PEROV project: perovskite devices for visible light and potential for X-ray detection

High Precision X-ray Measurements
22 June 2023

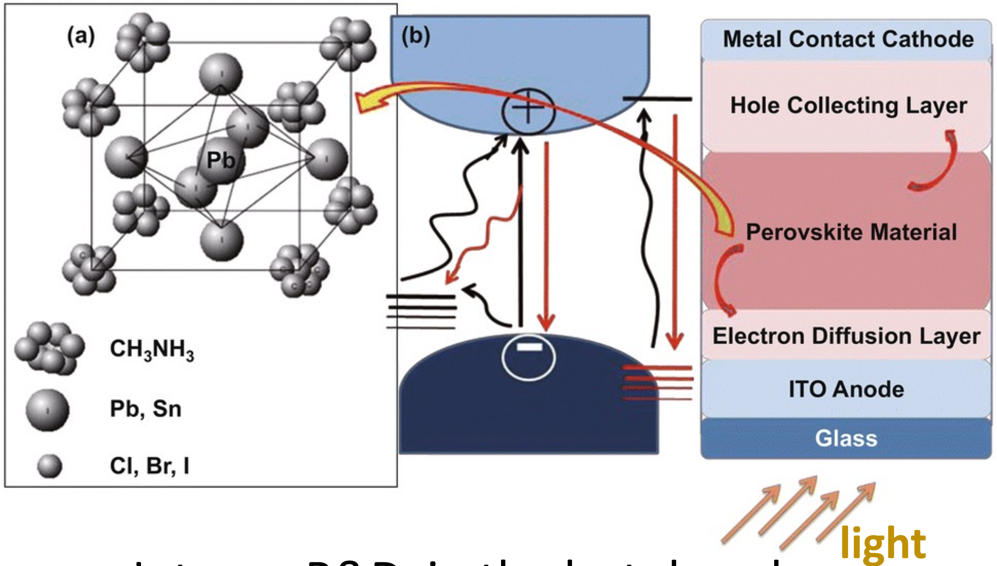
Marianna Testa (LNF-INFN)
On behalf of the PEROV collaboration:

- LNF-INFN A. De Santis, M. Testa
- INFN Sezione di Roma 1 C.Rovelli, S.Morganti
- Dipartimento Ingegneria Elettronica Tor Vergata : M Auf der Maur, F. Matteocci
- Dipartimento Chimica, Uni Milano: L. Lo Presti, S. Rizzato
- CNR – NanoTec, ISR, ISM: L. Di Marco, I. Viola, R. Mastria, S. Sennato
- TIFPA: Lucio Pancheri, Alberto Taffelli

LNF electronic services: G. Papalino, G. Felici

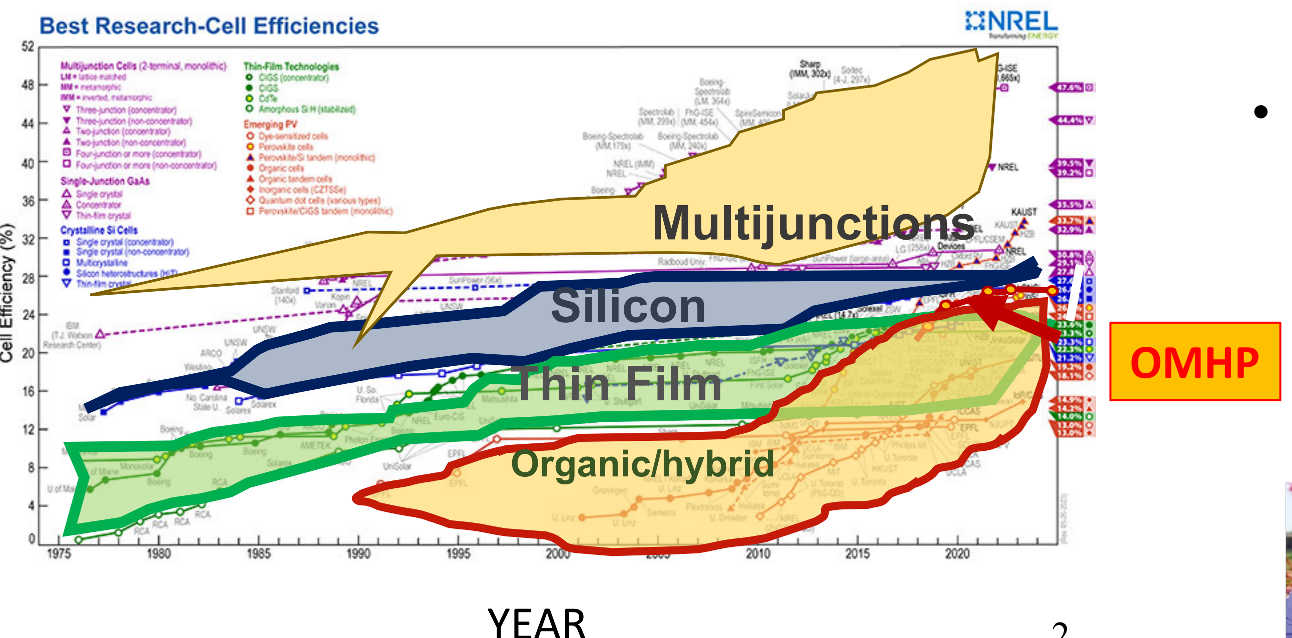
Organo-Metal Halide Perovskite

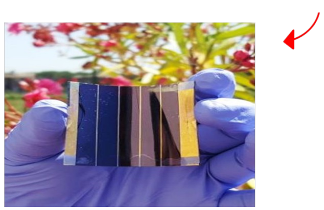
- **Organo Metal-Halide Perovskites (OMHP)** are a class of hybrid organic-inorganic semiconductor materials with a perovskite unit-cell structure **ABX$_3$** with
  - A = $CH_3NH_3^+$, B = metallic cation (Pb^{2+}), X= halide anions (Cl^-, Br^-, I^-)



- Opto-electronic properties combine **advantages from organic and inorganic semiconductors**

- Intense R&D in the last decade
  - OMHP are emerging as new generation photovoltaic material
  - **promising candidate**
    - large area and flexible sensitive photodetectors
    - More recently **for radiation detection**





Organo-Metal Halide Perovskite properties

OMHPs combine the advantages of inorganic and organic semiconductors.

Organic semiconductors:
- Disordered system
- Localized electronic states
- Hopping transport ⇒ low mobility
- **Low cost, low temperature processing**
- **Can be solution processed**
- **Scalable to large area**

Inorganic semiconductors:
- **Ordered periodic crystal ⇒ band structure**
- **Delocalized Bloch states**
- **band transport ⇒ high mobility**
- Usually wafer based technology
- Costly, high temperature processes

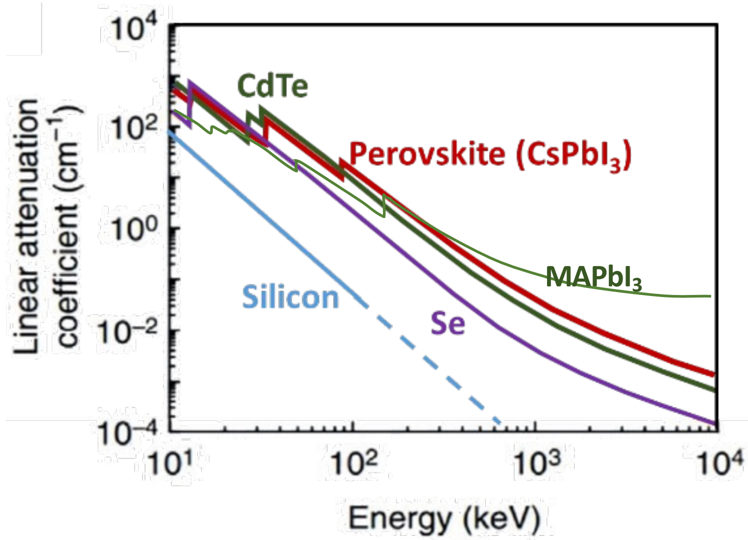
		Silicon	$CH_3NH_3Pb(I,Br)_3$
Density		2.33 g/cm^3	4.15 g/cm^3
Band gap (eV)		1.12 (indirect)	1.5-1.6 / 2.24 (direct)
Mobility (cm^2/Vs)	electrons	1400	< 70/190
	holes	450	< 160/220
Absorption (cm^{-1})		< 10^4	> 4x10^4
Threshold energy for impact ionization (eV)		1.2	~2 / 2.5 (estimated)
Mean free path (nm)		≤ 100	~100 (theory)

- band gap tunable changing halide (I,Br,Cl)
- contain highly mobile defects and have instabilities issues

Many features of interest for **visible light** detection and **Radiation** detection

Halide Perovskite for ionizing radiations

- The typical composition of HP contains heavy elements (Cs, Pb, Ag, Bi, Sn, I, Br) with atomic numbers in the range of 47-82, larger in comparison to widely used X-ray absorber - CZTS (max atomic number is 52).



Linear attenuation coefficient as a function of photo energy for several materials including halide perovskite

Adapted from (*)

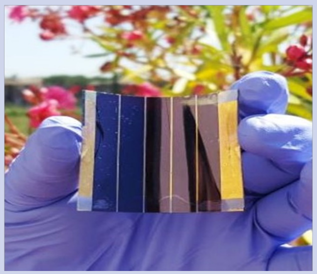
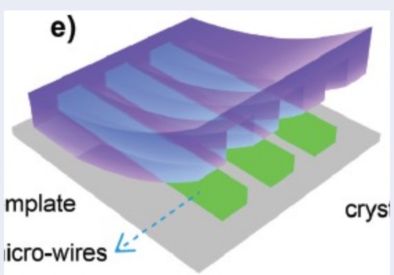
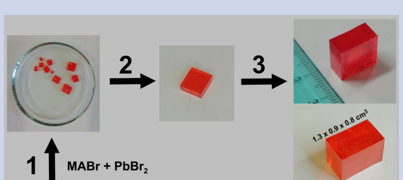
- ($\mu \times \tau$) product from 10^{-7} to 10^{-2} cm^2/V
- The typical values of the bulk resistivity for HPs exceed the level of 10^7 Ohm.cm (300K), good signal/noise ratio
- **Self Healing**

Egger et al. Adv. Mater. **2018**, 1800691

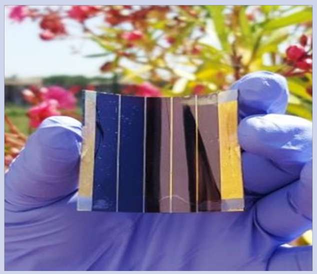
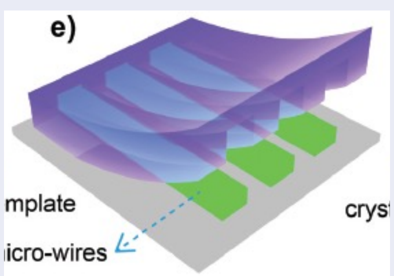
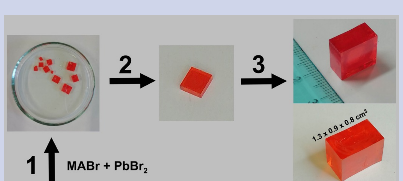
Material	h^+ effective mass [m_e]	e^- effective mass [m_e]	μ_{h+} [$cm^2 V^{-1} s^{-1}$]	μ_{e-} [$cm^2 V^{-1} s^{-1}$]
Si[b)]	0.54[109]	0.32[110]	500[109]	1500[110]
GaAs[b)]	0.53[113]	0.06[113]	400[113]	8000[113]
CdTe[b)]	0.72[115,116]	0.11[115,116]	100[117]	1100[117]
$CuInS_2$	≈1[120]	0.16[120]	≈20[120]	≈150[120]
$MAPbI_3$	0.26[122,123]	0.23[122,123]	≤160[124]	≤70[124]
$MAPbBr_3$[c)]	0.15[127]	0.25[127]	≤220[128]	≤190[129]

(*)Wei & Huang, J. Nat Commun 2019, 10, 1066; Del Sordo et al. Sensors 2009, 9, ; H.M. Thirimanne et al. Nature Comm 2018, 9, 2926

PEROV: Overview of CH_3PbBr_3 crystal growth

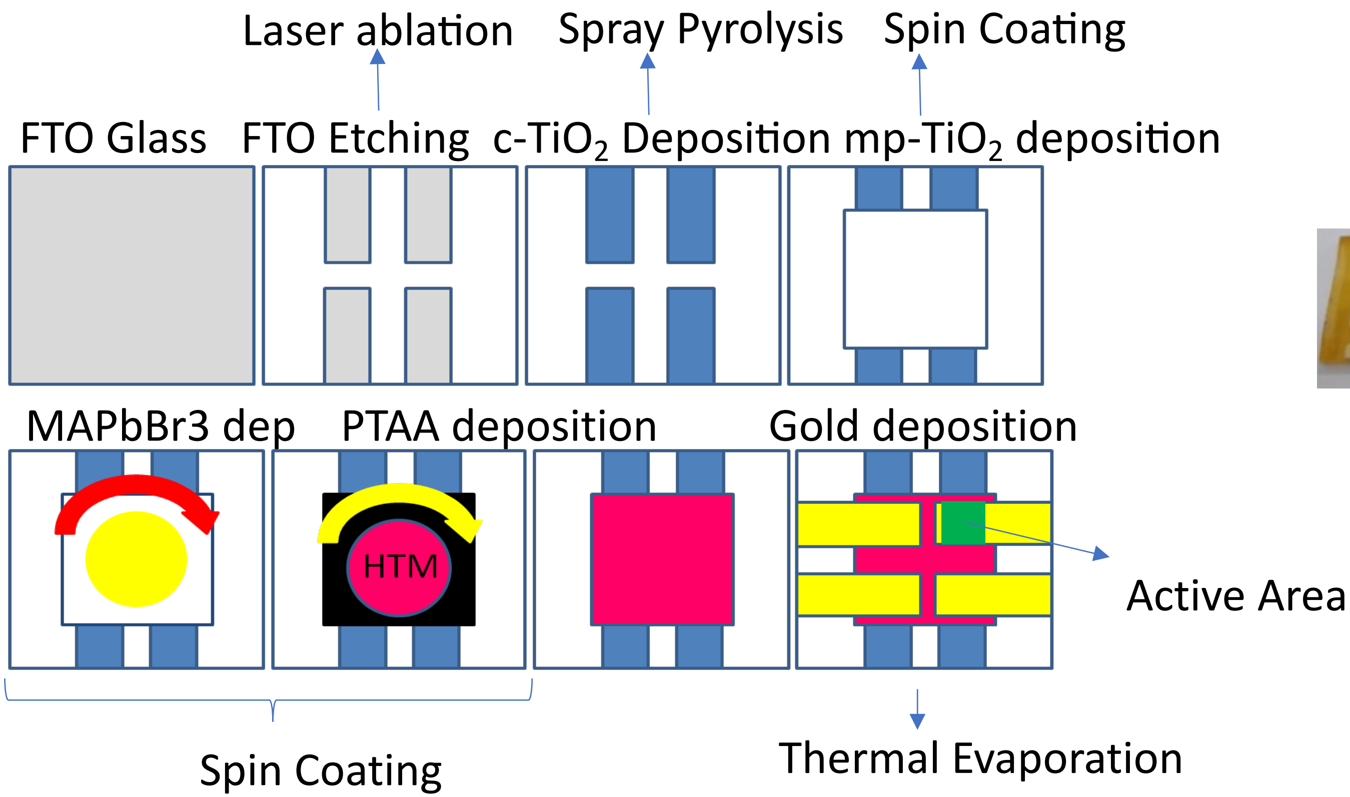
Technology and Thickness	Pro	Contra
Film 300 nm thickness 	• large area • small transit time due to low thickness • flexible substrate	• polycristalline • grain boundaries • large variability between samples
Micro channels 2-6 microns realized 	• large flexibility in dimension • moderate area • pixelization • flexible substrate • Deposited directly on substrate	• need high optimization of parameters (pressure, temperature)
Single crystals Up 0.5 cm realized 	• ideal for single crystal large dimension, up to O(1) cm^3 • low defects	• No scalability to large area systems • Need to be cut mechanically for low thickness

PEROV: Overview of CH_3PbBr_3 crystal growth

Technology and Thickness	Pro	Contra
Film 300 nm thickness 	• large area • small transit time due to low thickness • flexible substrate	• polycristalline • grain boundaries • large variability between samples
Micro channels 2-6 microns realized 	• large flexibility in dimension • moderate area • pixelization • flexible substrate • Deposited directly on substrate	• need high optimization of parameters (pressure, temperature)
Single crystals Up 0.5 cm realized 	• ideal for single crystal larg… dimension, up to O(1) cm^3 • low defects	• …ility to large area systems • …eed to be cut mechanically for low thickness

These two technologies can be adapted/used for direct Xrays detection

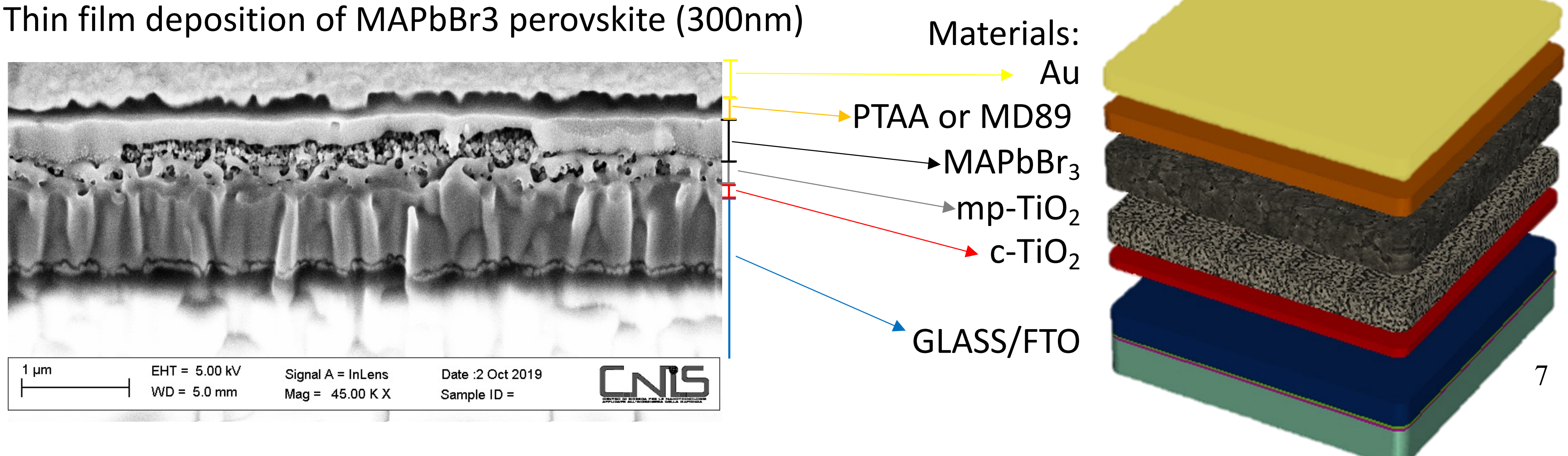
Film-based devices production



Ready devices with
different Optical Band-Gap

CHOSE lab
Dip Ing. Elettronica RM2

Thin film deposition of MAPbBr3 perovskite (300nm)



Film-based devices: gain observation and modelling

Experimental observation of

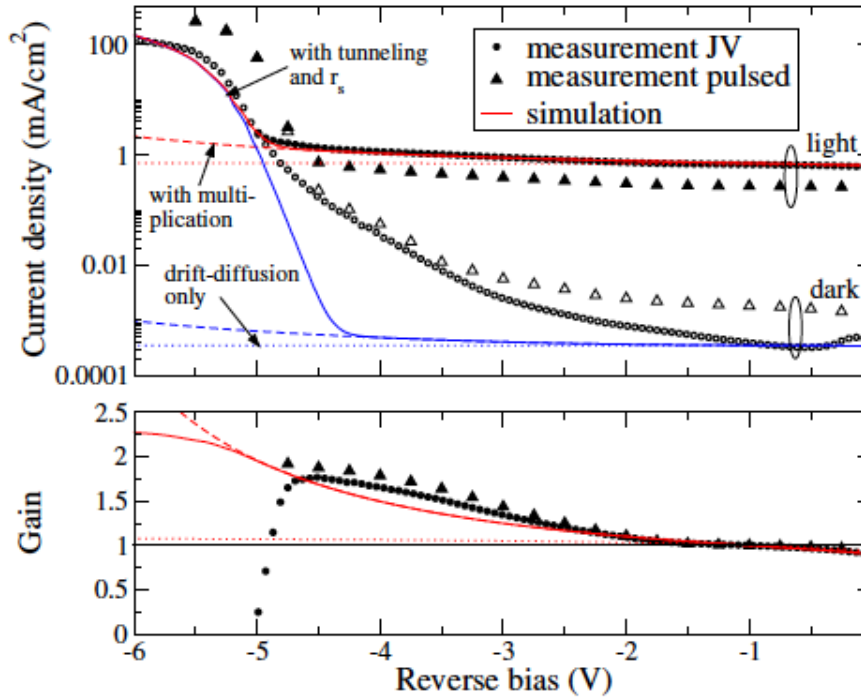
- Breakdown-like behavior at around -4–5 V
- Small amount of photocurrent **gain** of ~ 2
    - Incident photon to current efficiency $IPCE = J_{ph}\, hc / (P_{in}\, e\, \lambda) \sim 200\ \%$

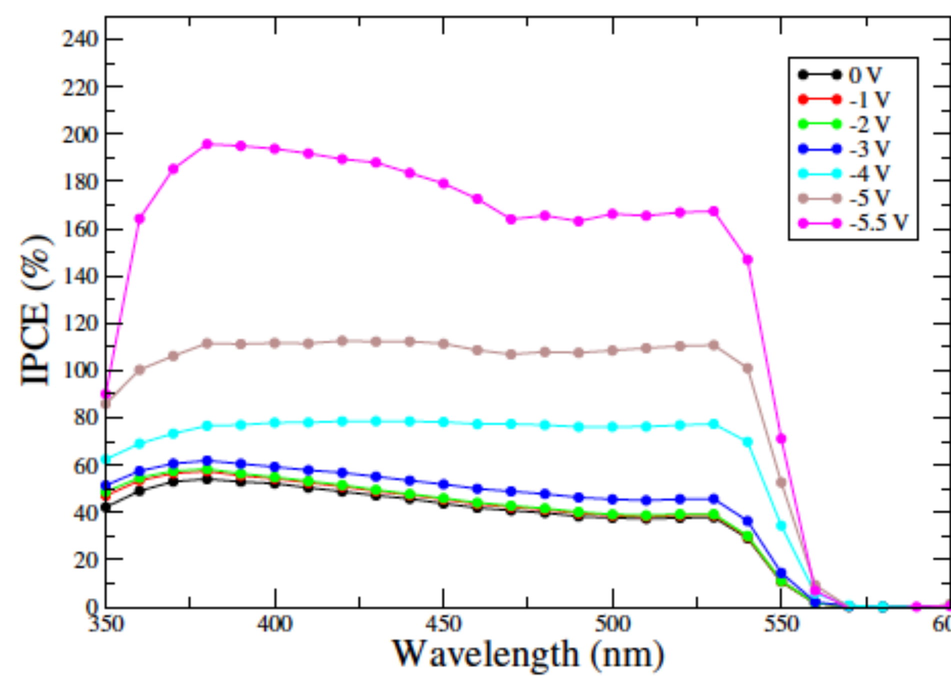
- Developed phenomenological **model** to explain the observed reverse bias behavior and gain though
    - *tunneling-assisted electron extraction at the TiO 2 /$MAPbBr_3$ interface*
    - *carrier multiplication*

- Both processes mediated by the electric field due to *mobile ions Br-*

- Mobile ionic species in halide play an important role in photodetector and solar cell performance and stability
    - Not fully understood but critical

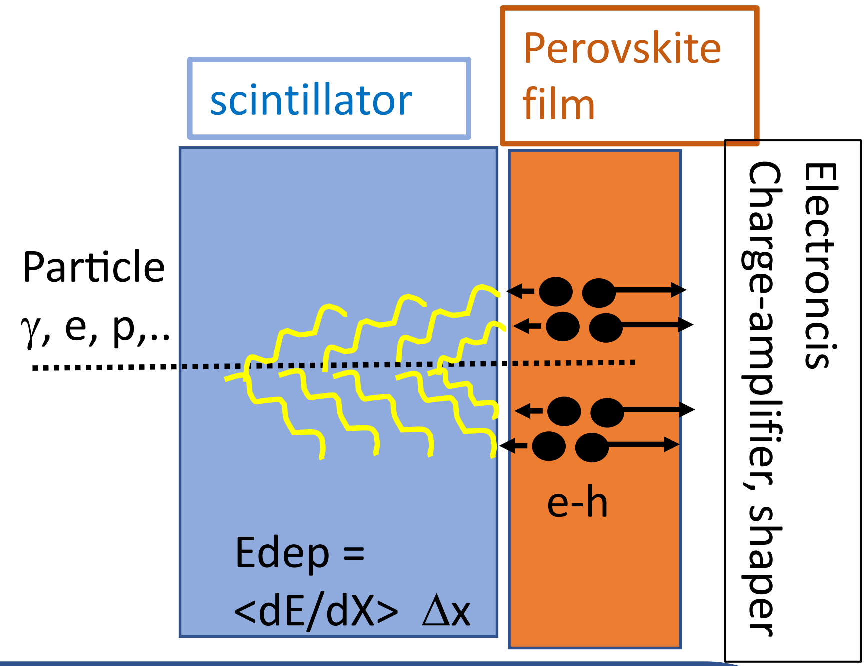
M. Testa, M. Auf der Maur, F. Matteocci, A. di Carlo
APPLIED PHYSICS LETTERS 10.1063/5.0082425

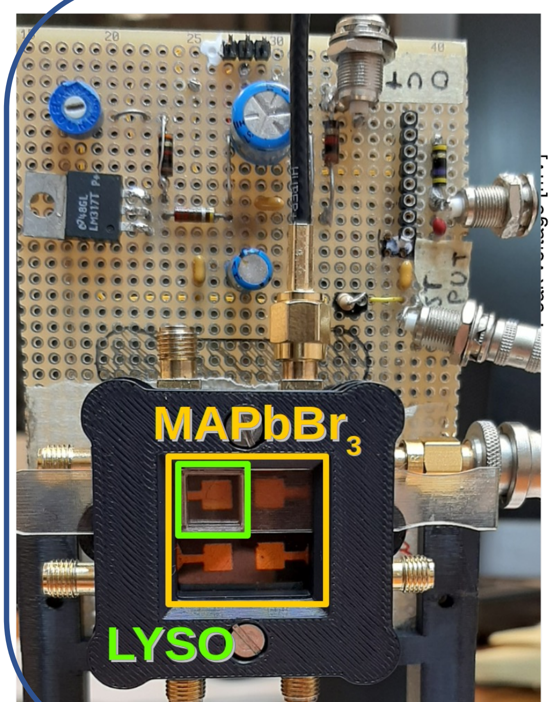




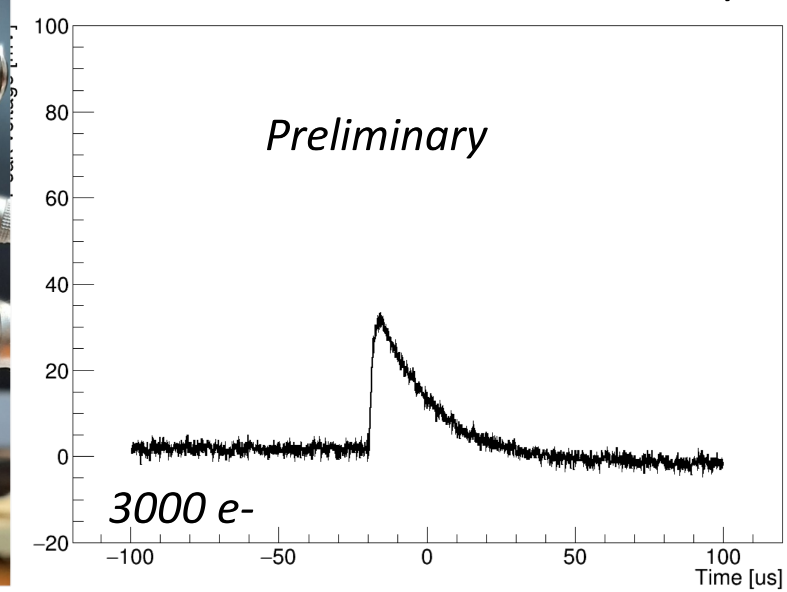
Film-based devices: application for radiation detection

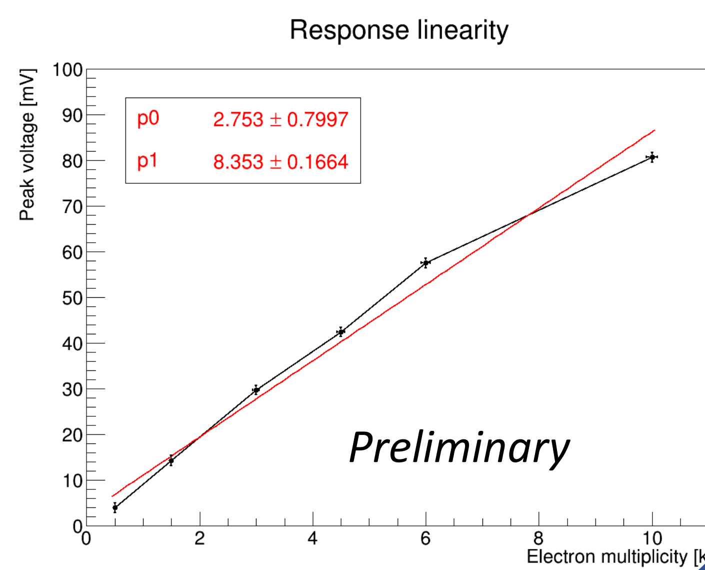
- Film devices can be used in combination with a scintillator (eg LYSO)
- Film not suitabble if sensitivity to single photon required (SiPM have gain ~10^6)
- If large areas need to be covered, light intesity is high and timing performance not stringent, films are good candidate





Test Beam performed with electrons of 450 MeV in bunch of 10ns, 3.5 mm width at Beam Test Facility at LNF

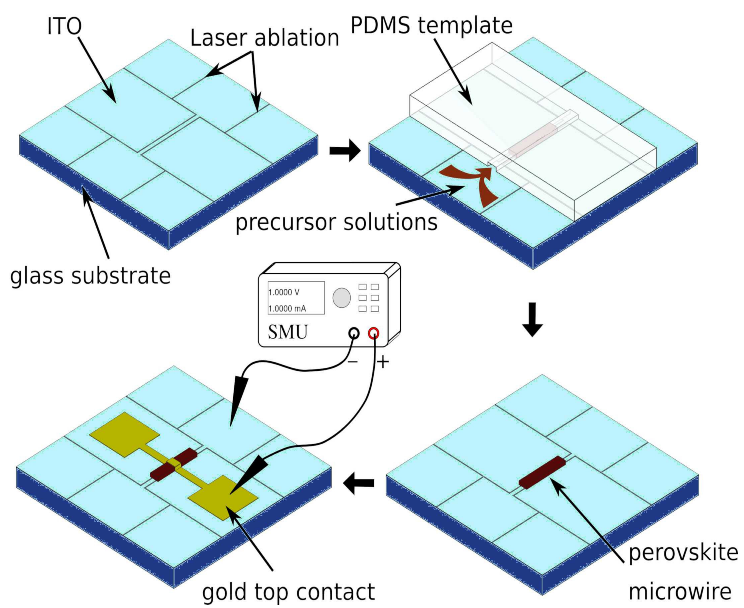




Micro-wires on patterned substrate

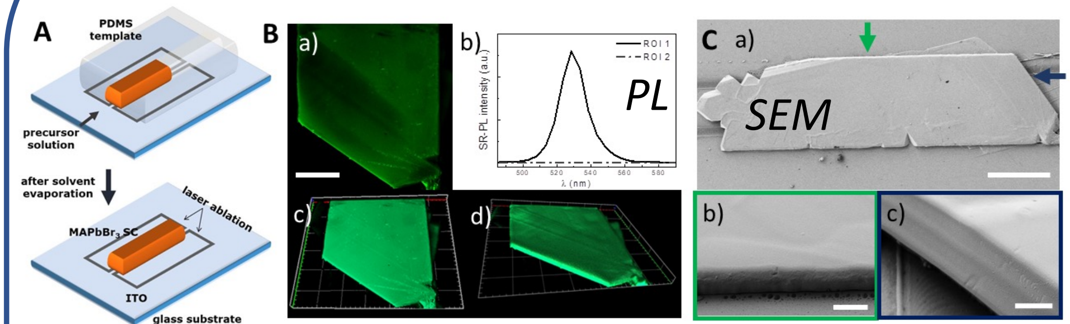
- Microfluidics-assisted technique to realize a controlled growth of OMHP single crystals, in the form of **microwires**, directly on a conductive **patterned substrates** W x L x H = 150 μm x 500 μm x 6(2) μm

Fabrication steps



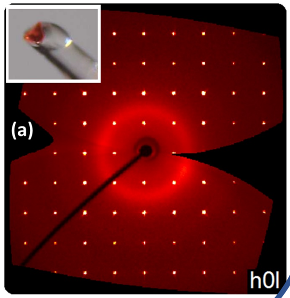
Advanced Material Technology
[10.1002/admt.202300023](https://doi.org/10.1002/admt.202300023)

Material Characterization

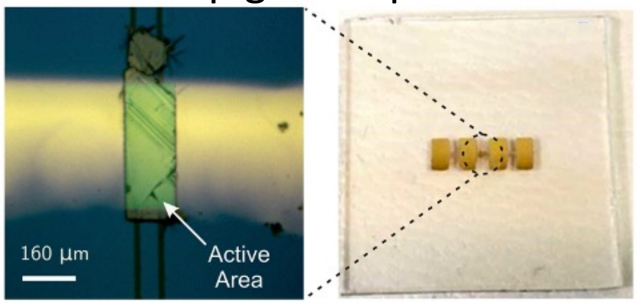


- homogeneous 3D crystalline microstructures, consistent with microchannel used for confinement
- typical photoluminescence of $MAPbBr_3$
- expected cubic phase with cell length a=5.927(2) Å

Xray diffraction



Top gold deposition

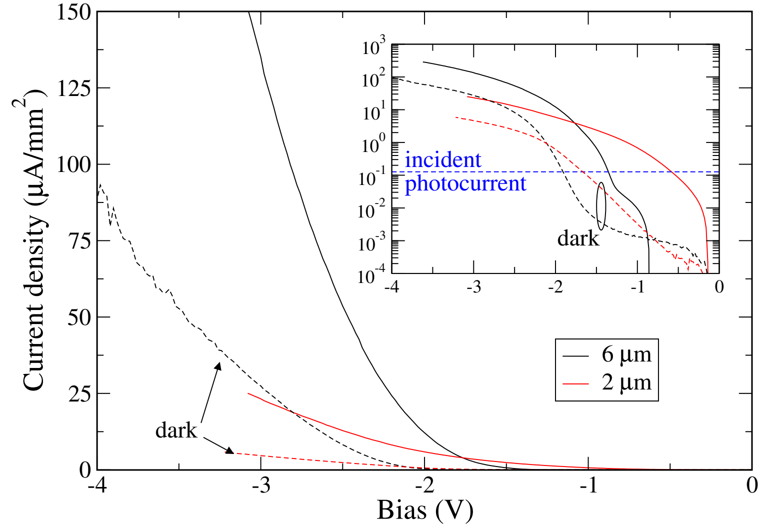


Final vertical device

Deposited patent
102022000010469

Characterization of micro-channels crystals: JV, IPCE

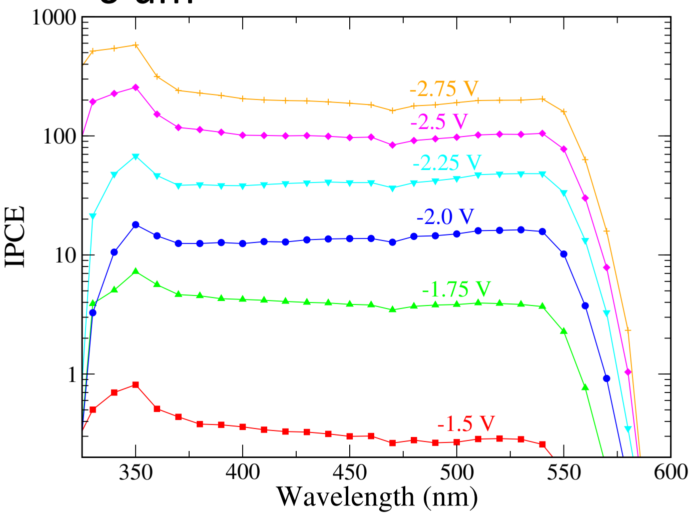
- 2 and 6 um thick-devices with active area of 0.034 mm^2 and 0.013 mm^2
- JV curve: trap-filled-limited region at 2 V
  - trap density ~ $10^{14} – 5 \times 10^{14}$ cm^{-3}.



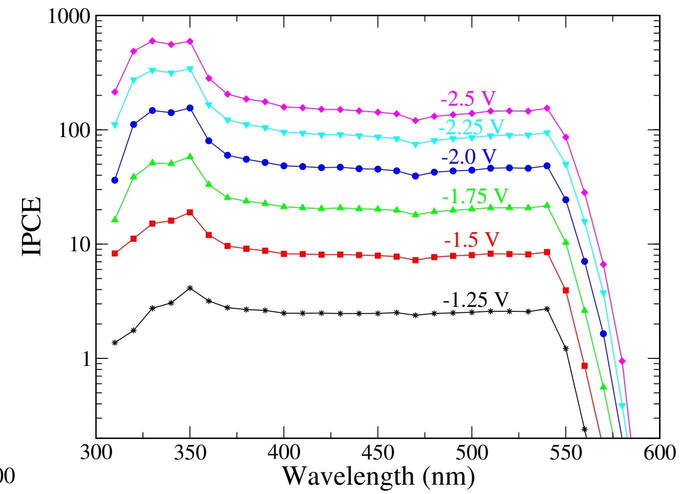
- Incident photon to current efficiency
  IPCE = J_{ph} hc / (P_{in} e λ) **> 100 %**
  at bias > 2-2.5 V→ **Gain** observed

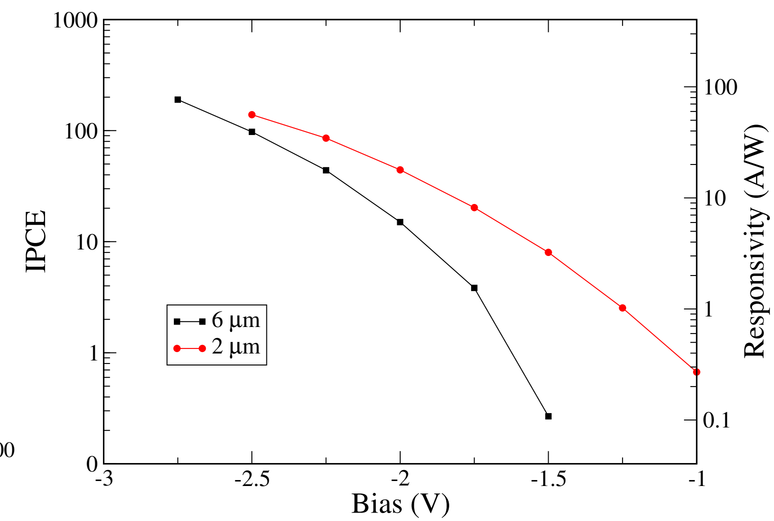
- Similar dark and light JV → gain probably due to photoresistive effect, possibly mediated by trap states

6 um



2 um



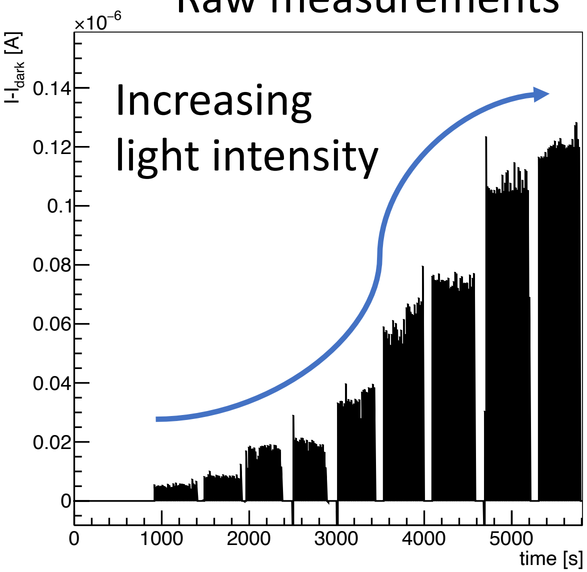


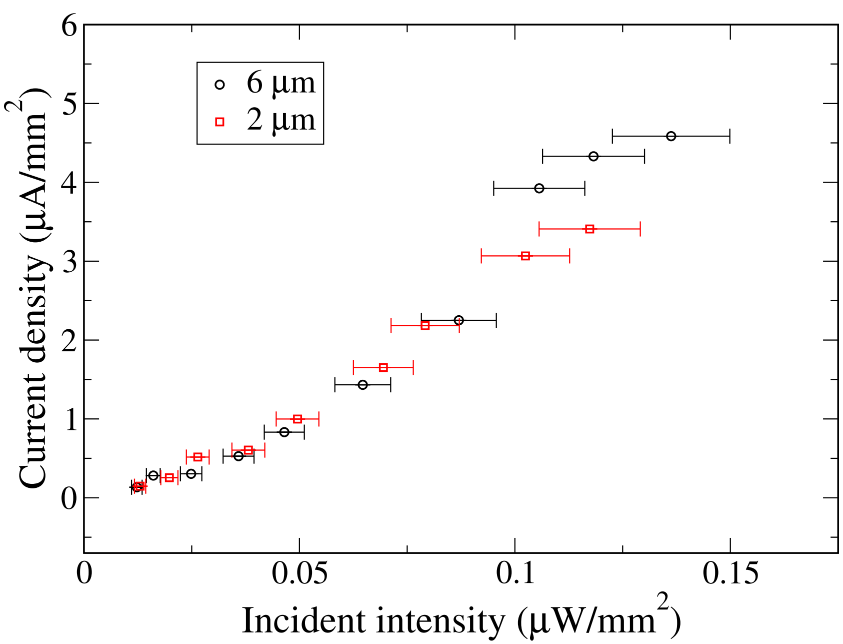
Advanced Material Technology **10.1002/admt.202300023**

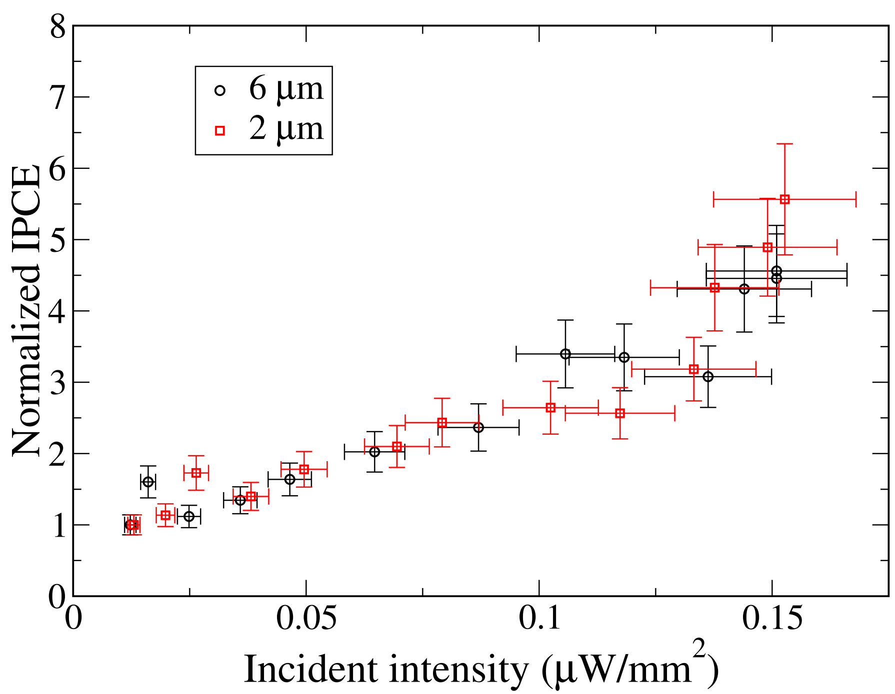
Characterization of micro-channels crystals: Light Intensity dependence

- A slightly super-linear behaviour is found within a light intensity variation of about a factor of eight
- Increase of IPCE as a function of the light intensity
  - at least a component of the gain mechanism is related to a photoconductive effect

Raw measurements





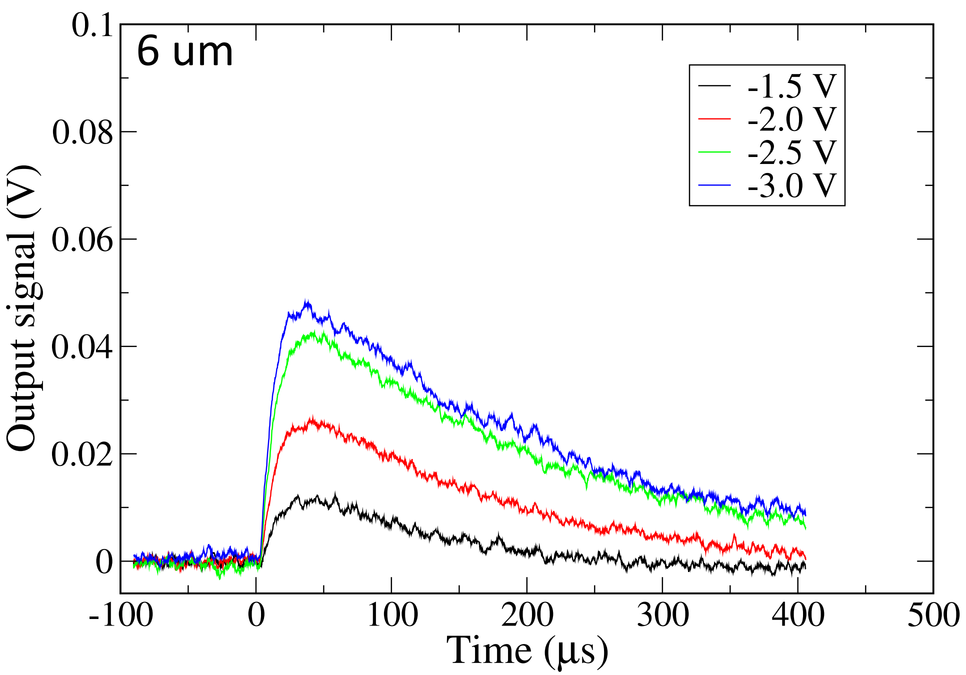


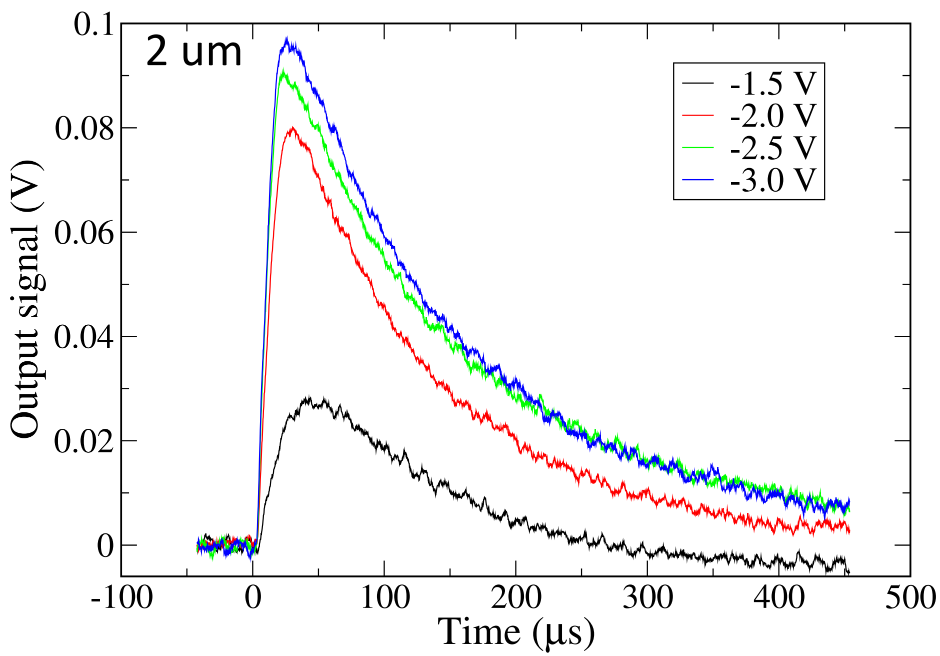
Advanced Material Technology **10.1002/admt.202300023**

Characterization of micro-channels crystals: Rise Time

- Rise-time measured with light intensity of 0.16 μW/mm^2
  - connection to preamplifier and a pulse shaper and the output voltage signal has been measured with an oscilloscope

- Rise-time decrease of ~40 μs to ~27 μs for applied voltages between -1.5 V and -3 V, corresponding to gain variation of 4
  - Does not suggest gain mechanisms that increase rise times, like those related to trapping

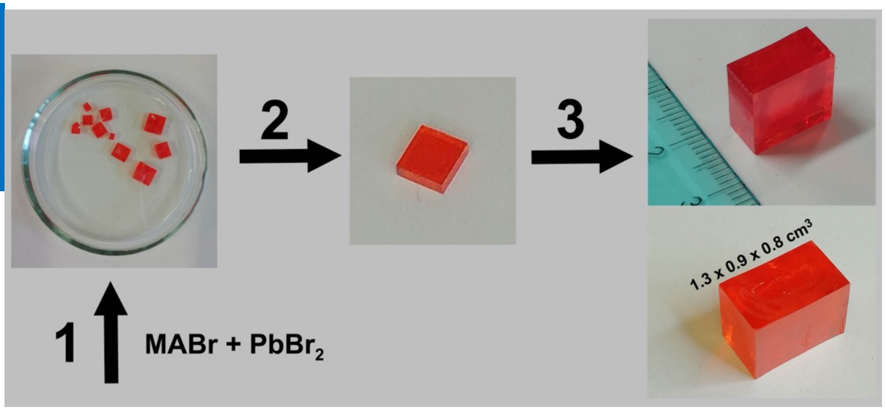




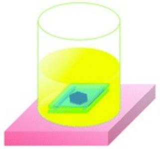
Advanced Material Technology [10.1002/admt.202300023](https://doi.org/10.1002/admt.202300023)

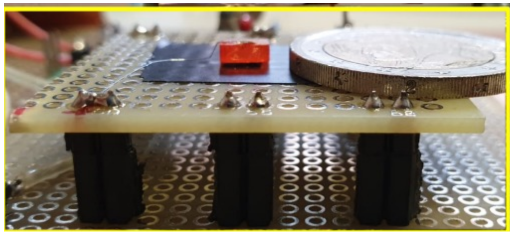
Large Single crystal

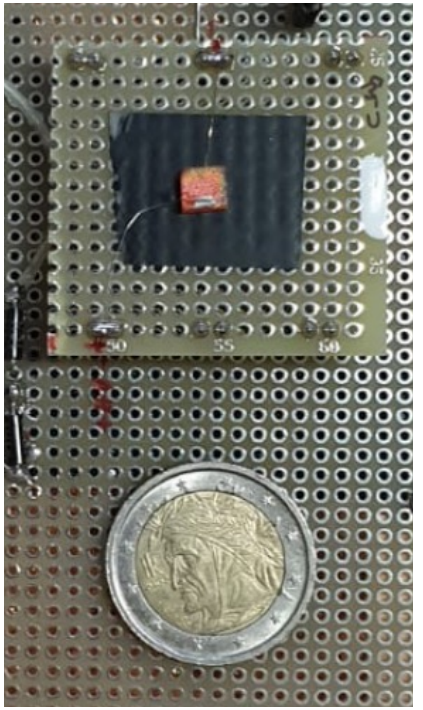
- Dimensions up to 1.0 x 1.5 cm^2 and up to 0.5 cm thick down to 300 μm by cutting the crystals along one of the {100}cubic planes
- Device realized with Indium Tin Oxide / $CH_3NH_3PbBr_3$ / Au
- Stable response measured
- Due to large thickness, suited for radiation detection (X-rays, charged particles)

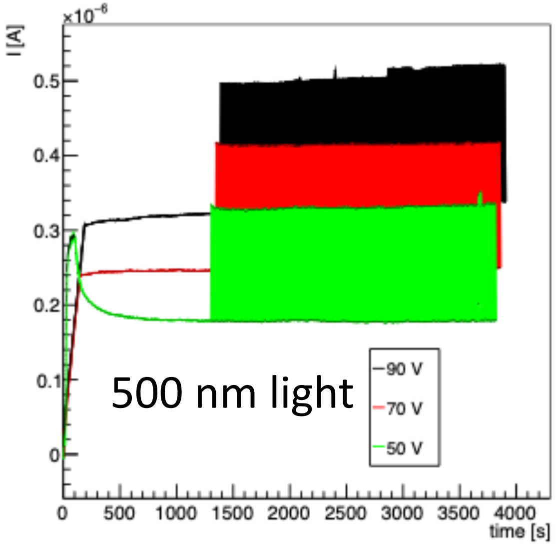


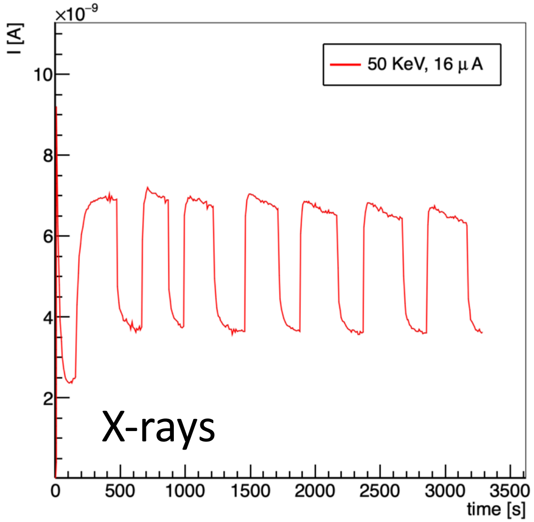
Seeding Techniques
Dip. Chimica Milano







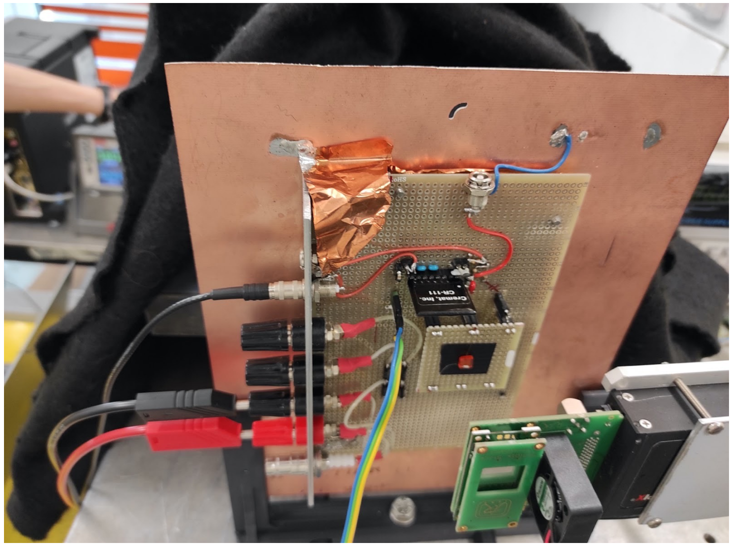


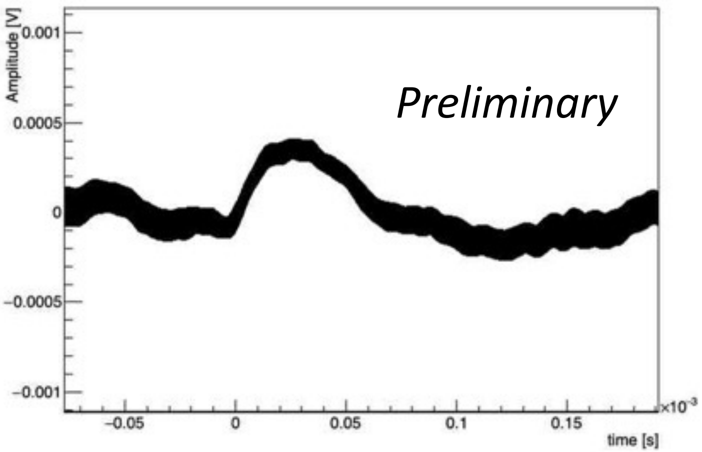


G. Tinti (LNF)

Charged particles detection

- Test Beam performed with **electrons** of **400 MeV** at Beam Test Facility at LNF
- Bunch of 10 ns, 3.5 mm width
- Beam multiplicity from 1 to 1000 measured from downadstream calibrated calorimeter
- Sensitivity down to single particle

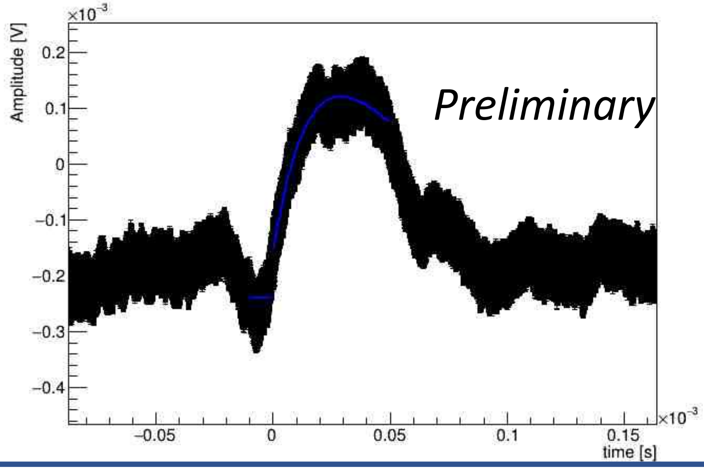




< Beam multplicity >= 1.4

- Observed **cosmics rays** passying through the crystal
- Similar response as single electrons, as expected (MIP)

Deposited patent 102023000012477



With help of G. Papalino, G. Felici. A. Paoloni (LNF)

Perovksite on CMOS for ionizing detection

- Goal: the feasibility of a hybrid X-ray detector structure combining a perovskite absorption layer and a CMOS silicon active layer
  - Principle: X-ray-generated electrons in the perovskite layer are transferred to silicon and collected by low-capacitance sensing diffusions coupled to in-pixel readout electronics
- The CMOS chips with an area of the order of 1cm^2 are available from ARCADIA INFN project

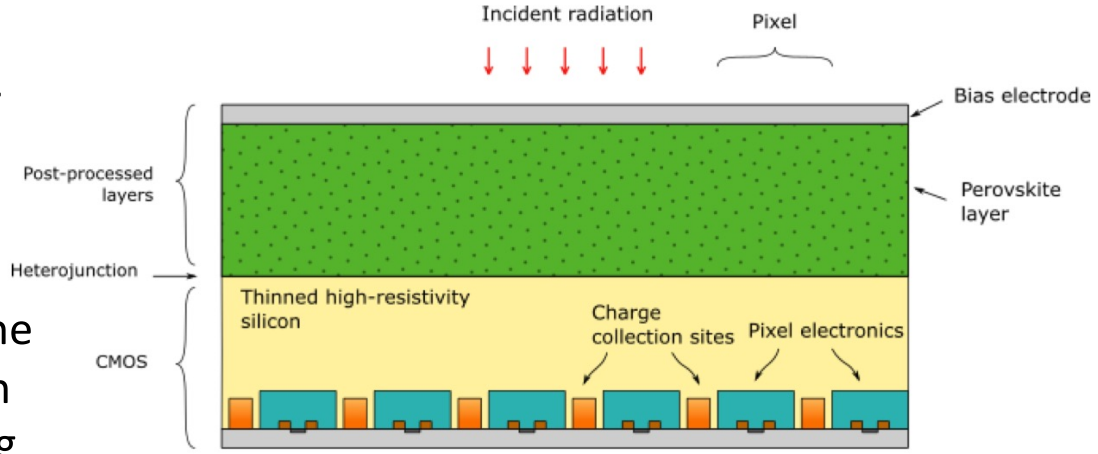
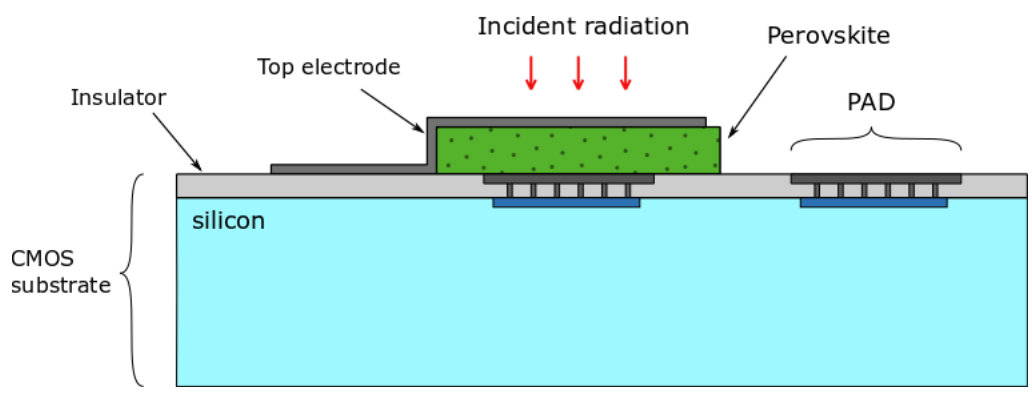


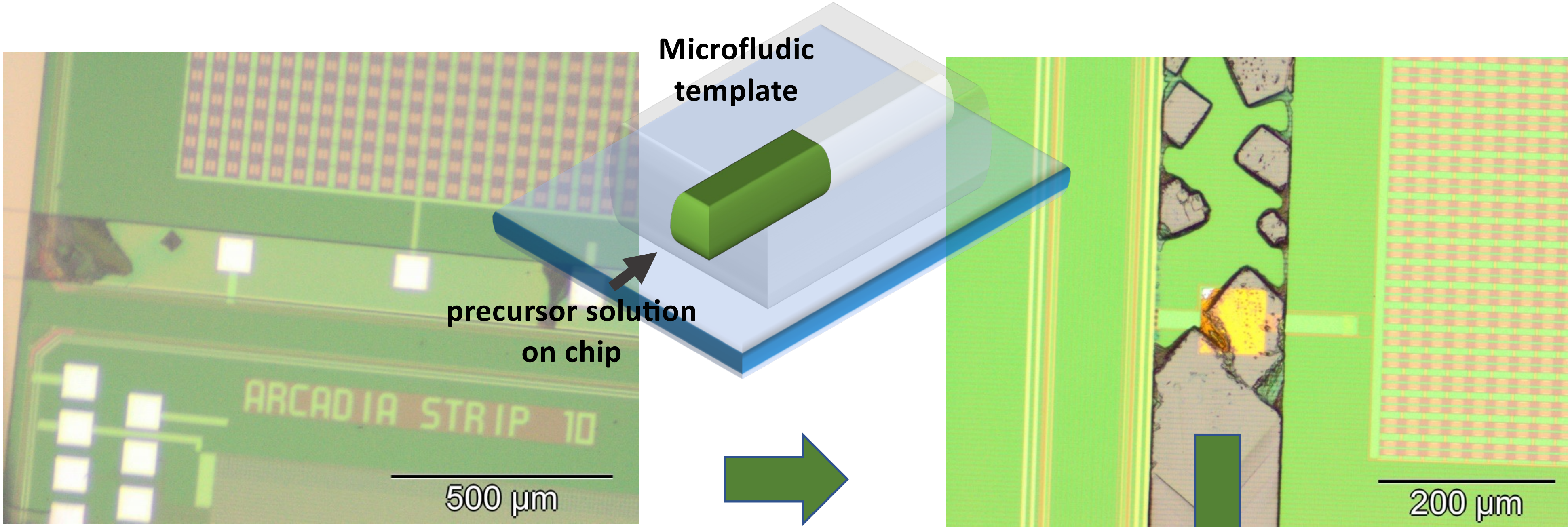
Figure 1. Simplified cross section of the proposed hybrid detector

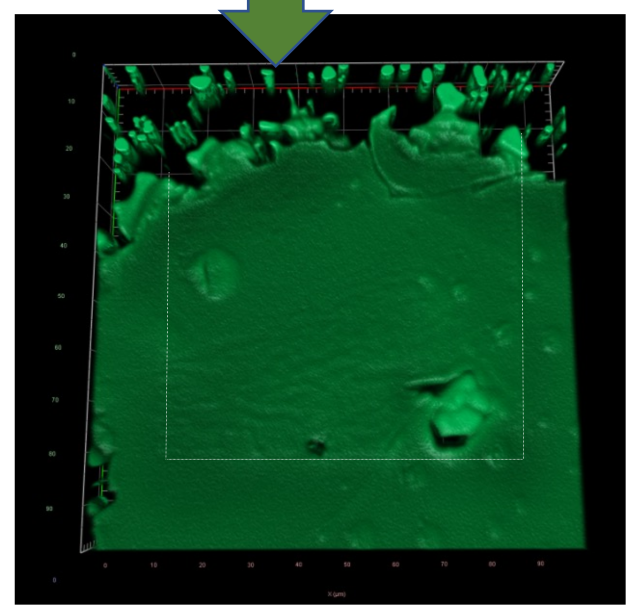
PRIN 2022 project granted
HyPoSiCX = Hybrid Perovskite on Silicon CMOS X-ray Detectors
L.Pancheri, M. Testa, I.Viola

- On going activity:
  - Test on deposition of perovskite micro-channels through microfluidics technique on CMOS substrates with aluminium pads, used as passive substrates



Perovksite on CMOS: Microfluidic-assisted growth





- High <u>crystalline quality</u> of each single crystal (SC);
- Controlled SC <u>dimensions</u> from 500 nm up to 200 µm;
- High <u>aspect ratios</u> for large area devices;
- Growth directly on the device interface;
- Tunability of precursor composition;
- Flexibility in the SC shapes.

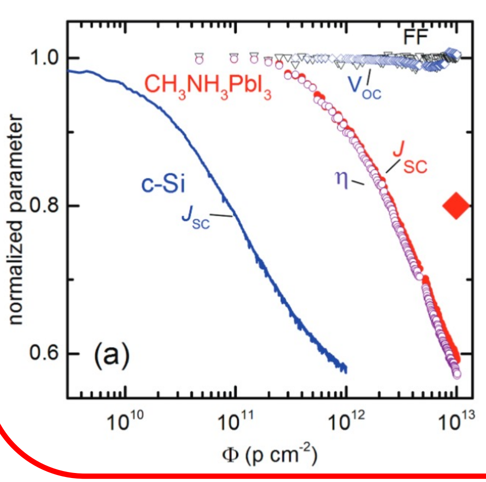
Confocal z-stack on a single crystal grown on the chip pad. Dotted lines indicate pad's position.

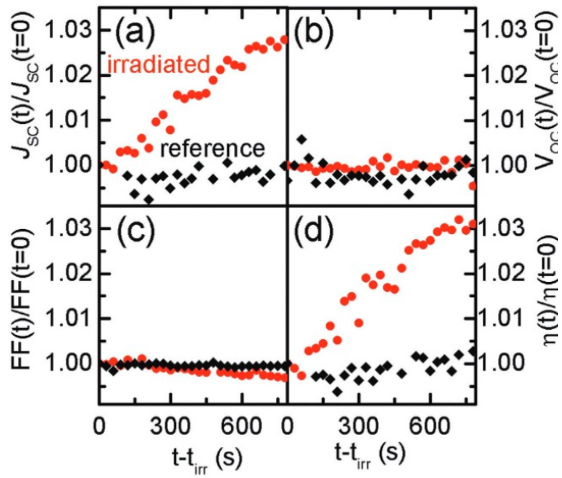
Photo courtesy: L. De Marco; R. Mastria; I. Viola – CNR-NANOTEC

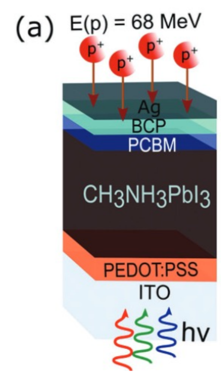
CNRNANOTEC
INSTITUTE OF NANOTECHNOLOGY

Radiation Hardness

Adv. Material 2016 10.1002/adma.201603326

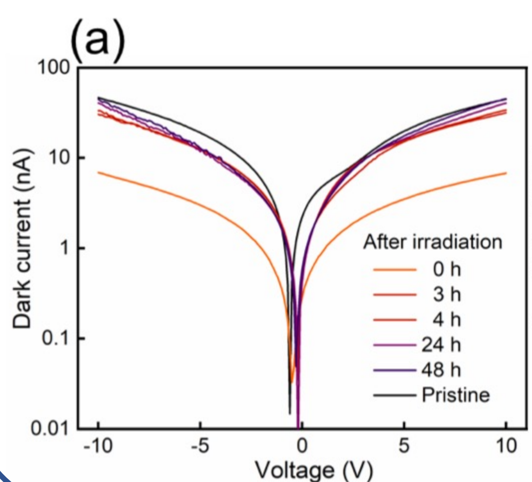


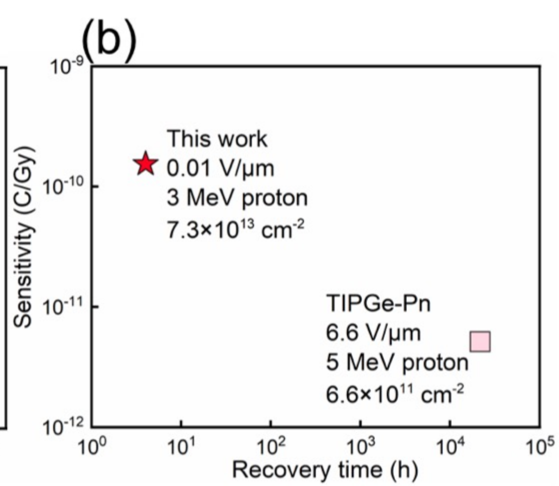




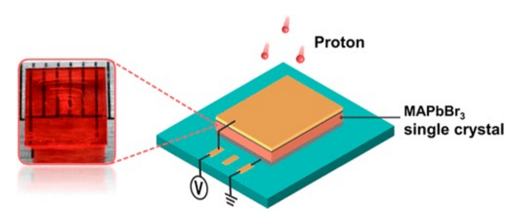
- Solar Cell thin perovskite films
- 68 MeV proton flux 10^{13} p/cm^2
- Damage thr. much larger than commercial silicon-cell
- **Self-healing** of perovskite
  - Displaced atoms migrate in lattice and passivates defects

ACS Appl. Electron. Mater. 2023
10.1021/acsaelm.2c01406





- Bulk Crystal 2×1.5×1 mm^3
- 3MeV protons flux of 7.3×10^{13} p/cm^2 (1MGy)
- **Self-healing** : performance recovered within hours



Conclusions and Outlook

- Halide Perovskite is a promising class of semiconductors for ionizing radiation detection

- Single Bulk crystals:
  - Stable response under visible light and X-rays
  - Sensitivity down to high energy single charged particles

- Single crystal microwires have been growth directly on patterned substrate with precise location and high aspect ratio
  - Visible light detection with high responsivity
  - Next steps:
    - testing with X-rays
    - Integration with CMOS technology

Backup

State of art for perovskite photodetectors

- **Thin films**, **single crystals** devices can be divided in two categories:
  - Vertical devices
    - without or with small gain and responsivity; short rise time
    - Rise time/decay time down to O(1) μs; EQE up to ~ 80%.
  - Lateral devices
    - with gain, slow; generally lateral devices

Table 2 Summary of the reported broadband perovskite photodetectors

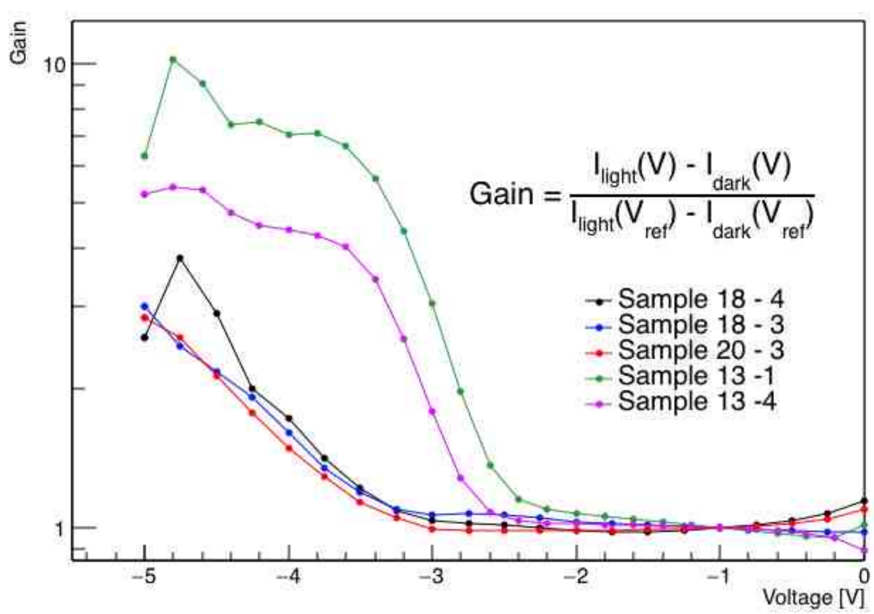
Materials (device structure)	Response range (nm)	EQE (%)	R (A W^{-1})	D^* (Jones)	τ_r/τ_f	Ref.
$MAPbI_3$ thin films (vertical)	400–800	—	0.4	10^{12} [c]	1.2/3.2 μs	174
$MAPbI_3$ thin films (vertical)	375–800	84	0.339	5×10^{12} [d]	—	175
$MAPbCl_3$ thin films (vertical)	300–400	24	0.071	2.87×10^{10} [d]	—	211
$MAPbI_3$ thin films (vertical-MSM)	300–800	$\sim 10^4$	>150	—	—/0.67 μs	172
$MAPbI_3$ thin films (lateral-MSM)	300–800	—	0.11	1.3×10^{11} [d]	<90/<20 ms	212
$MAPbI_3$ thin films (lateral-MSM)	440–800	4.1×10^4	219	3.1×10^{12} [d]	—	171
$MAPbI_3$ thin films (lateral)	400–800	80	320	—	6.5/5.0 μs	43
$MAPbI_{3-x}Cl_x$ thin films (lateral)	254 & 350–800	3832	7.85	—	0.2/0.7 μs	145
$MAPbI_{3-x}Cl_x$ thin films (lateral)	405–808	1808	11.5	4.93×10^{12} [d]	—	146
$MAPbBr_{3-x}I_x$ thin films (lateral)	300–600	—	0.055	—	<20/<20 μs	147
$MA_{0.5}FA_{0.5}Pb_{0.5}Sn_{0.5}I_3$ thin films (vertical)	350–1000	—	>0.2	>10^{12} [c]	—/7.4 μs	149
$(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ thin films (vertical)	300–1000	~80	>0.4	>10^{12} [c]	6.9/9.1 μs	47
$FA_{1-x}Cs_xPbI_3$ thin films (lateral)	240–750	—	5.7	2.7×10^{13} [d]	45/91 ns	150
$MAPbI_3$ single crystal (lateral)	275–790	2.22×10^5	953	—	74/58 μs	182
$MAPbI_3$ single crystal (lateral)[a]	600–950	22	0.15	—	0.12/0.08 s	183
$MAPbBr_3$ single crystal (lateral)[a]	400–890	25	0.1		0.08/0.09 s	
Integrated $MAPbCl_3$ single crystals (lateral)	340–430	100 (G)	11	10^{12} [d]	—/1 ms	185
Integrated $MAPbBr_3$ single crystals (lateral)	375–575	1.4×10^4 (G)	4500	>10^{13} [d]	25/25 μs	184
$FAPbI_3$ single crystalline wafer (lateral)	—	900	4.5	—	8.3/7.5 ms	186
$MAPbI_3$ thin single crystal (vertical)	350–800	62	0.32	>10^{13} [c]	—/3.1 μs	187
$MAPbBr_3$ thin single crystal (vertical)	350–550	60	0.26		—/7.2 μs	
$MAPbBr_3$ single crystalline thin film (vertical)	—	5×10^7 (G)	1.6×10^7	—	81/892 μs	188

J. Mater. Chem. C, 2019, 7, 1741

- **Micro-sized** photodetector development steadily growing [*Adv. Funct. Mater.* **2022**, *32*, 2200385]
  - Few examples for vertical devices with low responsivity and/or slow rise time
    - 0.38 AW^{-1} [*Li et al Advanced Optical Mate-rials 2021, 9 210037*]
    - Slow rise time [*Weng et al, Advanced Materials 2020, 32, 1908340,11*]

Film-based devices: what we learned

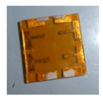
- Gain observed in a fraction of devices
  - Not dependent on different hole transport layers: PTAA or MD89, none 🙂
- Significant differences among devices and pixels on the same devices ☹️

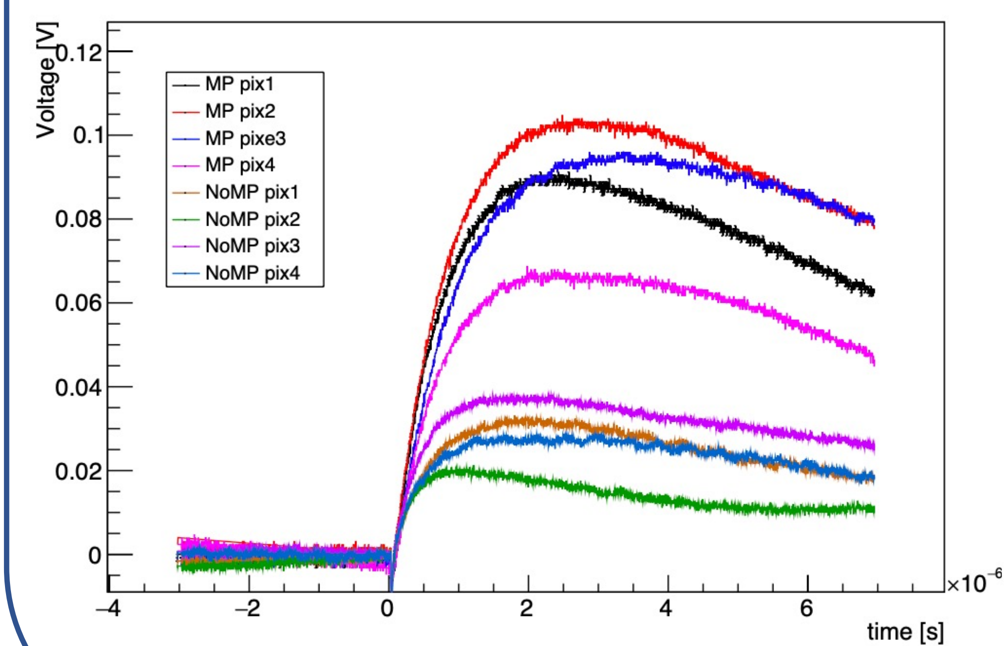


- Rise-time of ~ 2μs dominated by transport in the mesoporous TiO2 transport layer.
- Less impact from area
- Planar TiO_2: 0.5 – 1 μs
- Mesoporous TiO_2: 1.3-2 μs
- Small area Mesoporous TiO_2: ~1 μs

Def Area

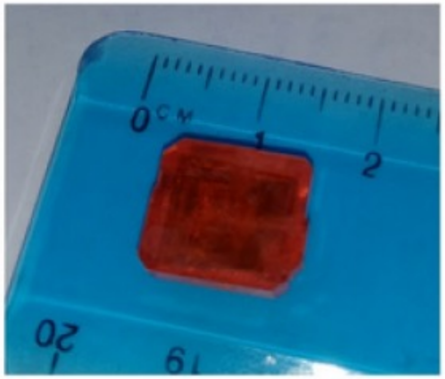
Small Area



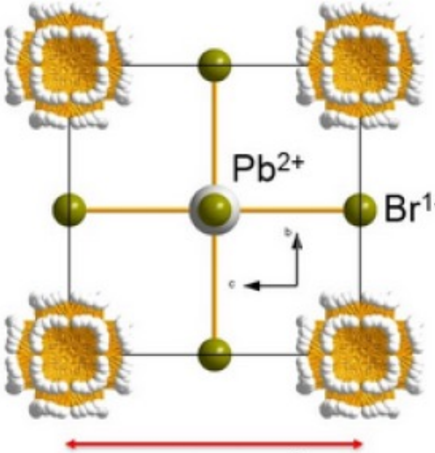


Large Single crystal production

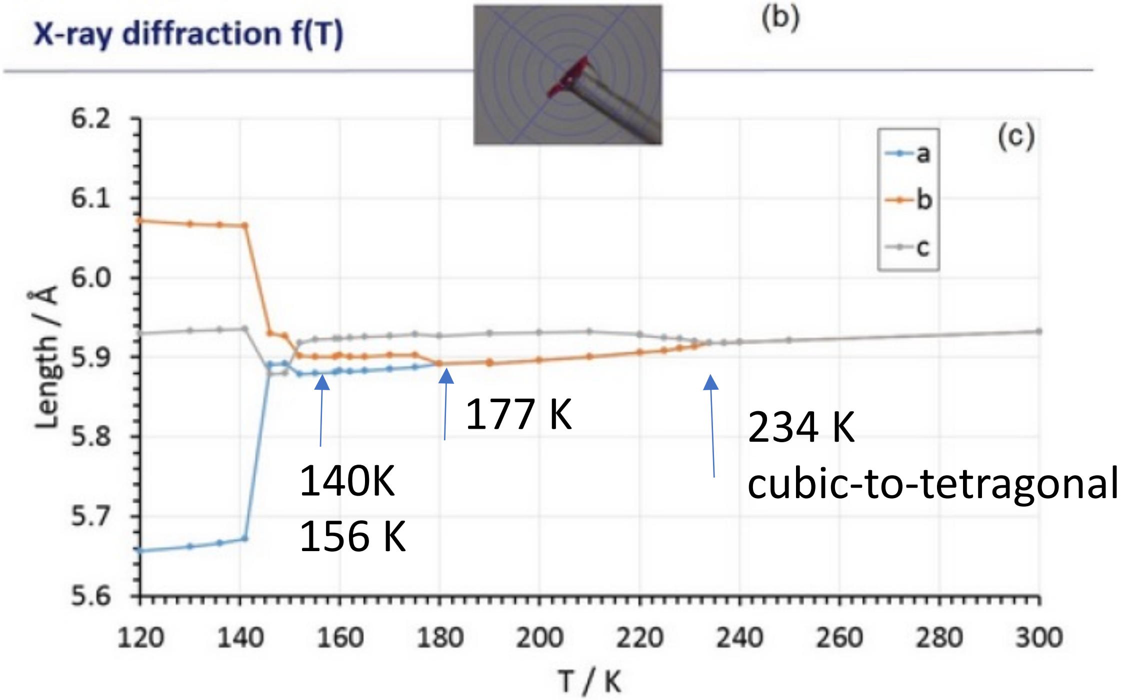
- $CH_3NH_3PbBr_3$ single crystals synthesized by temperature raising method from a dimethylformamide solution of the reactants
    - Dimensions up to 1.0 x 1.5 cm^2 and up to 0.5 cm thick down to 300 µm by cutting the crystals along one of the $\{100\}$cubic planes
- X-ray diffraction:
    - Transitions observed at various temperatures in agreement with literature
    - At T_{room} complete full sphere of data: The methylammonium cation occupies the cuboctahedral sites and is disordered over 48 crystallographic equivalent directions



(a)

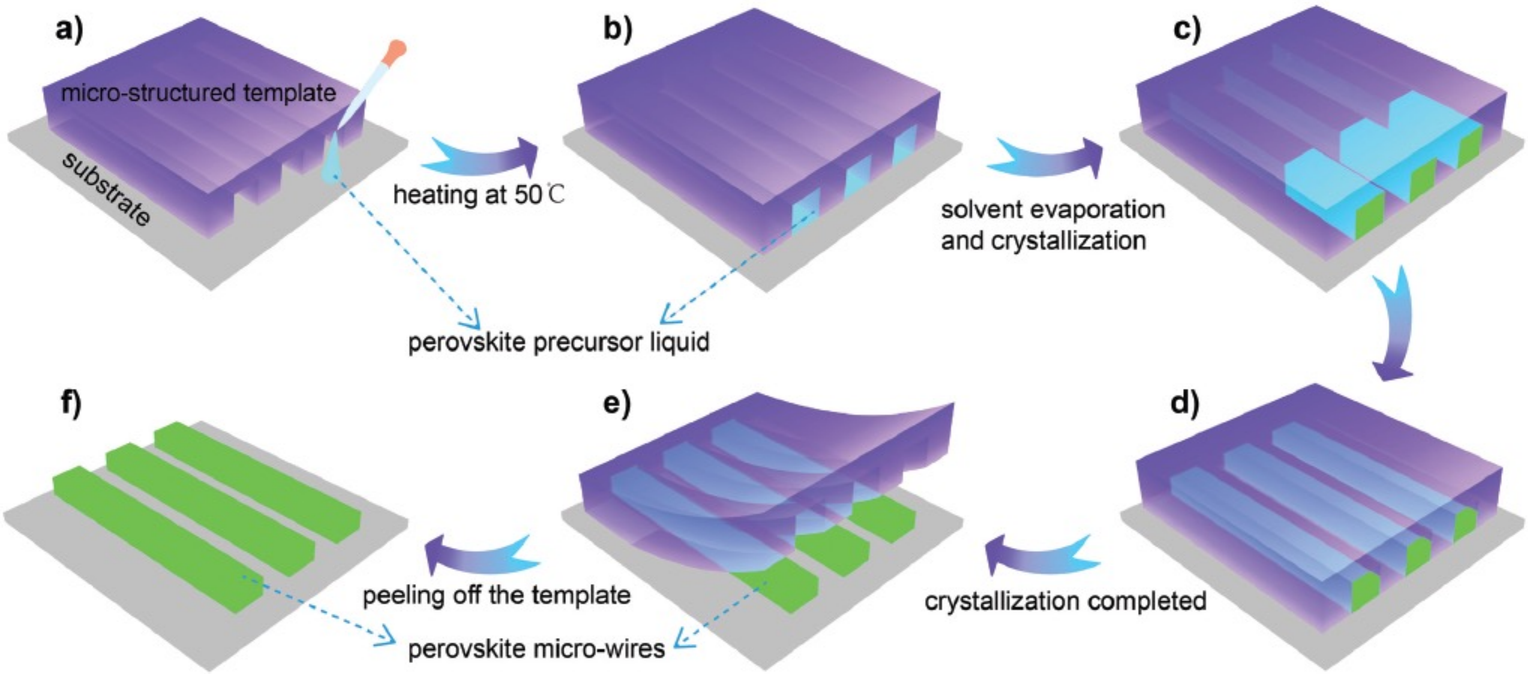


(b)



L. Lo Presti, S. Rizzato
Dip. Chimica Univ. degli studi di Milano

Microfluidic-assisted perovskite crystallization



S.-X- Li, Nanoscale, 11, **2019**

- Manipulation of fluids at the microscale
- High control over the crystallization kinetics

⬇

- Excellent uniformity, crystallinity and structural quality
- Allow perovskite crystallization on functional device
- Reduce significant batch-to-batch variability
- Allow patterning over large area, on nonplanar surfaces, with sub-micrometer resolution

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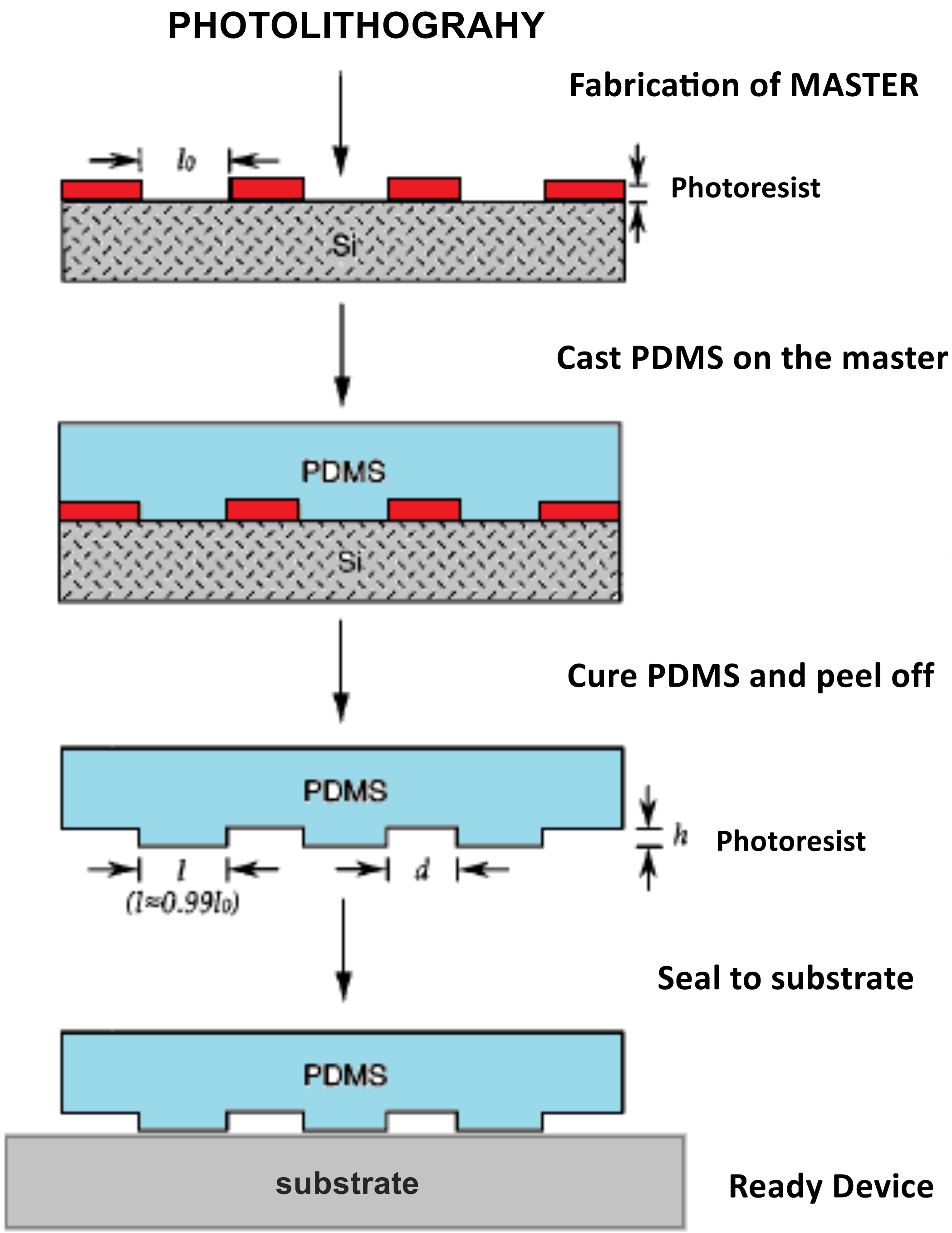
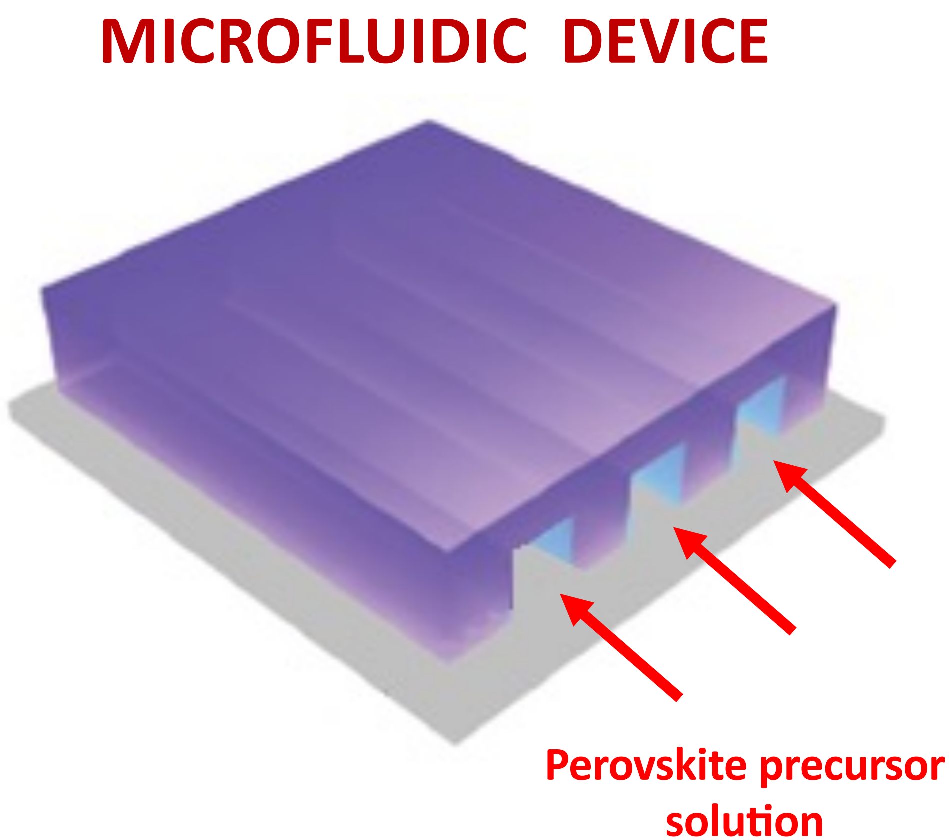
Microfluidics: Soft-Lithography fabrication technique





Y. Xia, G.M. Whitesides, **Ann. Rev. Mater. Sci**, 28, 1998
I.Viola et al., **Anal. Chem.**, 77, 2005

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Electronic/Optical Properties

Material	h^+ effective mass [m_e]	e^- effective mass [m_e]	μ_{h+} [$cm^2 V^{-1} s^{-1}$]	μ_{e-} [$cm^2 V^{-1} s^{-1}$]
Si[b)]	0.54[109]	0.32[110]	500[109]	1500[110]
GaAs[b)]	0.53[113]	0.06[113]	400[113]	8000[113]
CdTe[b)]	0.72[115,116]	0.11[115,116]	100[117]	1100[117]
$CuInS_2$	≈1[120]	0.16[120]	≈20 [120]	≈150[120]
$MAPbI_3$	0.26[122,123]	0.23[122,123]	≤160[124]	≤70[124]
$MAPbBr_3$[c)]	0.15[127]	0.25[127]	≤220[128]	≤190[129]

Egger et al. Adv. Mater. **2018**, 1800691

Electronic properties are aligned with conventional semiconductors and much better than typical solution process organic semiconductors.

Absorption coefficient