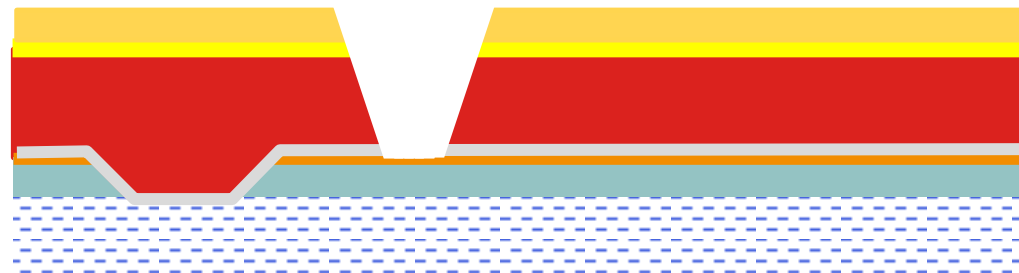
P3



D3: gold



P2

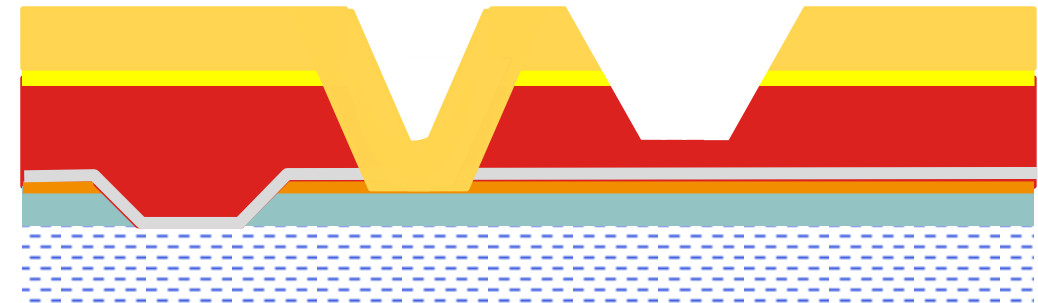


P1

transfer



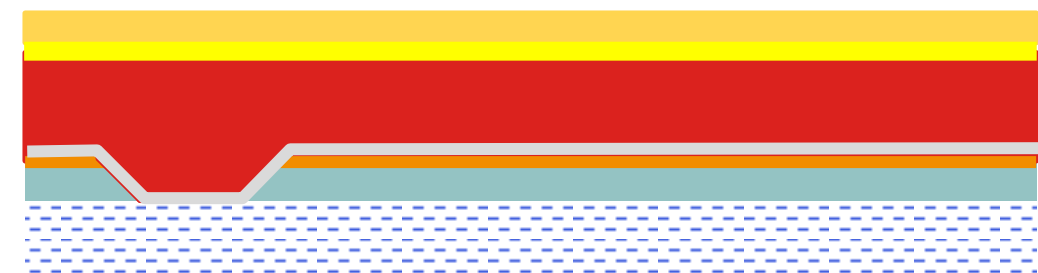
EMPA



Module characterization



D2: Full Perovskite film stack



D1: TCO preparation



IOM

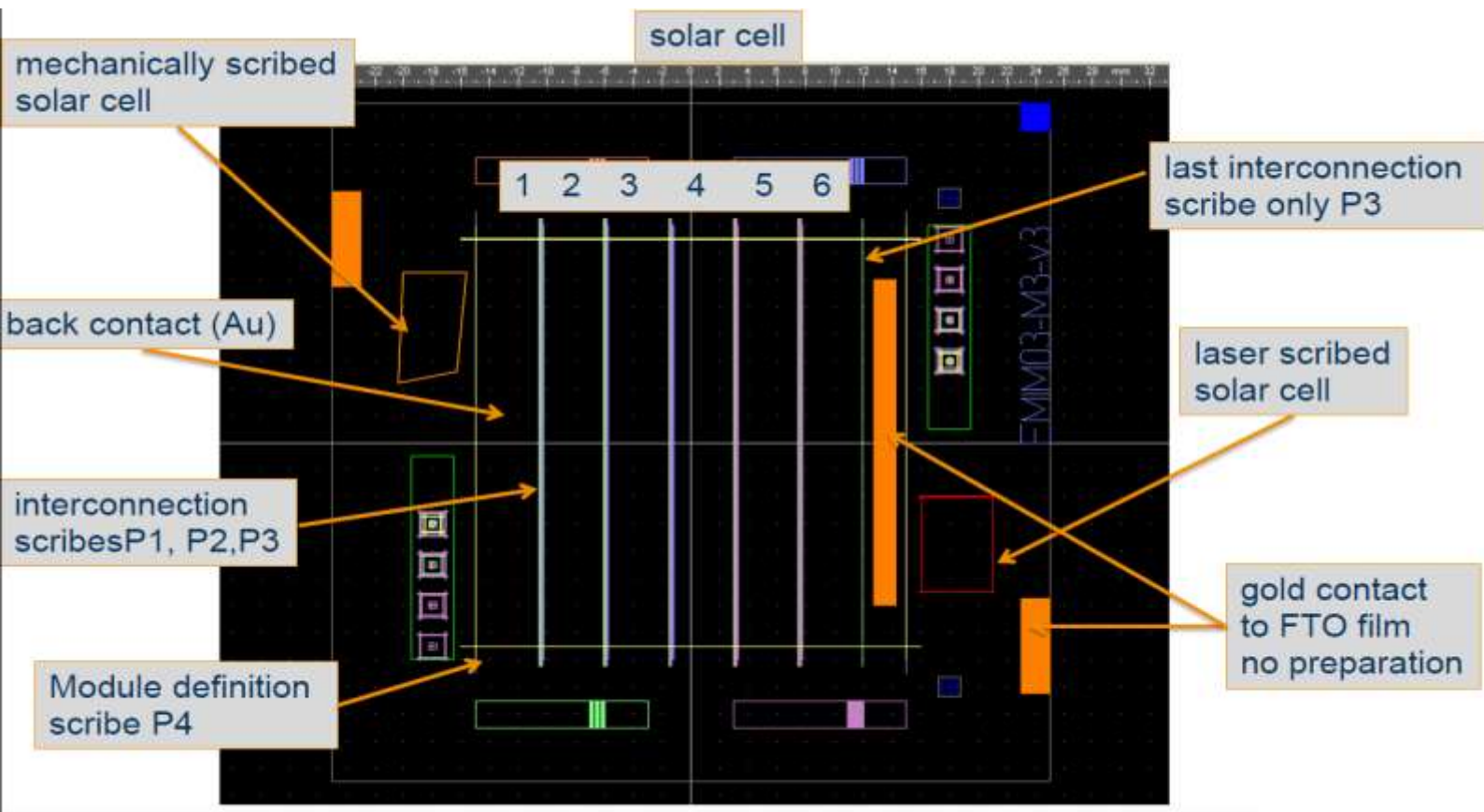
Perovskite mini-modules:

Nominal area: 8.6 cm²

Dead area: appr. 400 μm (per interconnection)

Cells: 6

Principal thin film design: Glass/FTO/TiO₂/PCBM/MAPbI₃/Spiro/Au

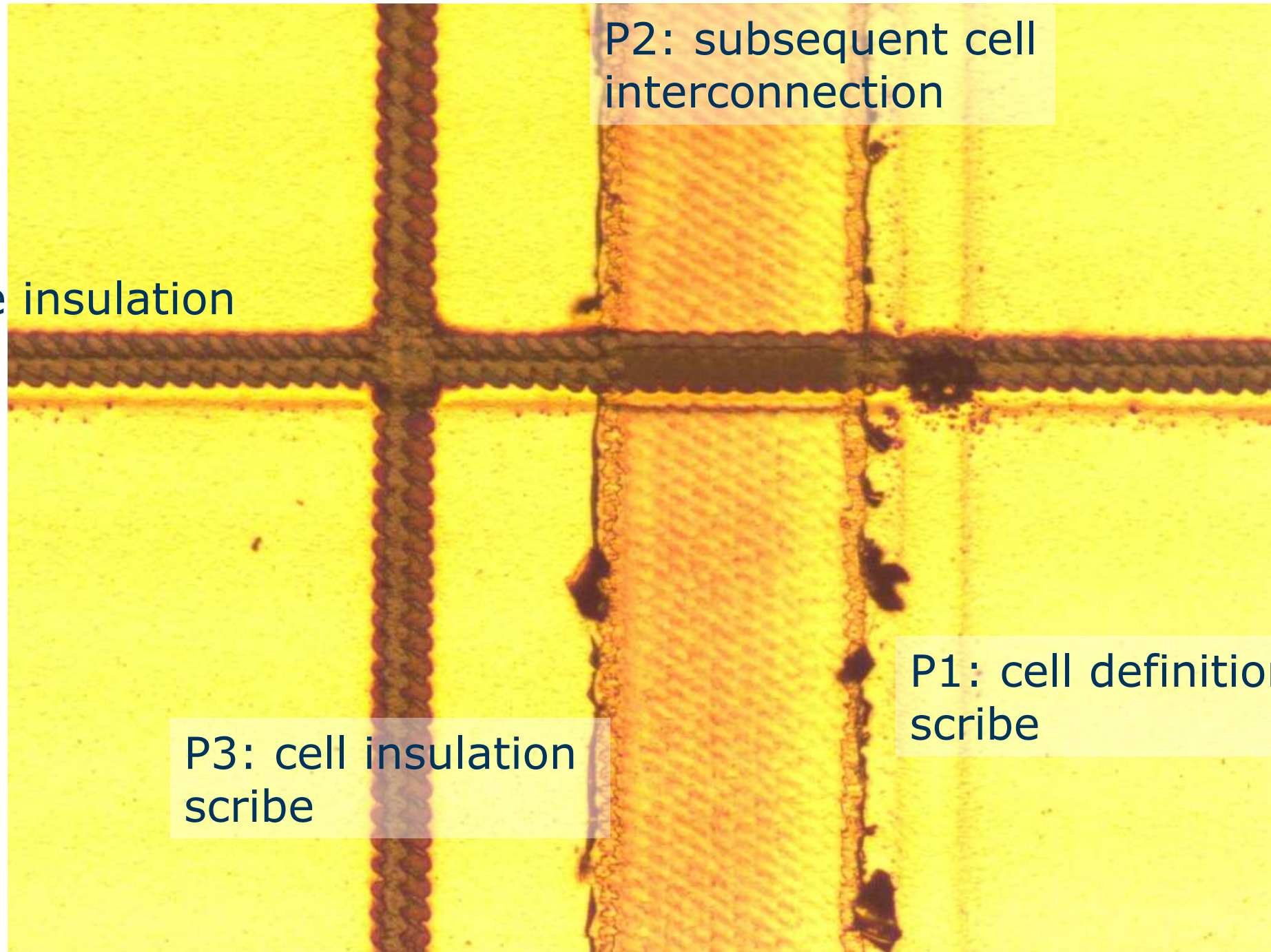


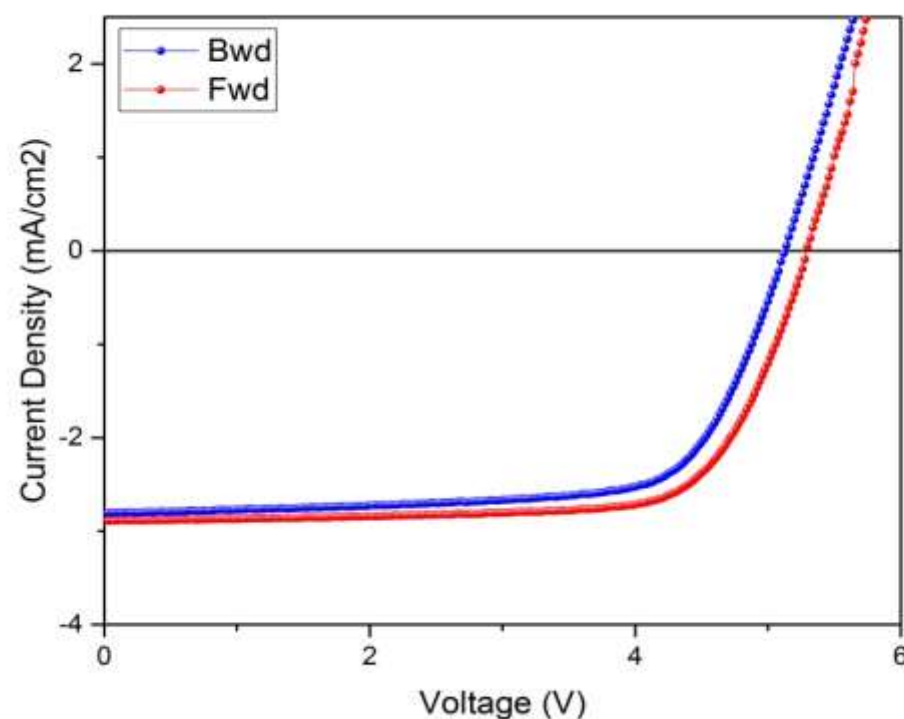
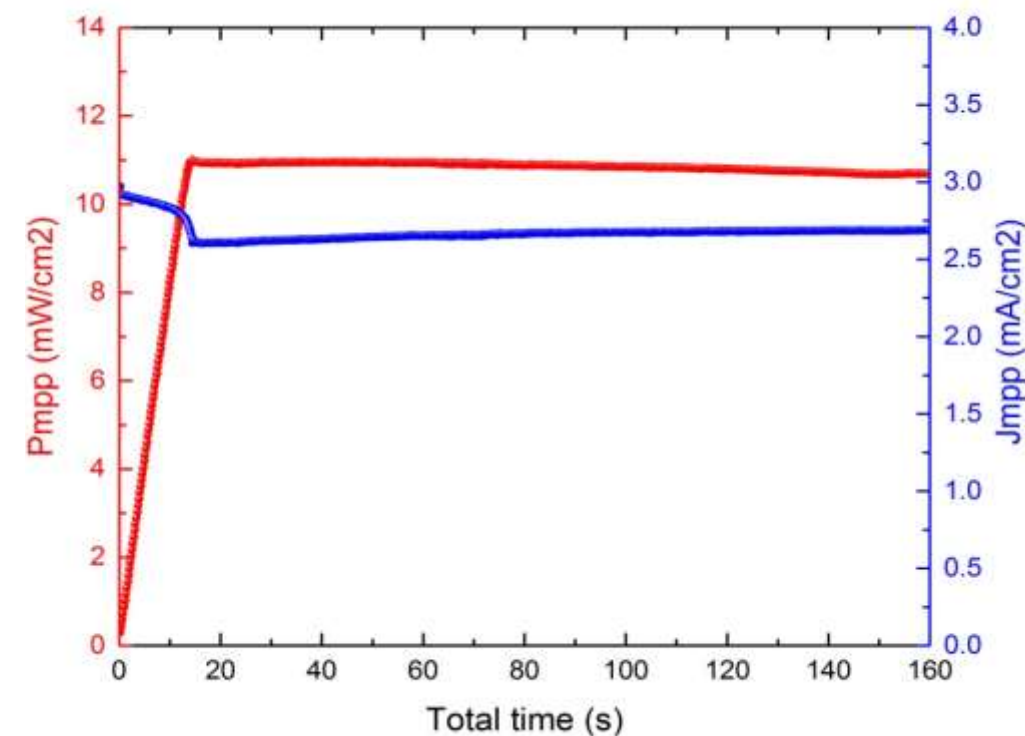
Layout for laser machining



Image of a module

P4
module insulation





Fife cells

Module area
6.73 cm²

Sample area
15 cm²

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)	η_{mpp} (%)
Fwd	5.3	2.9	72.8	11.13	10.65
Bwd	5.1 3	2.8	71	10.2	

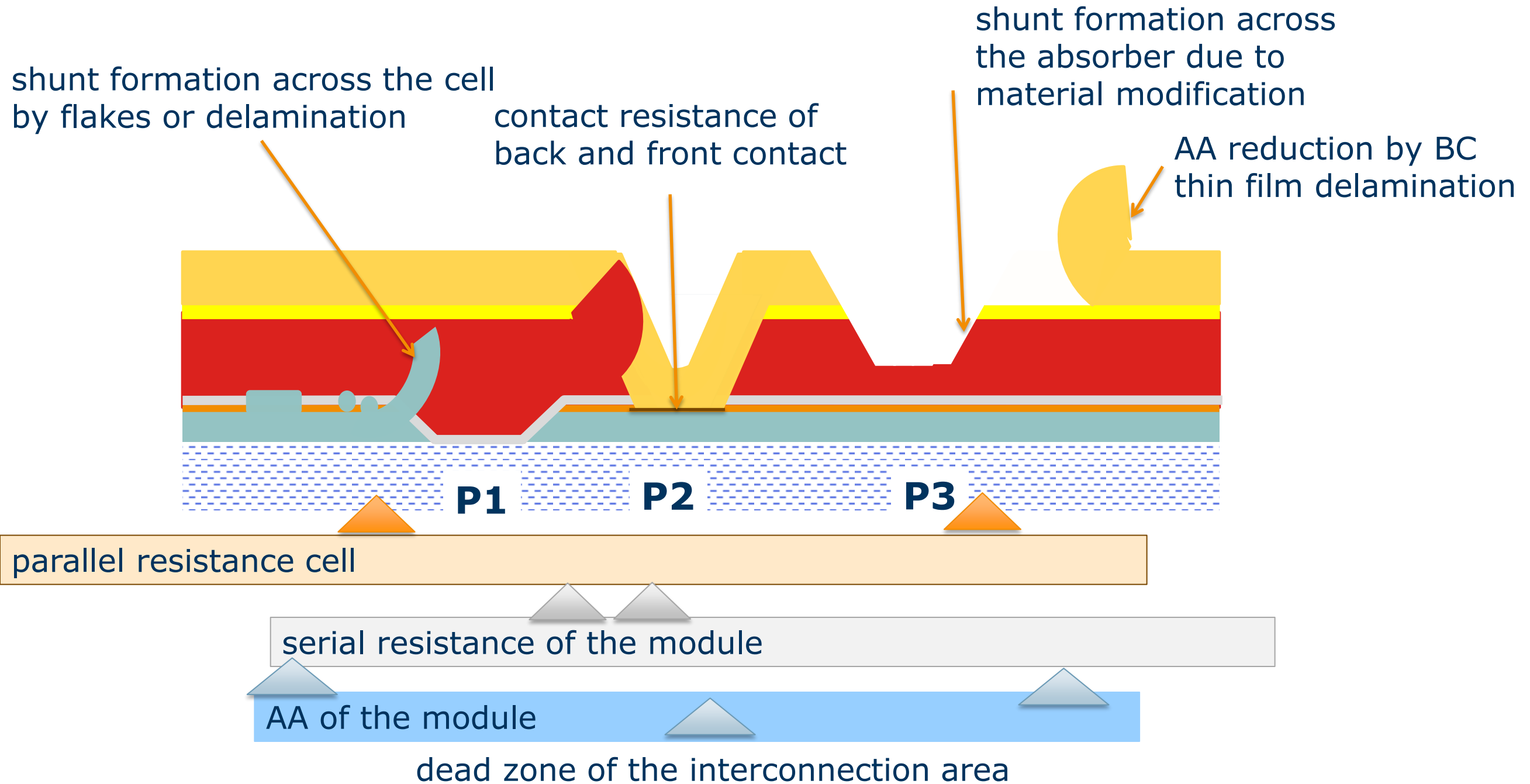
All laser scribed perovskite module with an efficiency of >10.5 % has been achieved so fair.

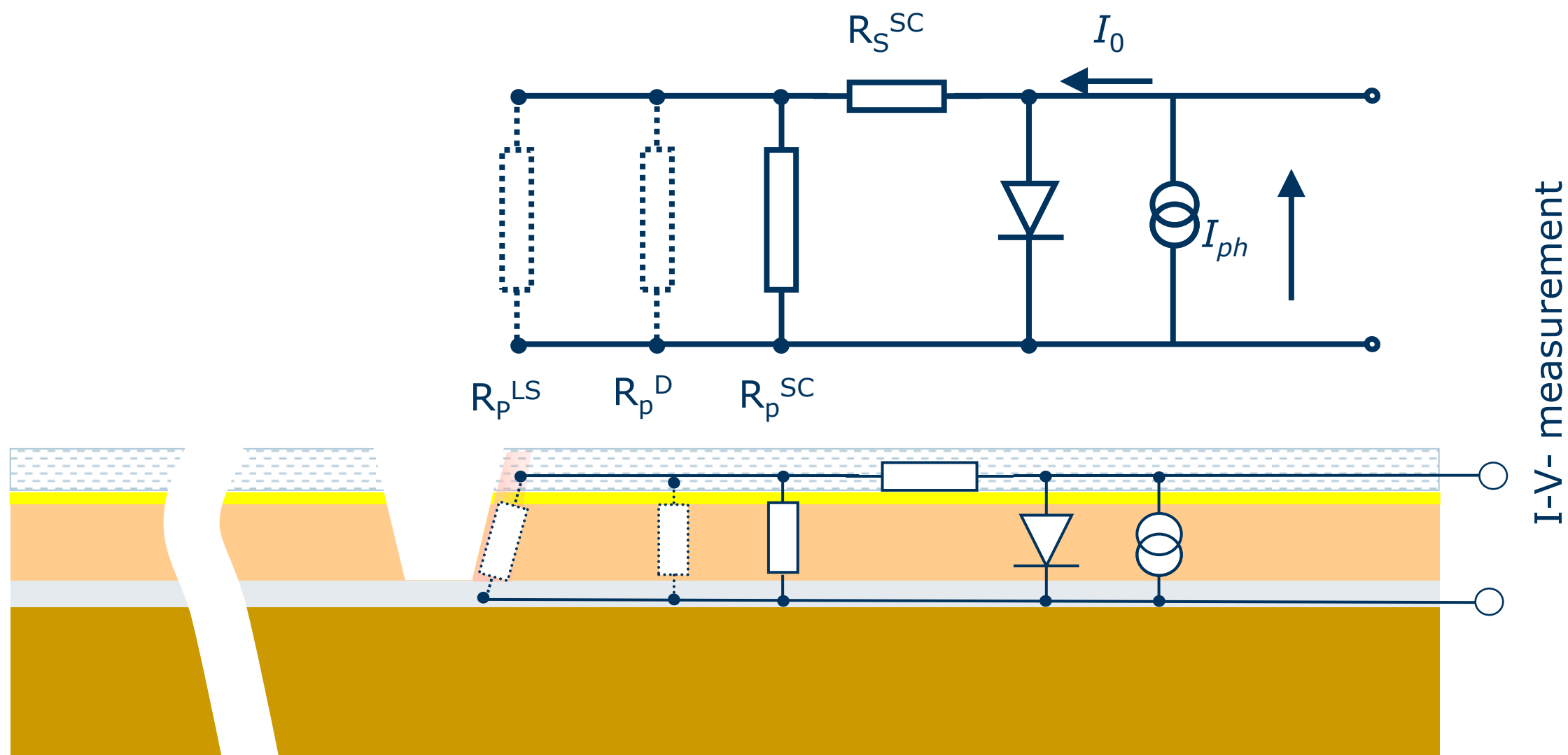
- All laser scribed thin film CIGS and Perovskite mini-modules have been demonstrated with good efficiencies (in comparison to cells).
- Understanding the ablation mechanism in relation to the functional properties of the scribes provides guidelines to:
 - limit material modification and defect formation
 - increase the processing speed
 - and reduce the interconnection area keeping the functionality.

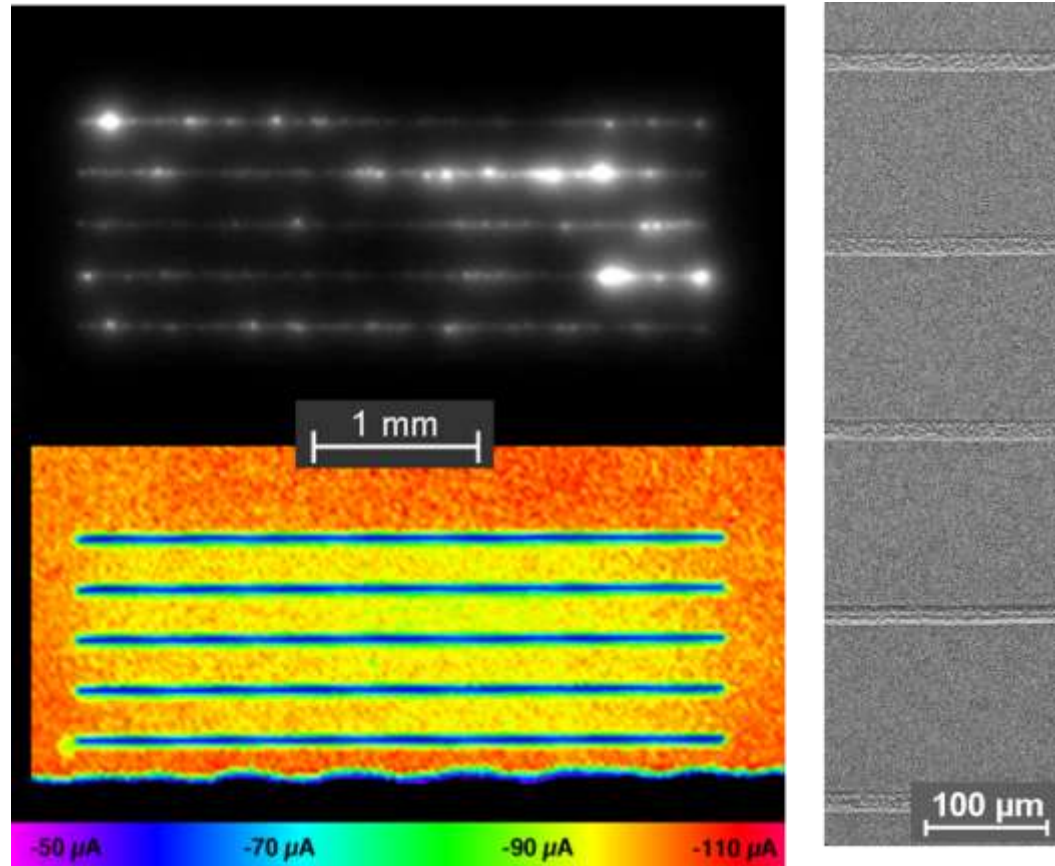


This work was partially supported by FP7 grant APPOLO No. 609355.

Thank you for your attention!







DLIT and LBIC of laser P3
scribes with significant defects
reducing the photocurrent.

LASER SCRIBING FOR SERIAL INTERCONNECTION

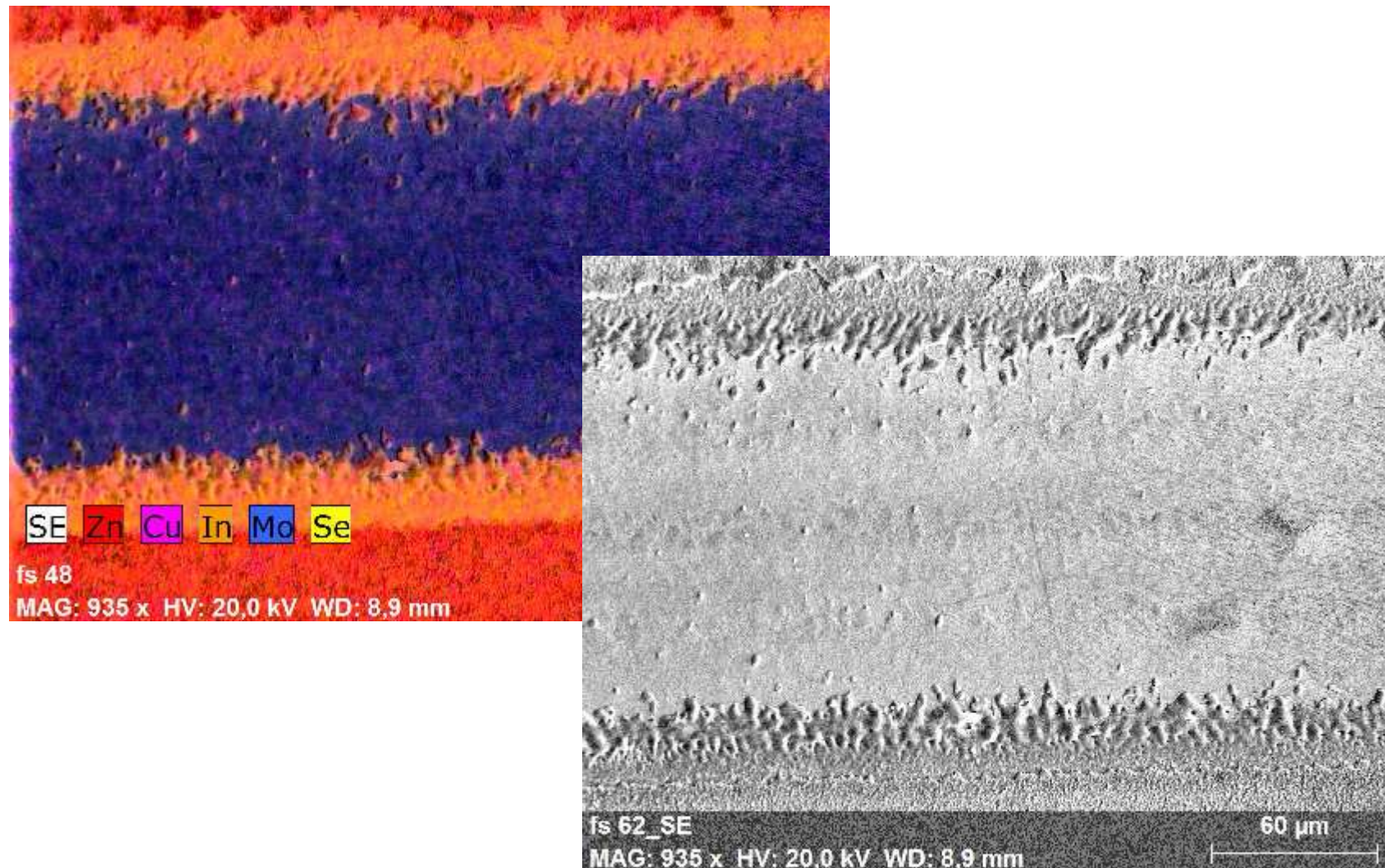
efficiency

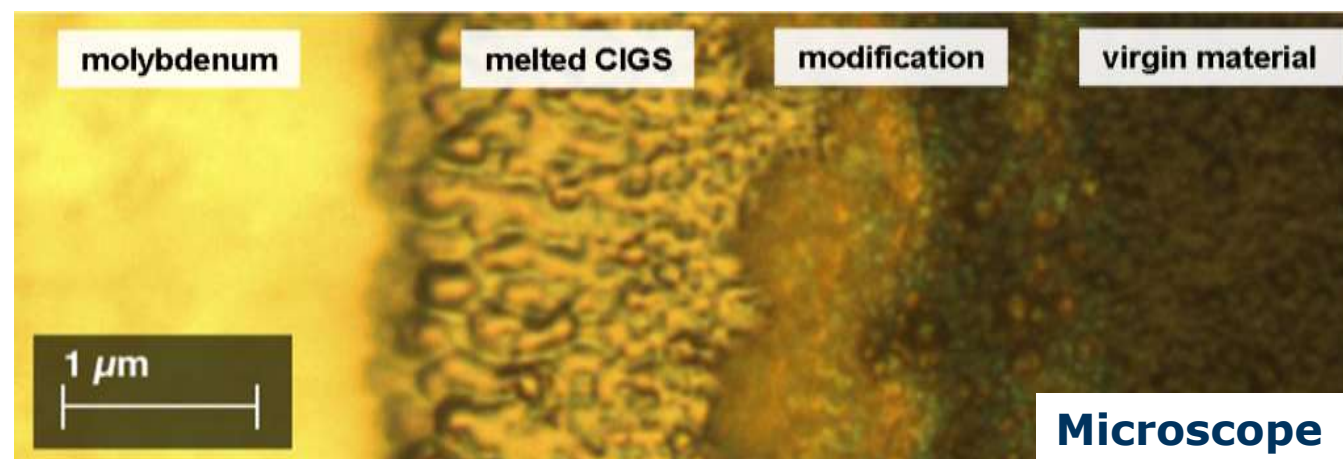
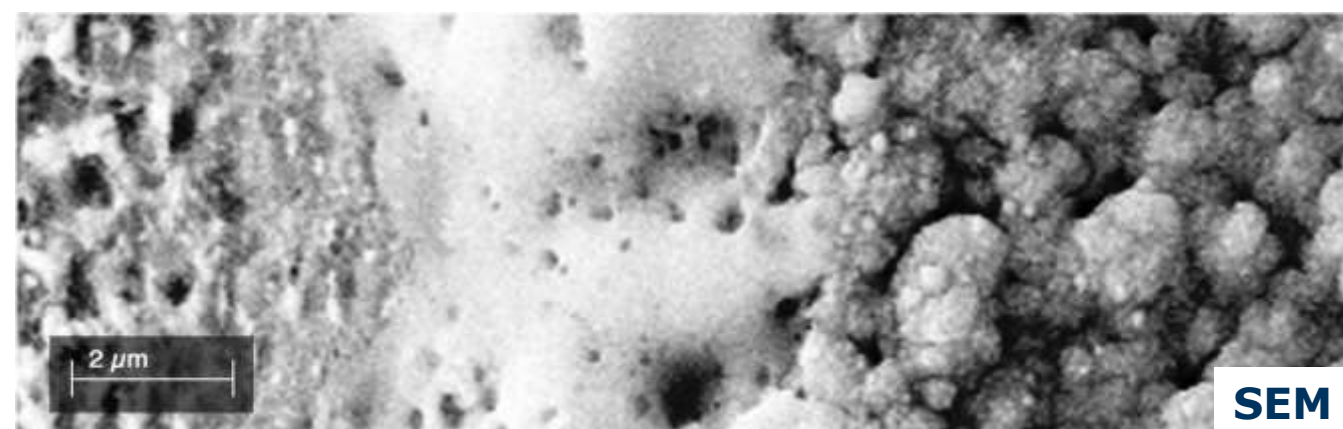
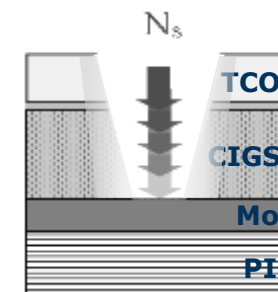
narrow scribes → small dead zone
scribing with low defects e.g.
morphological, electrical
selective processing → material
selective / interface related

technical

fast scribing – high speed
reliable process
low cost process

High-efficient, high-quality laser scribing is one key technology.





Schematic cross section of a P3 scribe

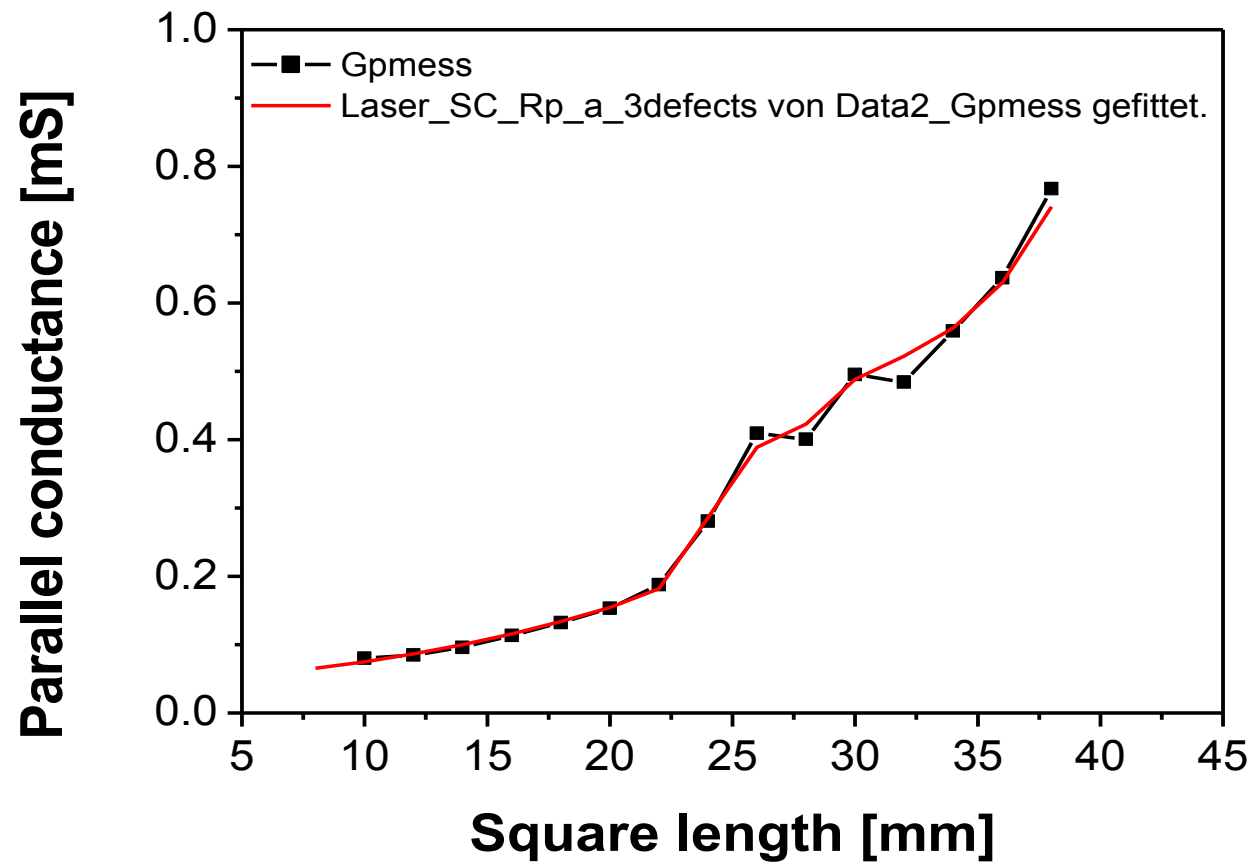
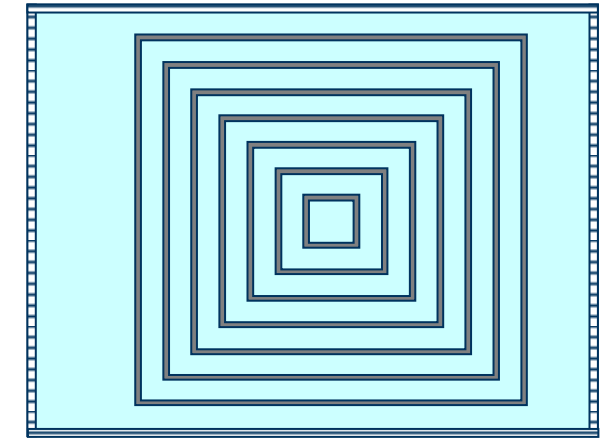
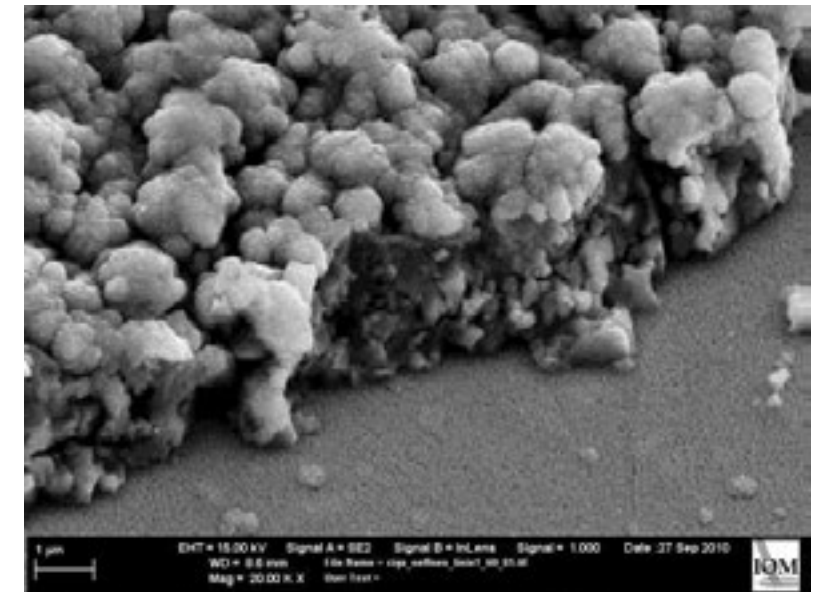
Microscope image

Brigth molydenum, modified & partially melted CIGS, virgin material
Change in colour and reflectivity → internal material modification

SEM image

Small amounts of debris, melted CIGS
No modified region → topological map

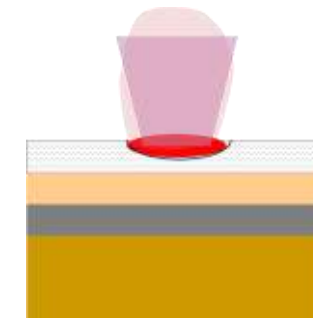
Real scribed CIGS solar cell



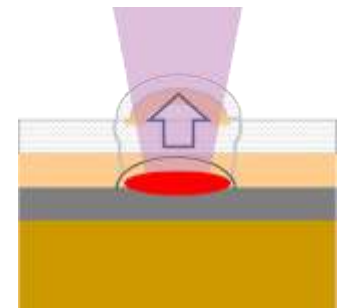
Quadratic equation: → defect free scribed solar cell
Steps → defects

Defect	Gp [mS]	Rp[kOhm]	a
b1	0.034	29.112	xc1=28.997
b2	0.164	6.099	xc2=37.338
b3	0.166	6.031	xc3=23.977

	E [μ J]										
	5,8	9	14	18	22	25	29	34	39	43	49
v [m/s]	0,01	a	a	a	s	s	s	s	s	s	s
	0,02	a	a	a	a	s	s	s	s	s	s
	0,05	a	a	a	a	a	a	s	s	s	s
	0,08	ü	a	a	a	a	a	a	s	s	s
	0,1	ü	a	a	a	a	a	a	a	a	s
	0,12	ü	a	a	a	a	a	a	a	a	a
	0,15	ü	a	a	a	a	a	a	a	a	a
	0,2	ü	ü	a	a	a	a	a	a	a	a
	0,3	ü	ü	ü	ü	a	a	a	a	a	a
	0,5	l	l	l	l	ü	ü	ü	ü	a	a
	0,8	l	l	l	l	l	l	l	l	ü	ü
	1	l	l	l	l	l	l	l	l	l	ü
	1,5	l	l	l	l	l	l	l	l	l	l
	2	l	l	l	l	l	l	l	l	l	l
	2,5	n	l	l	l	l	l	l	l	l	l
	3	n	l	l	l	l	l	l	l	l	l
	5	n	n	n	n	l	l	l	l	l	l
	10	n	n	n	n	n	n	n	n	n	n



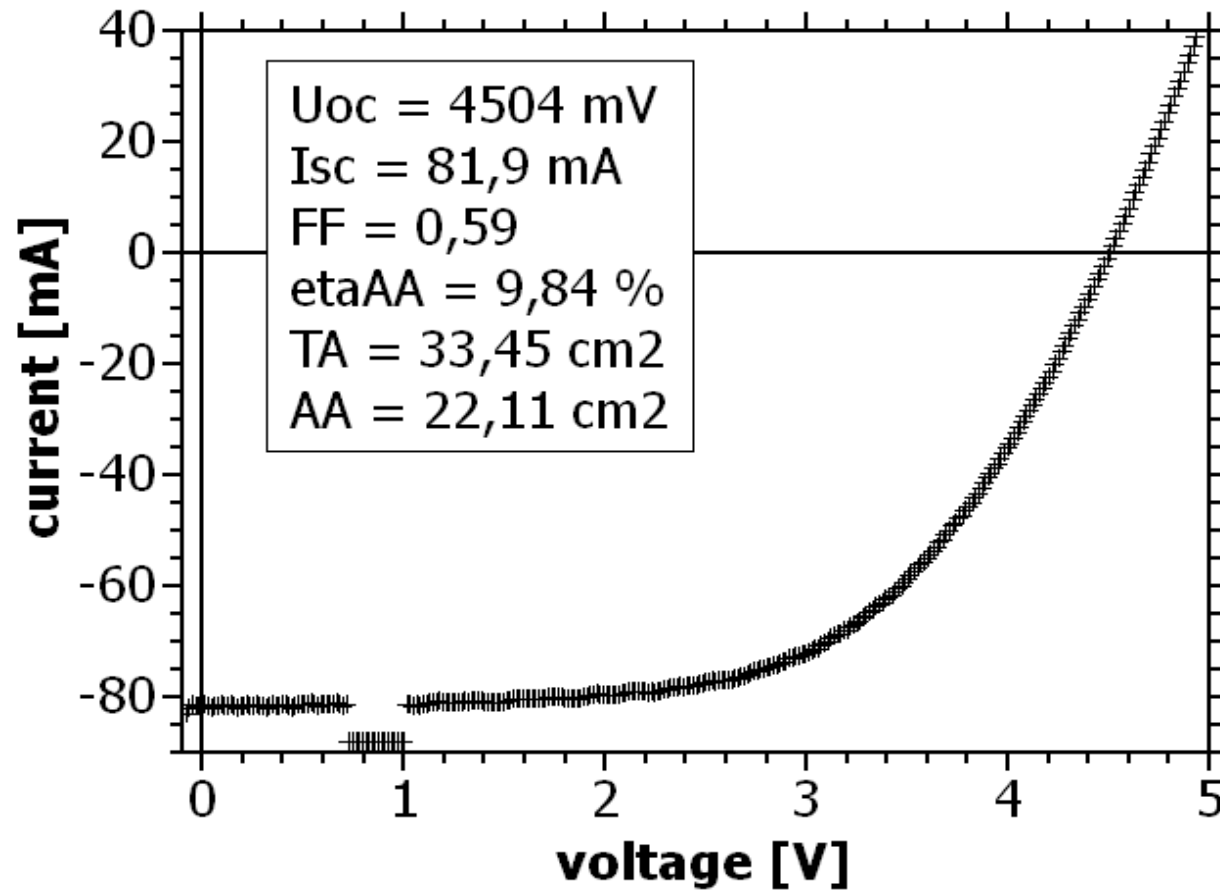
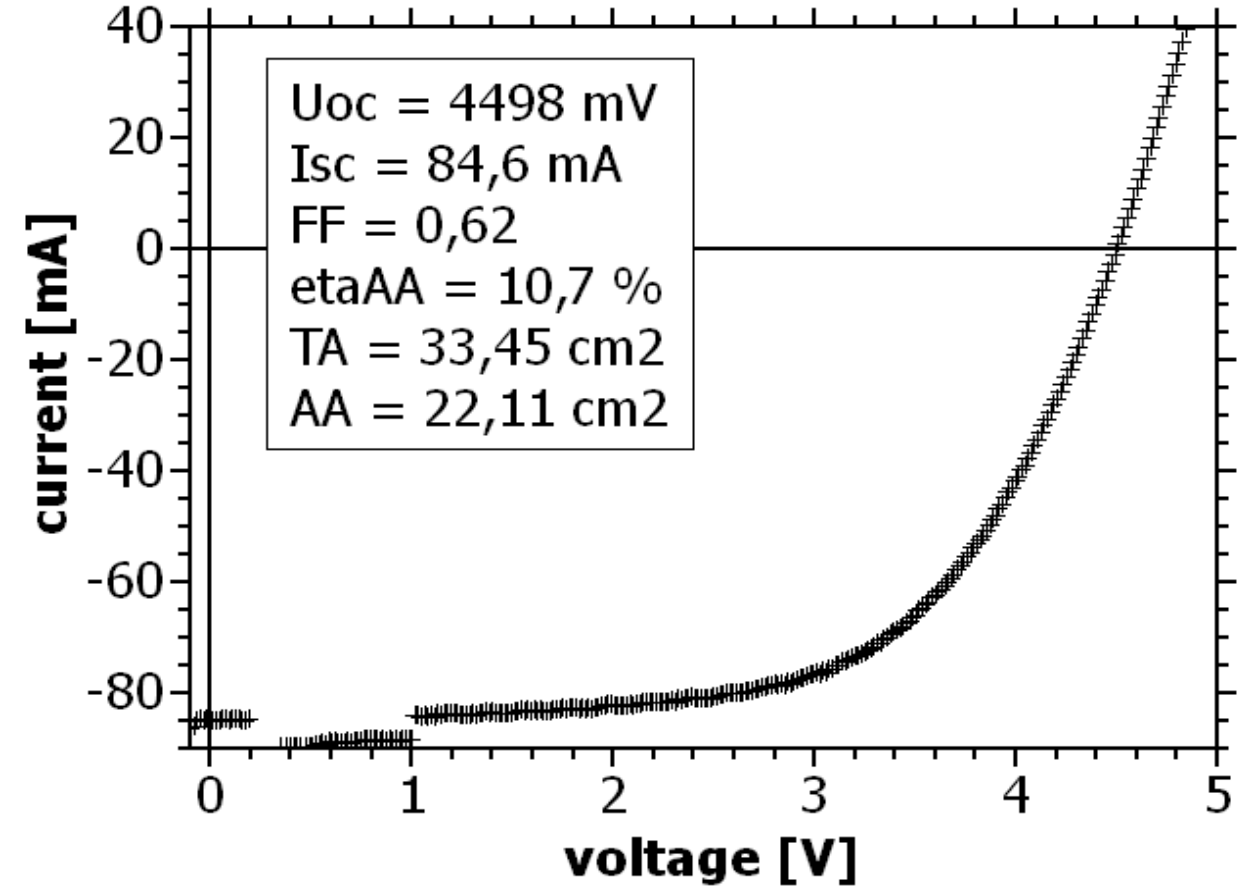
ablation



delamination
lift off

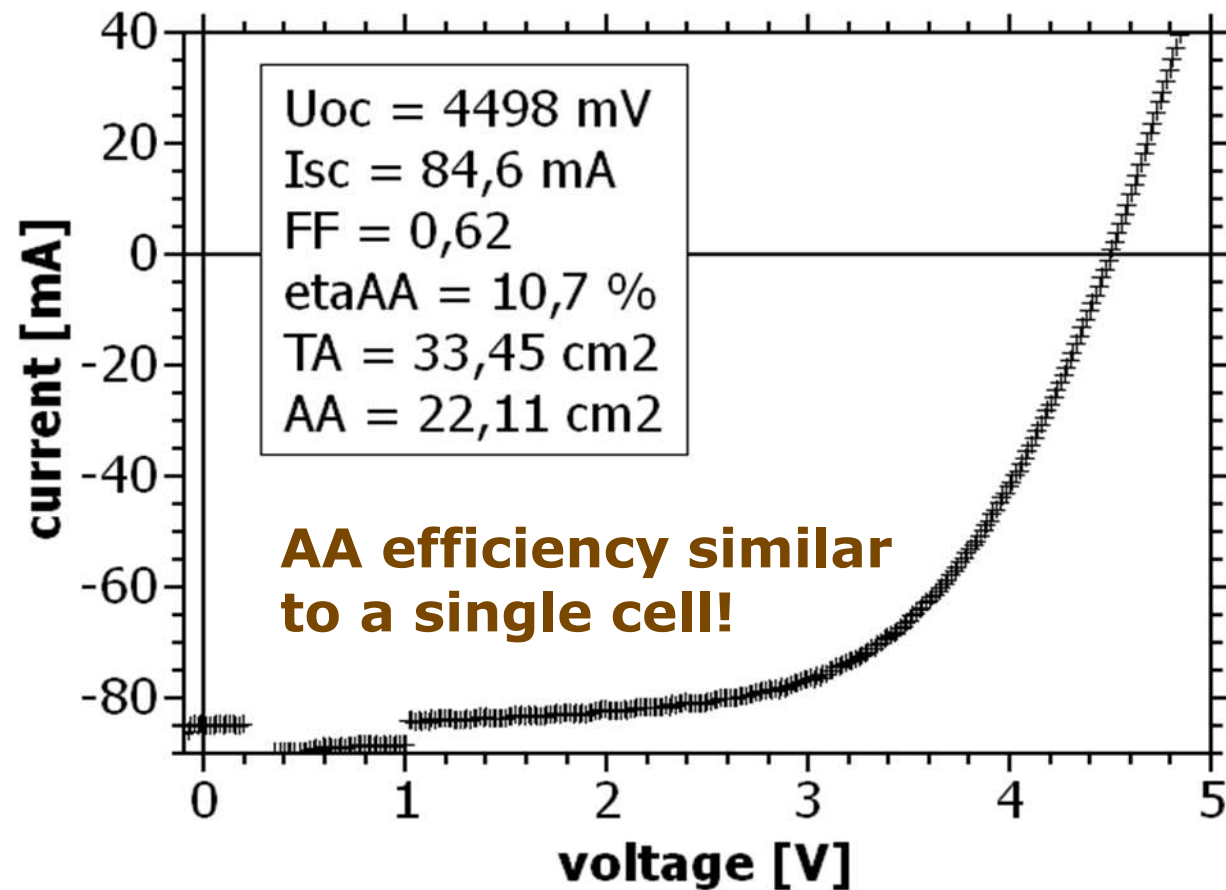
green: laser ablation
dark green: laser lift-off
yellow: transition from
ablation to lift-off;
red: Mo film damaged
blue: separated pulses

Fertige Module - Kennlinien

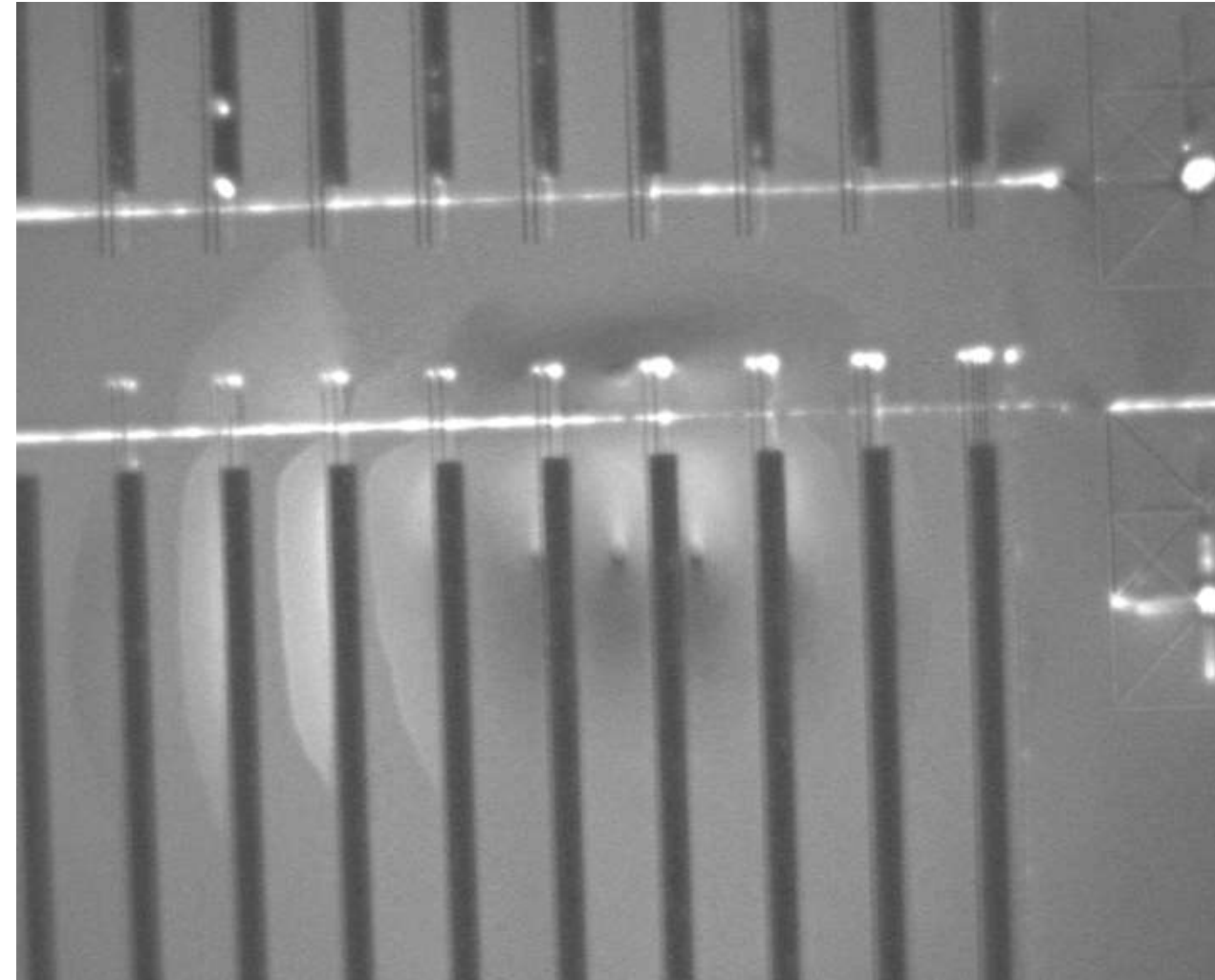


(Ursache für die Sprünge in den Kennlinien müssen noch geklärt werden.)

Zelle	TA [cm ²]	AA [cm ²]	Uoc [mV]	Isc[mA]	Umpp[mV]	Impp[mA]	Pmpp [W]	Füllfaktor	etaTA [%]	etaAA [%]
A_links_unten	33.45	22.11	4503.79	81.68	3055.63	71.19	217.54	0.59	6.50	9.84
A_rechts_unten	18.91	12.50	4473.06	48.62	3119.38	40.27	125.62	0.58	6.64	10.05
B_links_unten	33.45	22.11	4498.19	84.62	3294.69	71.79	236.53	0.62	7.07	10.70
C_links_unten	33.45	22.11	4490.29	85.37	3199.06	72.89	233.17	0.61	6.97	10.55
C_links_oben	18.91	12.50	4025.13	46.87	2720.94	38.94	105.94	0.56	5.60	8.48
C_rechts_oben	33.45	22.11	4495.48	81.96	3055.63	71.57	218.69	0.59	6.54	9.89



I-V-curve of a external integrated interconnected mini module



DLIT image of the mini module

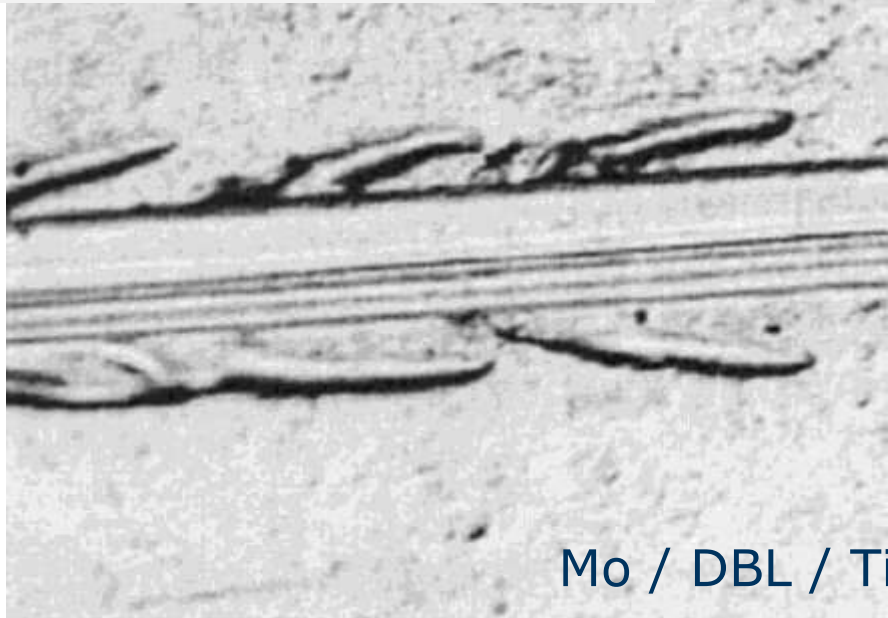
Technology	material	patterning step
PET/ITO substrates		
Masking and wet etching	ITO	P1
FTO/glass substrates		
Laser scribing	ITO	P1
screen printing	TiO ₂	
tape masking		P2
solving/mechanically	Perovskite	P2
masked metal deposition	Au	P3
FTO/glass substrates		
Laser scribing	ITO	P1
lift off with metal mask	c-TiO ₂	P2
masked metal deposition	Au	P3
solving/mechanically		P2

Former work on patterning of Mo on DBL/foil

former results

reference results

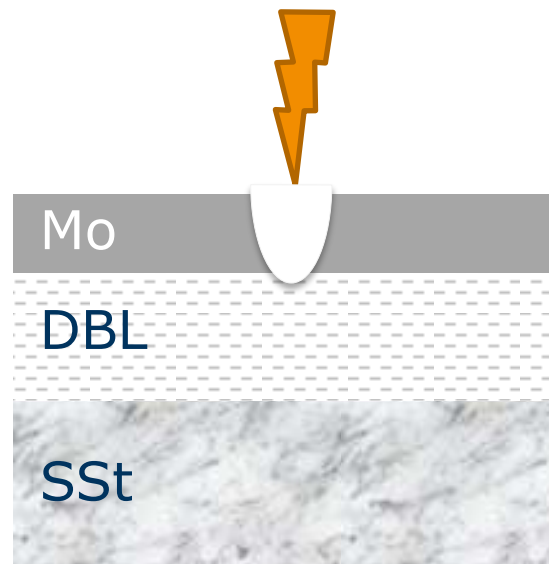
mechanical scribing of Mo



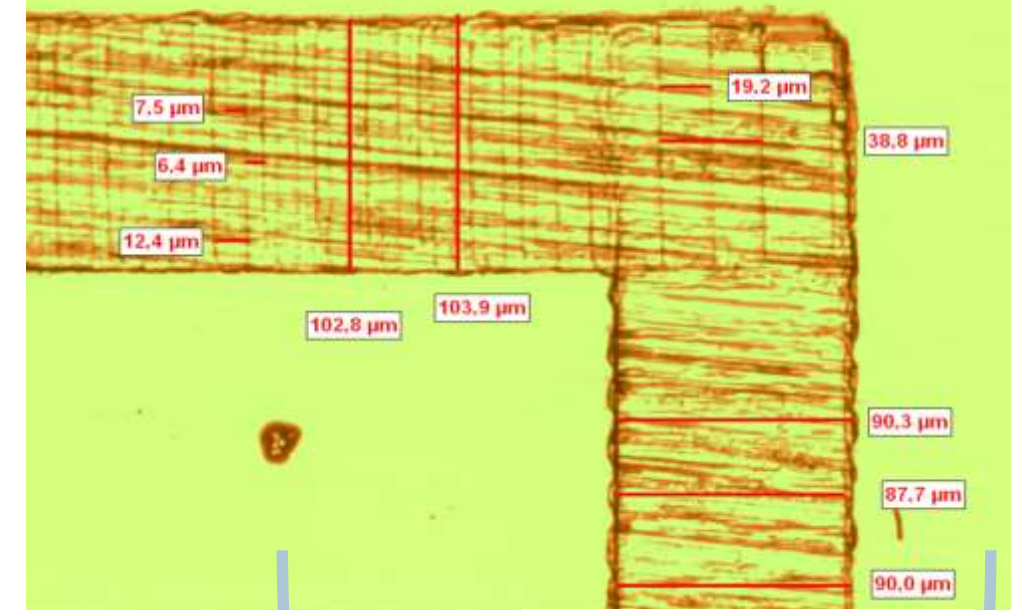
Nd:YAG-laser scribing of Mo



the problem



λ : 248 nm, t_p : ~20 ns, A: 100 μm^2 , F: 2.14 J/cm²

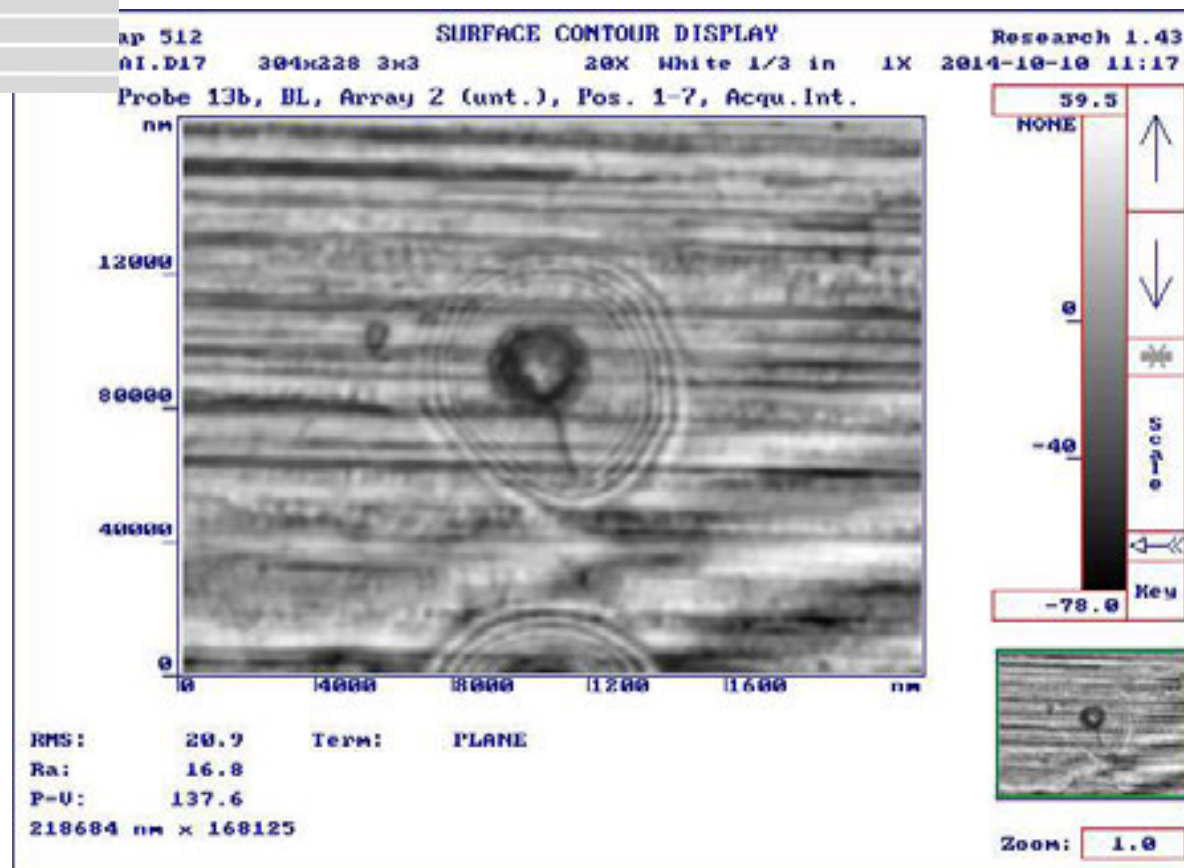


$\Omega = \infty$

- selective ablation of Mo film
- slightly damage (ablation) of the topmost part of DBL
- full isolating DBL
- DBL withstand breakdown voltage to SSt

λ : 355 nm, t_p : ~10 ps, r_g : 13 μ m

Understanding the damage and ablation of the mechanism of materials involved in P1 scribing

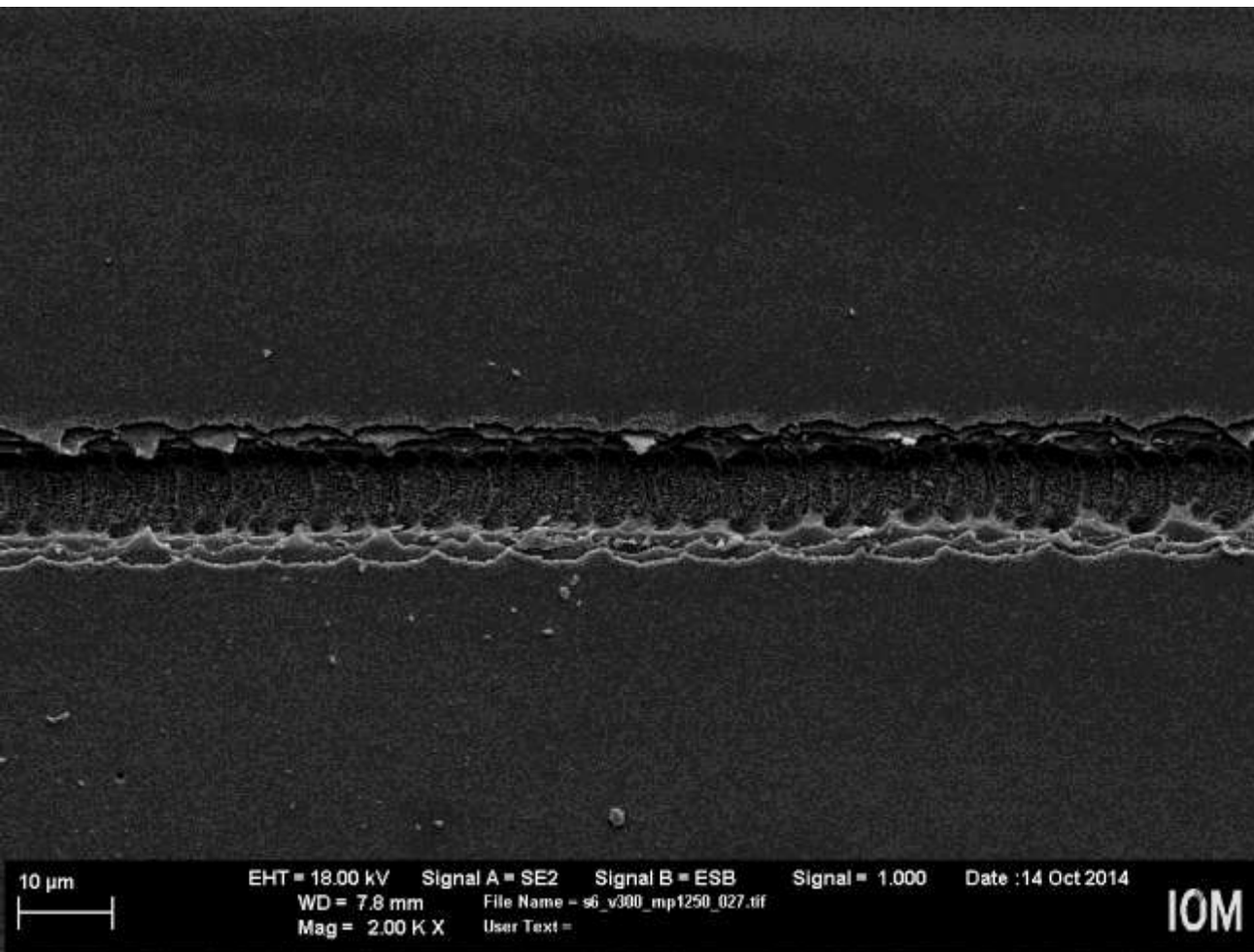


355 ps -

Possible damage features of the DBL upon laser irradiation

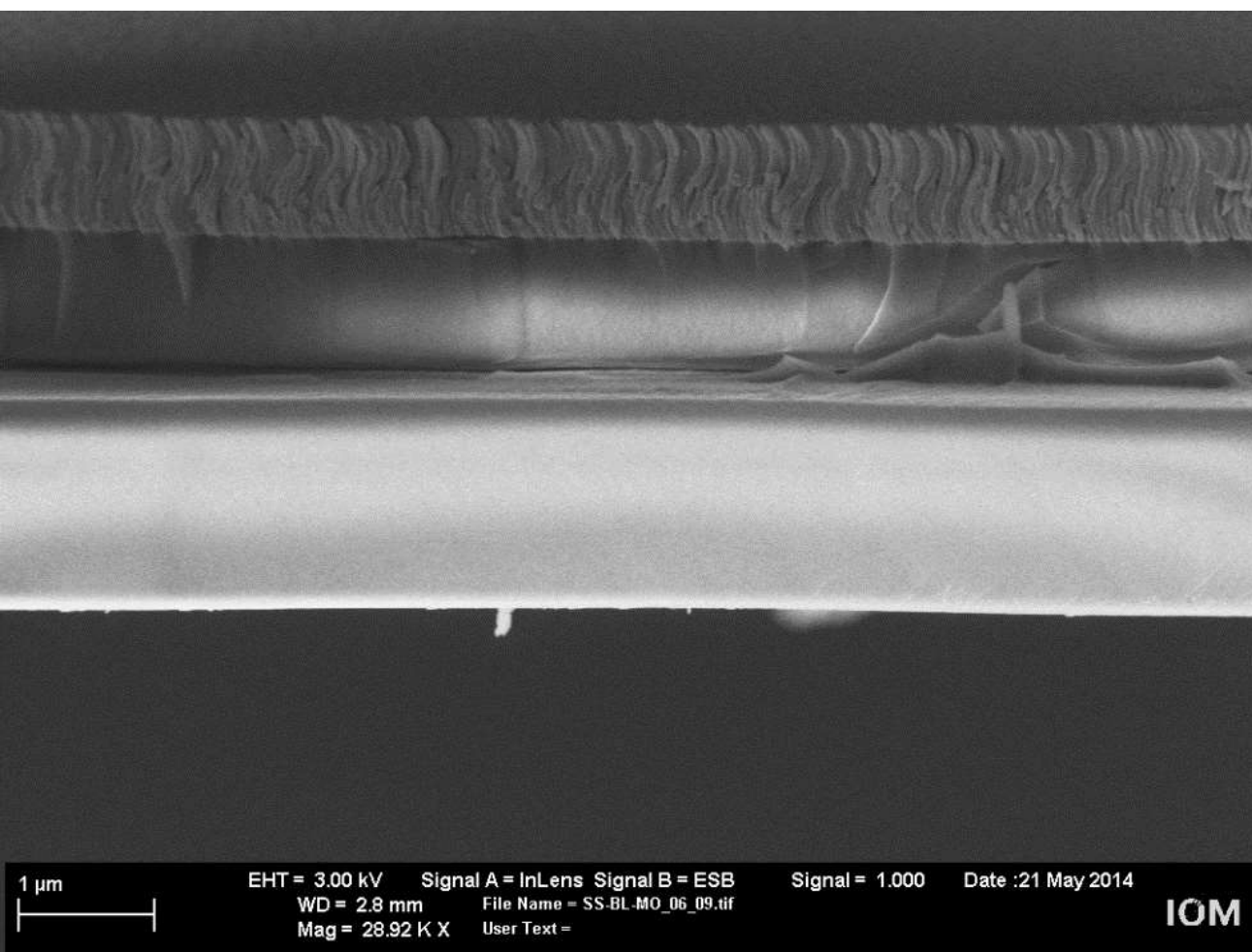
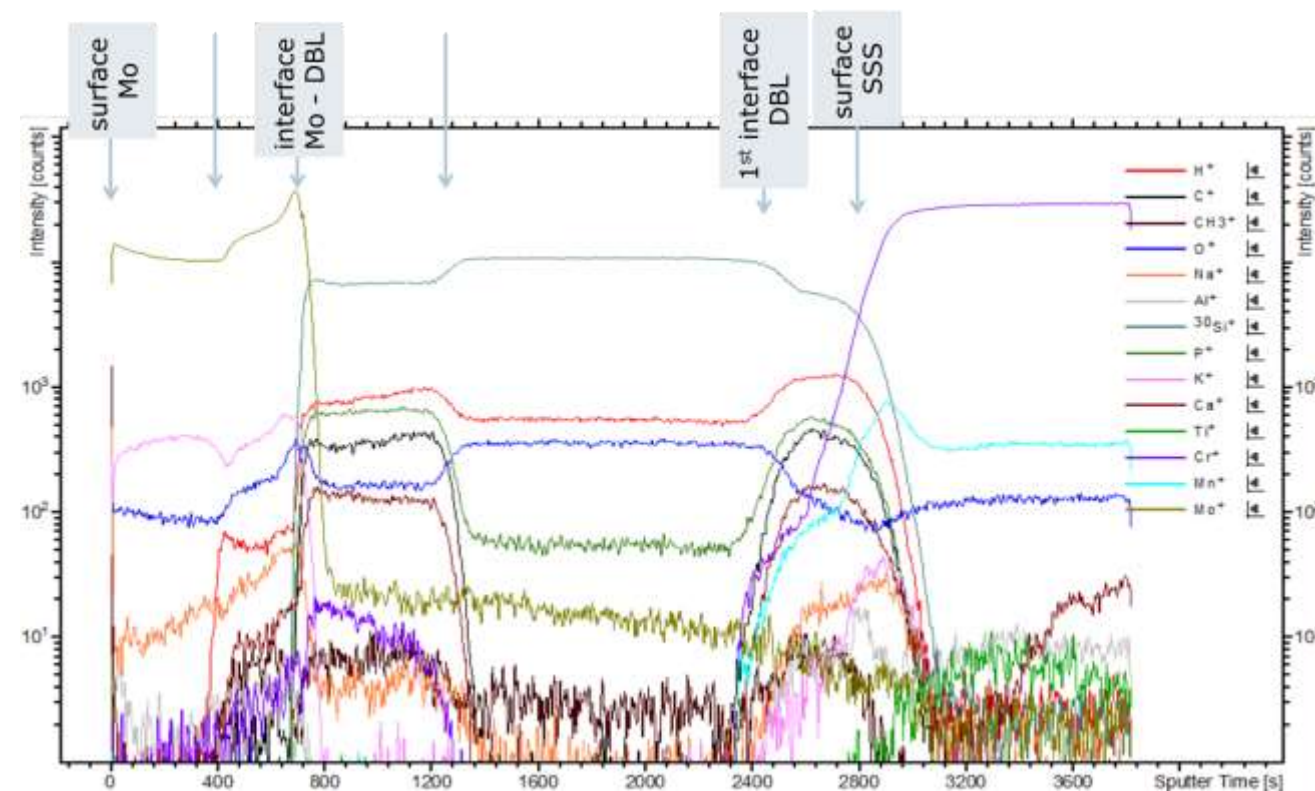
- SST surface damage or melting
- defects / roughness at the interface
- ablation of the DBL
- bulging of the DBL-surface
- cracks in the DBL

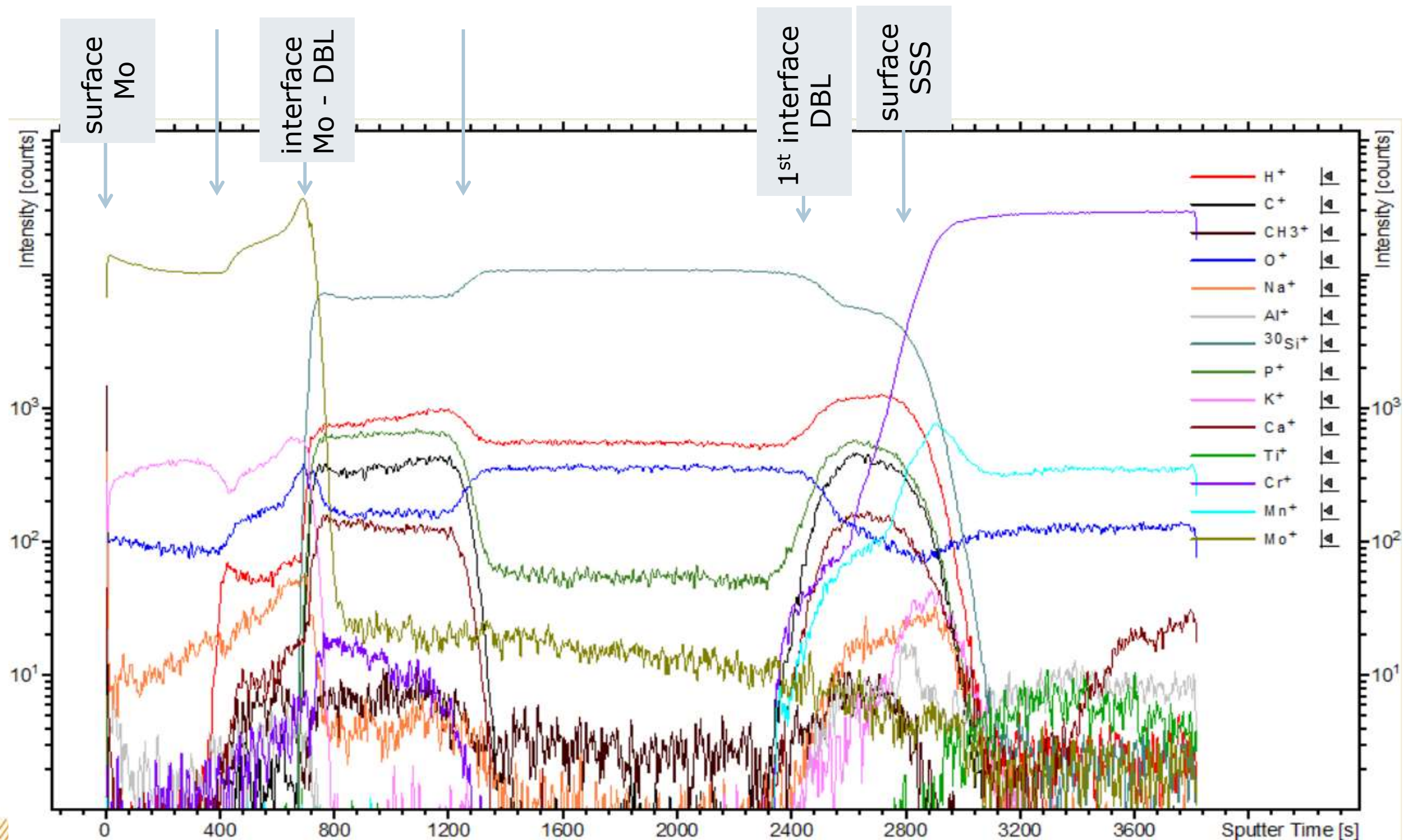
Interference microscopic image of a laser pulse damage of the DBL



PL: 0.037 W; f: 50 kHz; vs: 300 mm/s

Partial ablation of the DBL to a depth of $\sim 2 \mu\text{m}$





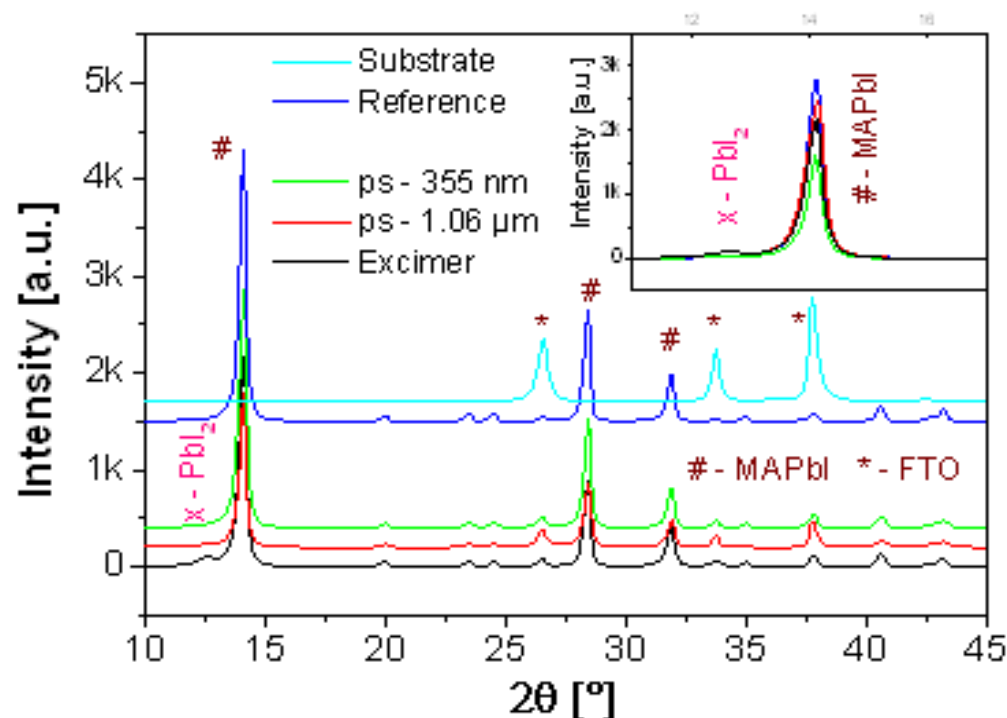
DETECTION OF LASER-INDUCED MATERIAL ALTERATIONS BY XRD

Laser-scanning of approx. $1.5 \times 1.5 \text{ cm}^2$ areas with

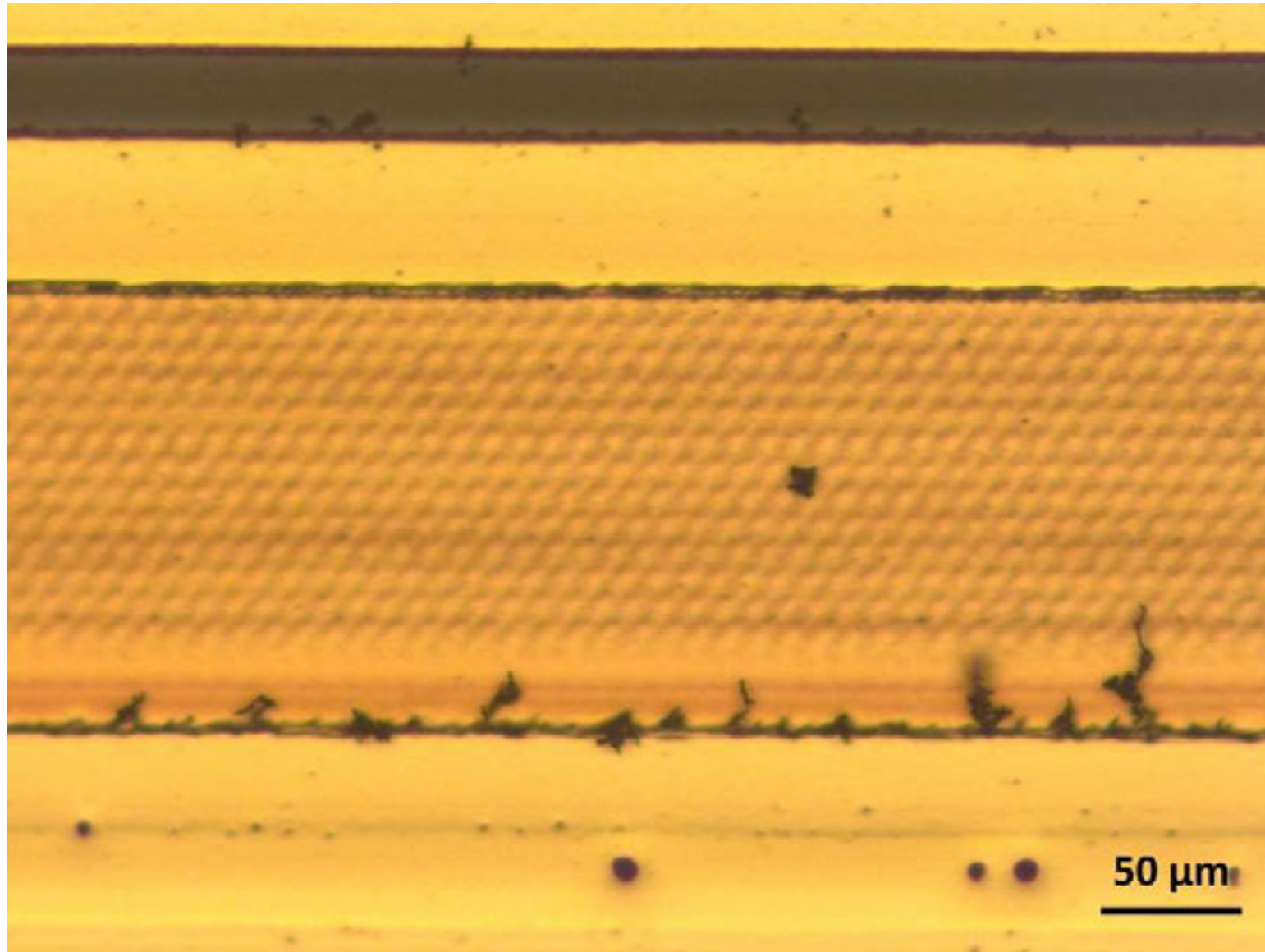
- Excimer
- 355 ps laser
- 1064 ps laser

Detection of additional PbI_2 in the case of UV ns laser irradiation

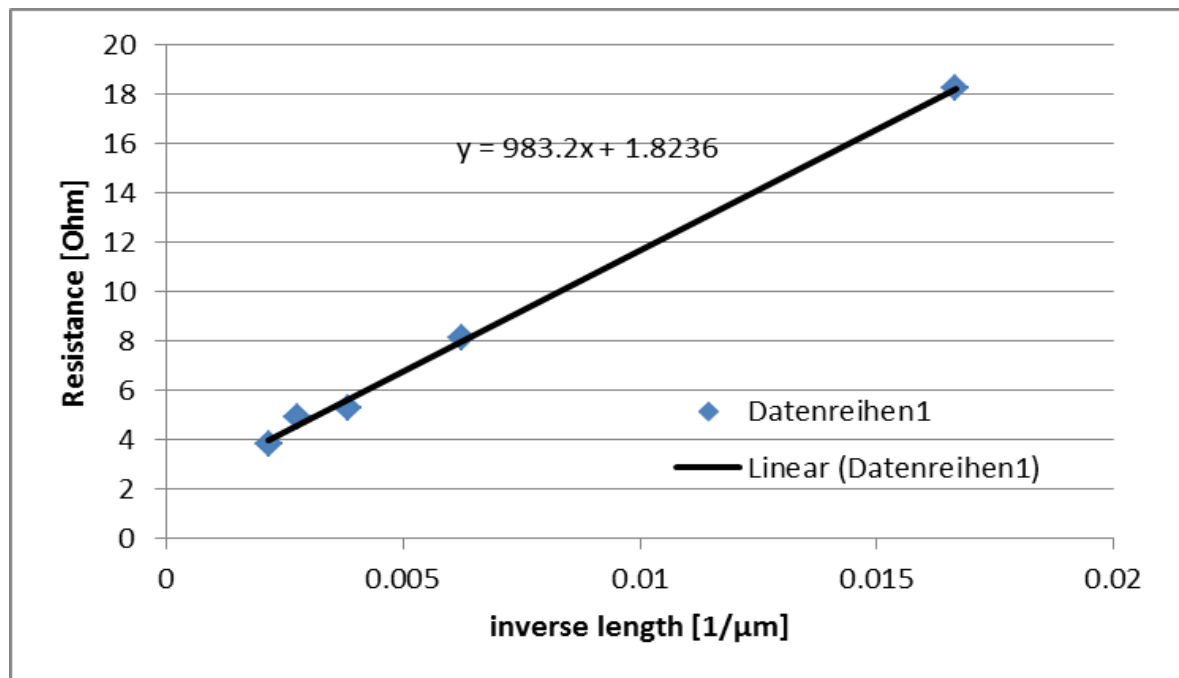
Reduction of the peaks intensity due to partial ablation of the perovskite film



XRD spectra of near threshold laser irradiated areas using different laser sources



Integrated interconnection
area of a perovskite module



specific resistance of the sputtered gold film:

magnetron sputtern

d: 150 nm

(IOM)

$$R/\square = 0.49 \, \Omega$$

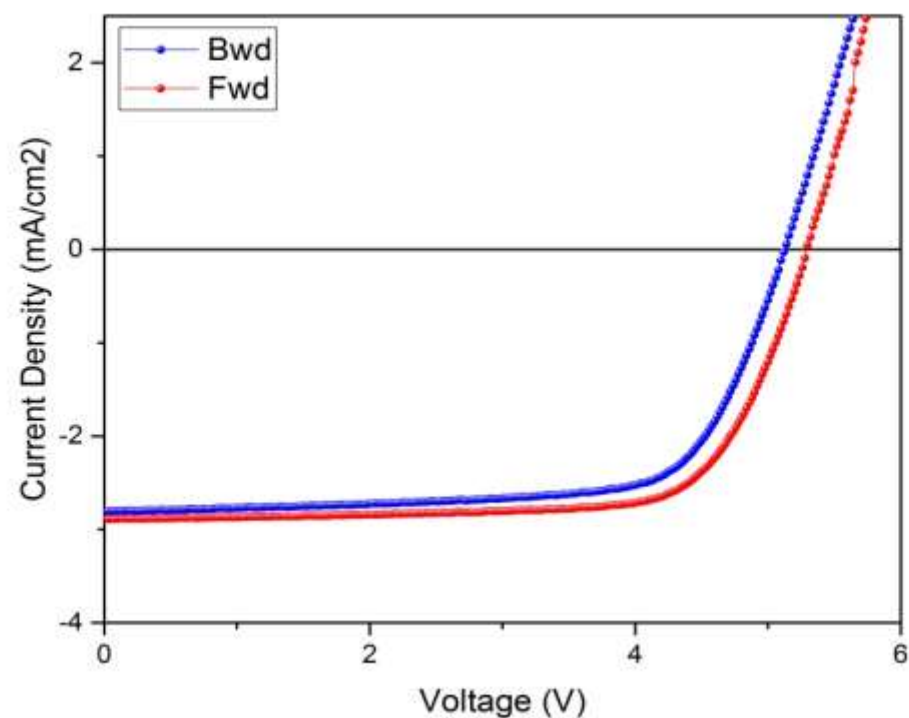
$$\rho_{\text{iom}} = 7.4 \, \text{e-8} \, \Omega \, \text{m}$$

(references)

$$\rho_{\text{bulk}} = 1.74 \, \text{e-8} \, \Omega \, \text{m}$$

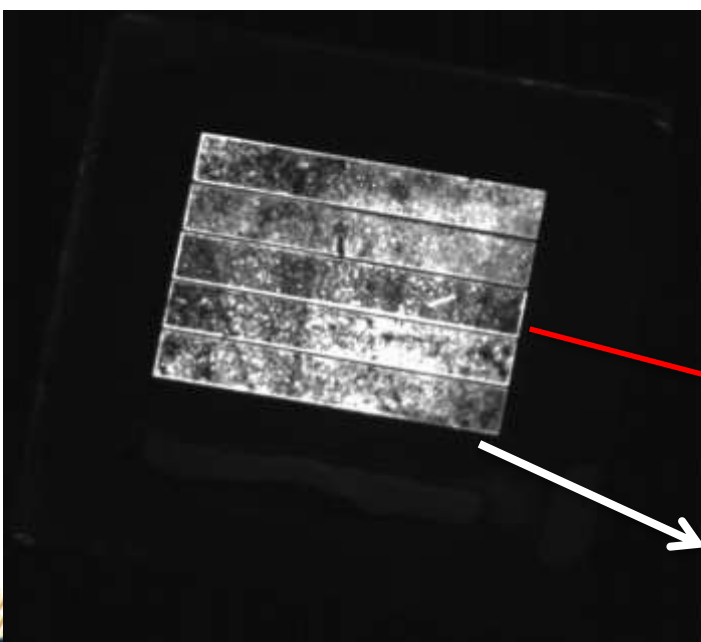
$$R/\square = <15 \, \Omega$$

All laser scribed champion module



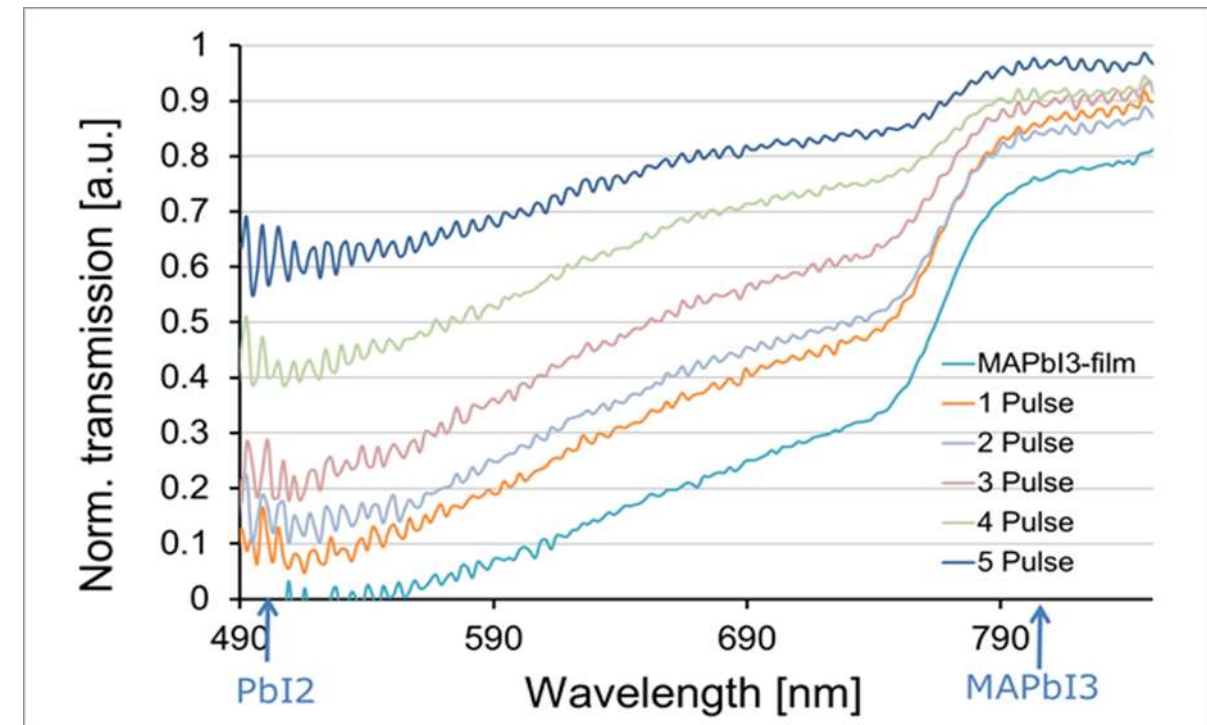
EL measurements

Module area
6.73 cm²



Only 5 subcells NOT 6
This subcell is dead

	V_{oc} (V)	J_{sc} (mA/cm²)	FF (%)	η (%)	η_{mpp} (%)
Fwd	5.3	2.9	72.8	11.1 3	10.65
Bwd	5.13	2.8	71	10.2	



FTP instrument – a reflectometer for thin film thickness measurements with the resolution of a optical microscope.

primary transmission data for reference and real MAPbI₃ samples
Influence of the pulse number is clearly seen