PEROV_XRAD project:
R&D for radiation detectors based on Organo-Metal Halide Perovskites

Consiglio di Laboratorio
6 July 2023

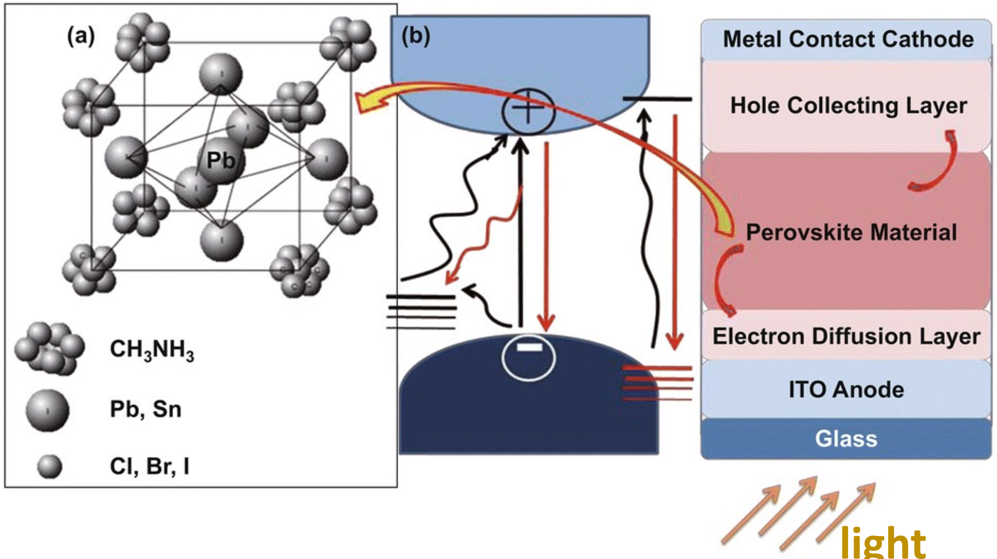
Marianna Testa (LNF-INFN)

- Participants structures:
  - LNF, A. De Santis RL
  - Universita' di Trento – TIFPA, Lucio Pancheri RL
  - CNR-NANOTEC
  - Dip. Ingegneria Elettronica di Tor Vergata
  - Dip. Chimica Universita' di Milano
- Collaborazione esterna: ENEA

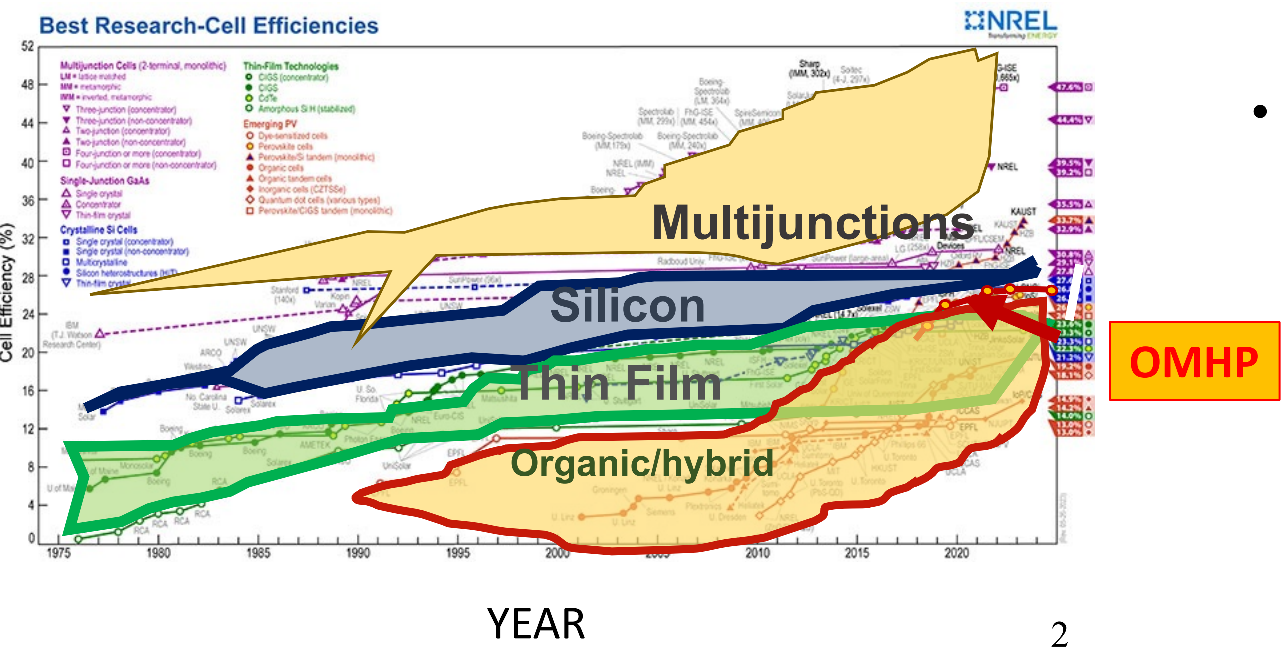
Organo-Metal Halide Perovskite

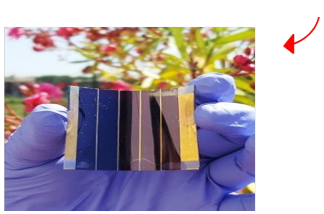
- **Organo Metal-Halide Perovskites (OMHP)** are a class of hybrid organic-inorganic semiconductor materials with a perovskite unit-cell structure **ABX_3** with
  - A = $CH_3NH_3^+$, B = metallic cation (Pb^{2+}), X = halide anions (Cl^-, Br^-, I^-)

- 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

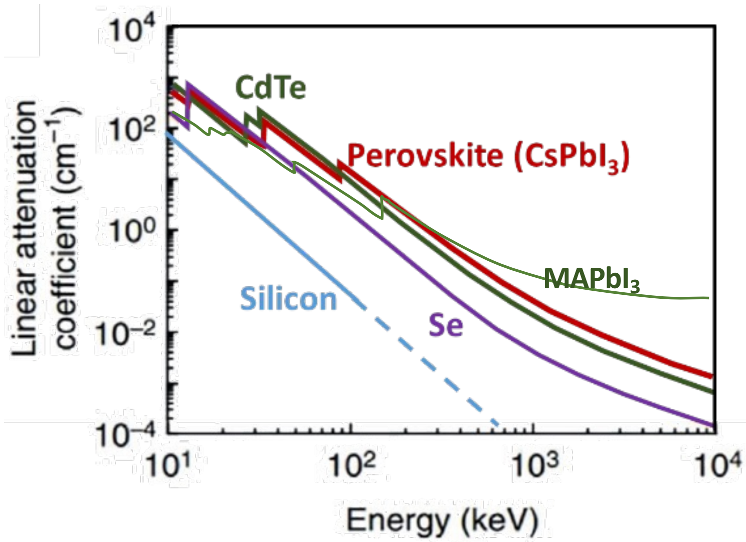
		Silicon	$CH_3NH_3Pb(I,Br)_3$
Density		2.33 g/cm^3	4.15 g/cm^3
Band gap (eV)		1.12 (indirect)	1.5-1.6 / 2.24 (direct)
Mobility (cm^2/Vs)	electrons	1400	< 70/190
	holes	450	< 160/220
Absorption (cm^{-1})		< 10^4	> 4×10^4
Threshold energy for impact ionization (eV)		1.2	~2 / 2.5 (estimated)
Mean free path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

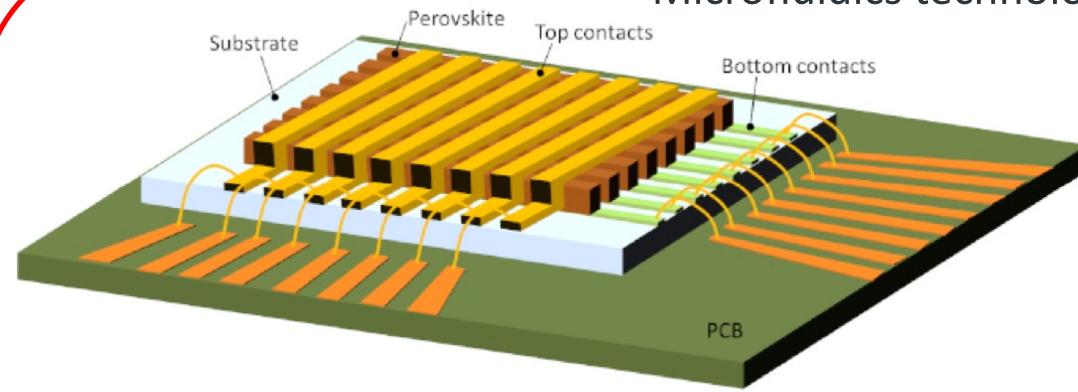
(*)Wei & Huang, J. Nat Commun 2019, 10, 1066; Del Sordo et al. Sensors 2009, 9, ; H.M. Thirimanne et al. Nature Comm 2018, 9, 2926

PEROV_XRAD: First Goal

- Prototypes of **multi-pixel** imaging devices
  - three benchmark thickness in the range of O(10)-O(100) mm
  - target detection of charged particles, X-rays and gammas

- Microfluidics technology:
  already developed in PEROV project
- for PEROV_XRAD:
  - multi pixel
  - higher thickness

Microfluidics technology



Dewetting technology

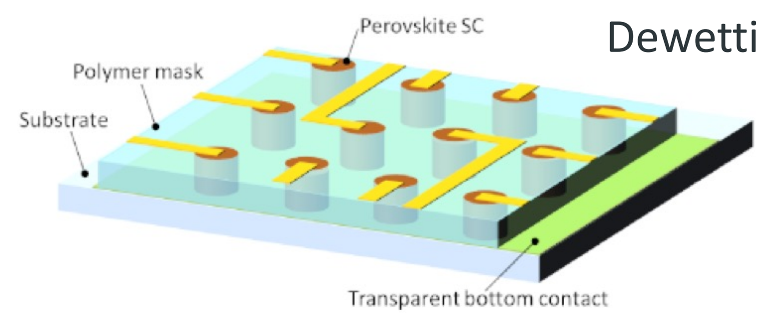
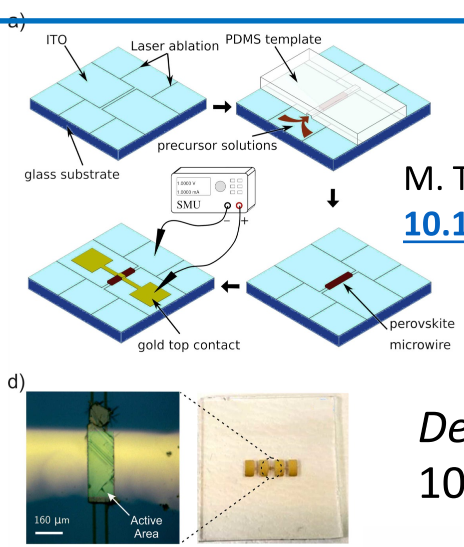


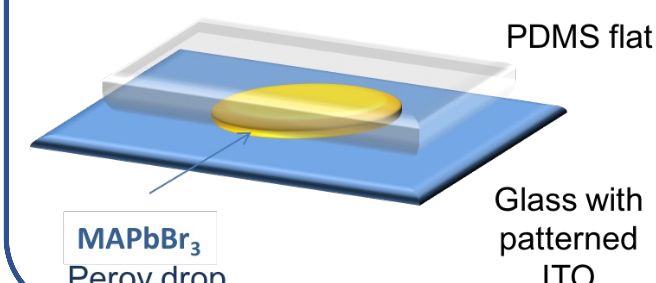
Fig 3: Device schemes for the two types of arrays, with matric addressing (top) and direct addressing (bottom).

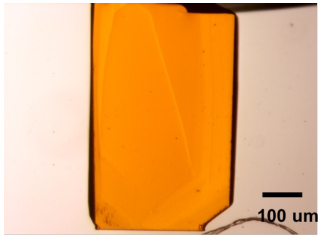


M. Testa, A. De Santis et al
[10.1002/admt.202300023](https://doi.org/10.1002/admt.202300023)

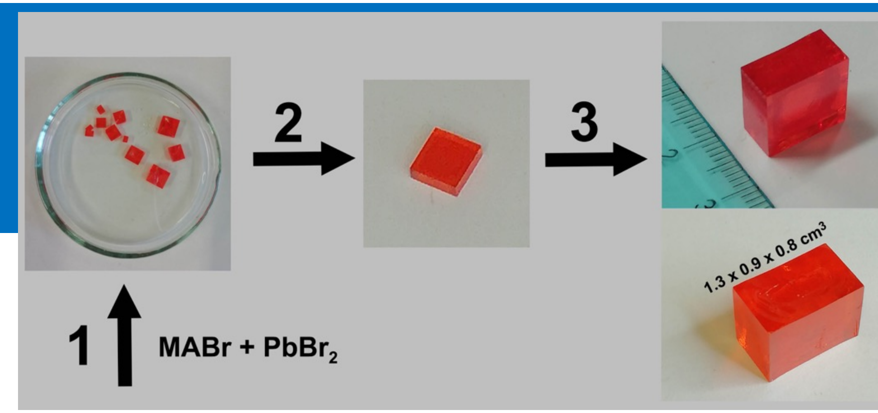
Deposited patent
102022000010469

Dewetting already developed in PEROV project
~ 100 micron thickness reached

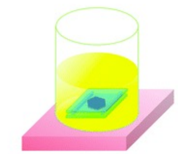




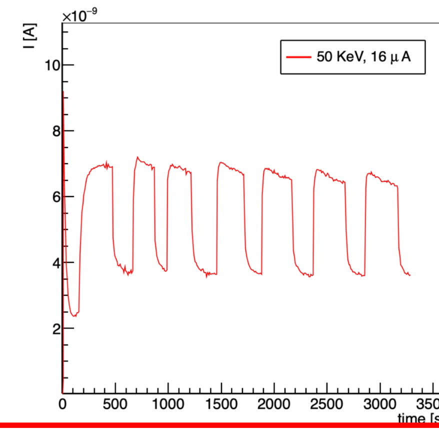
PEROV_XRAD: First Goal

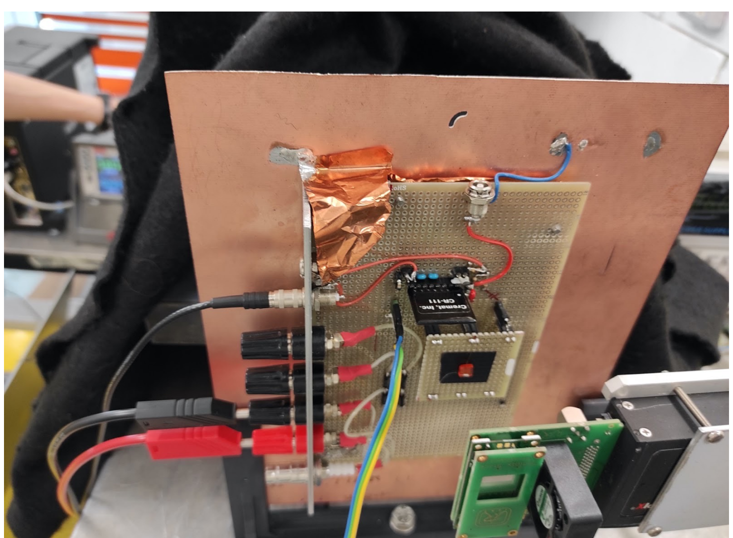


Seeding Techniques
Dip. Chimica Milano

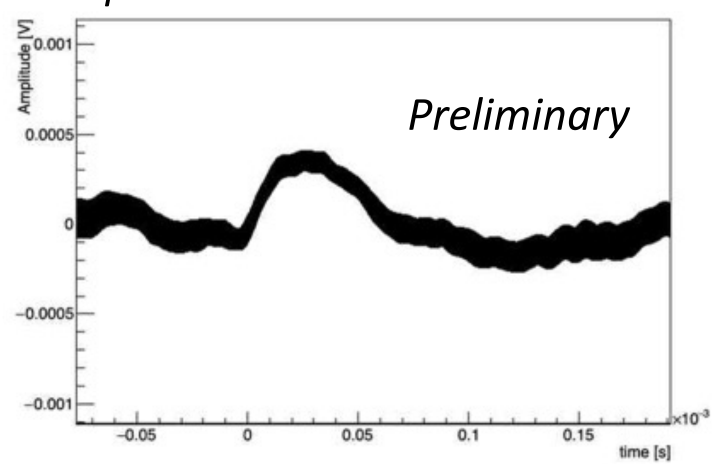


- Comparison with bulk high purity crystals
- Already developed for PEROV project
- Sensitive to:
  - high energy charged particles
    - Demonstrated at Test Beam at BTF
    - Xray
- LNF Facilities to be used
  - Xray tube (LEMRAP lab)
  - BTF





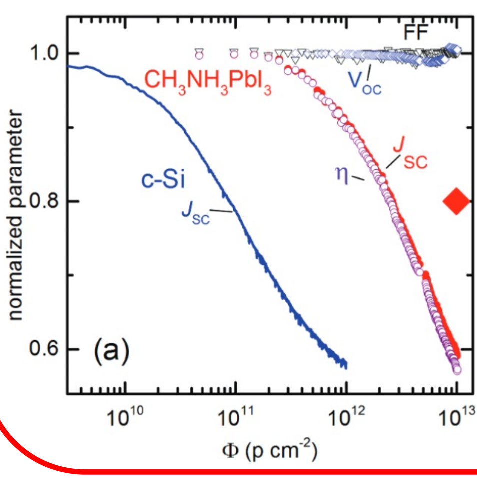
Deposited patent 102023000012477

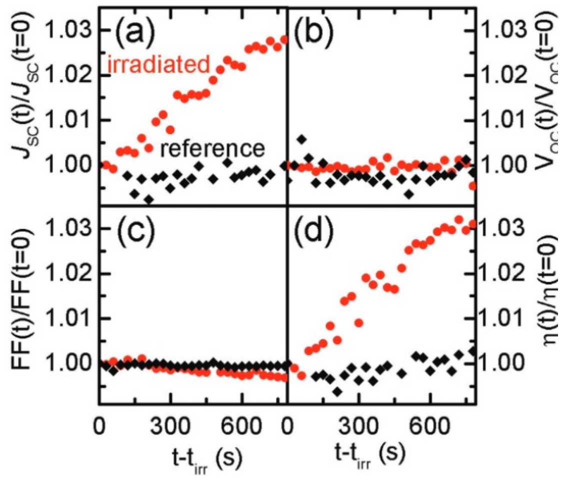


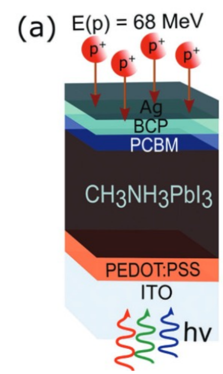
< Beam multplicity >= 1.4

Perovskite Radiation Hardness: State of Art

Adv. Material 2016 10.1002/adma.201603326

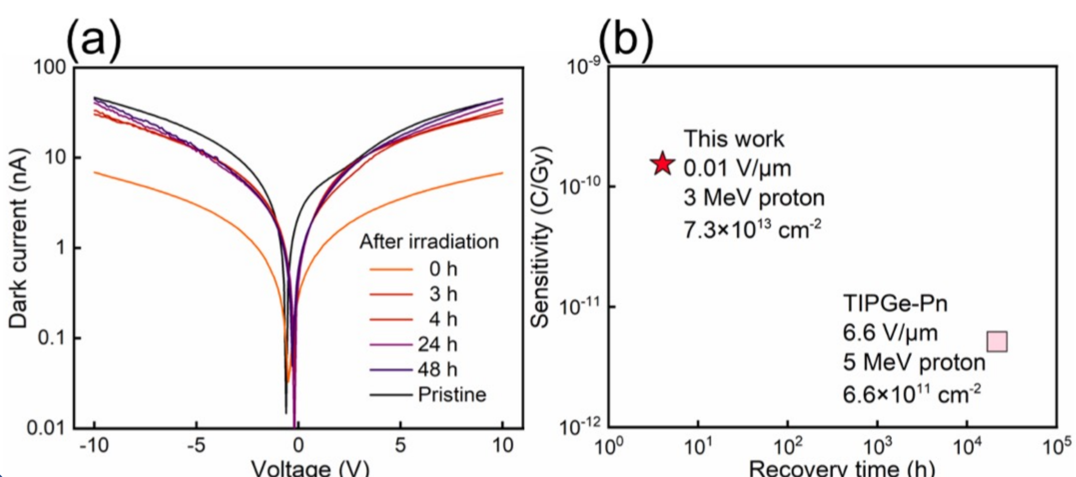




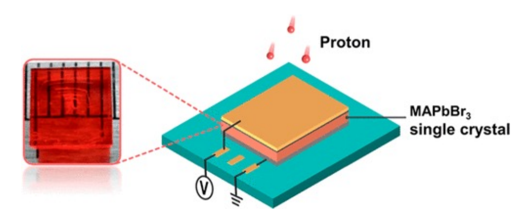


- Solar Cell thin perovskite films
- 68 MeV proton flux 10^{13} p/cm^2
- Damage thr. much larger than commercial silicon-cell
- **Self-healing** of perovskite
  - Displaced atoms migrate in lattice and passivates defects

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



Perovskite Radiation Hardness: State of Art

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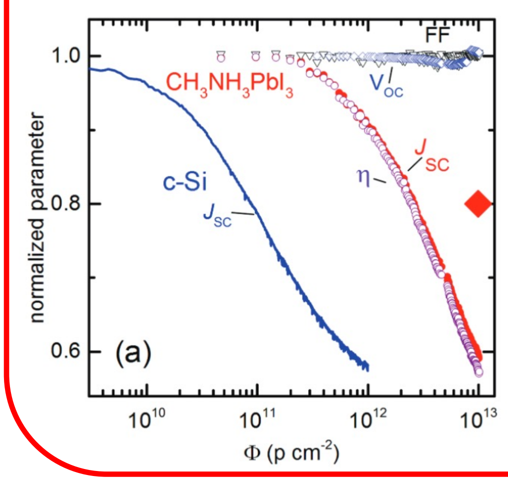
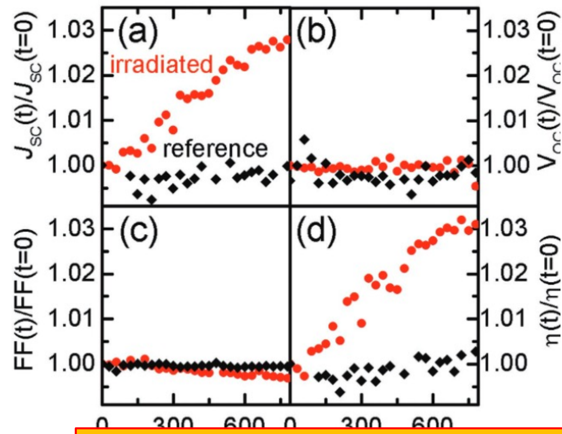
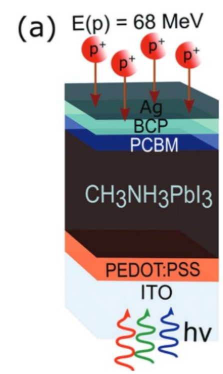






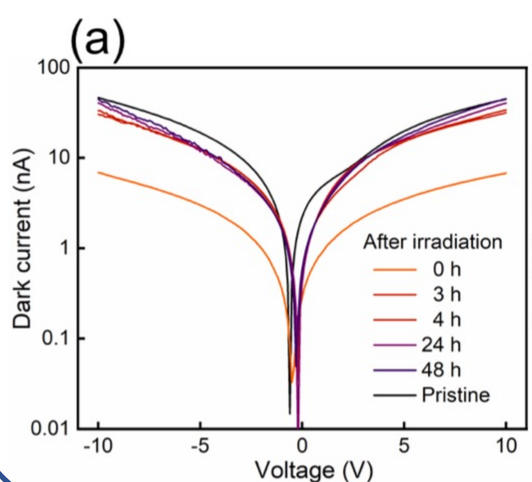
- Solar Cell thin perovskite films
- 68 MeV proton flux 10^{13} p/cm^2
- Damage thr. much larger than commercial silicon-cell
- **Self-healing** of perovskite
  - Displaced atoms migrate in lattice and passivates defects

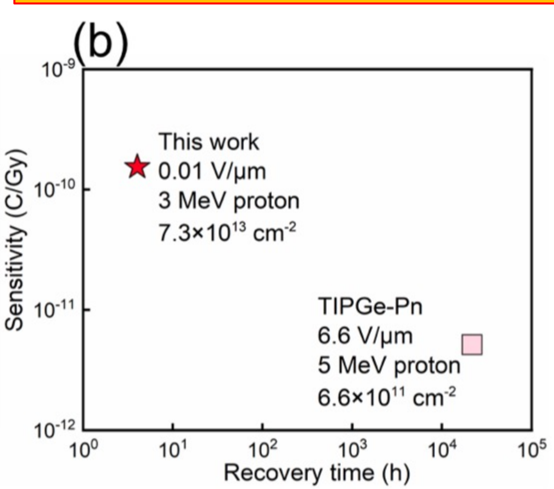
Not clear if self healing properties are still there with different thickness of the crystals, other topologies and energies of incident particles.

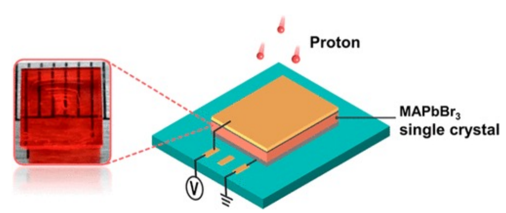
ACS Appl. Electron. Mate

10.1021/acsaelm.2c014

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







PEROV_XRAD: Second Goal & Synergy

- **Second Goal:** Study of the eventual presence of self-healing after radiation exposure
- Collaboration with ENEA Frascati
- Granted beam time at PARTREC (NL) within RADNEXT call

- Strong **synergies** with the funded PRIN project "HyPoSiCX: Hybrid Perovskite on Silicon CMOS X-ray Detectors”:
  - the feasibility of a hybrid X-ray detector structure combining a perovskite absorption layer and a CMOS silicon active layer

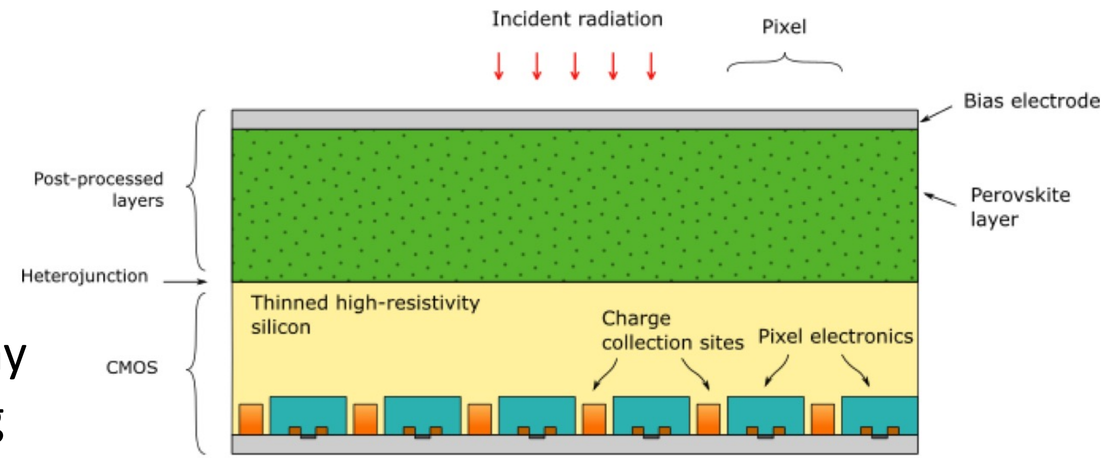


Figure 1. Simplified cross section of the proposed hybrid detector

L.Pancheri, M. Testa, I.Viola

SYNERGY: X-ray irradiation unit with ISO reference fields

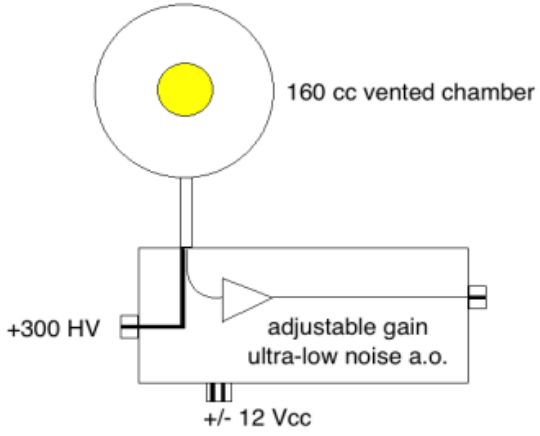
- Medical fluoroscopy tube 40-100 kV, 1 mA, recently established at LEMRAP
- In-beam dose rate up to Gy/h
- In order to have REPRODUCIBLE X spectra, the ISO reference qualities will be implemented. This means:
  - Using standardised voltage and filtration (ISO 4037)
  - Measuring the Dose in air with a spherical air-filled ion-chamber
  - Monitoring real-time the tube output with transmission air-filled air chamber
  - Measuring the energy distribution of the beams

What we have:

- X-ray equipment fully operational
- Filtrations
- A self-built spherical ion-chamber

What we need:

- Build the transmission chamber
- X-spectrometer CZT 0.5 cm^3 from RITEC
- Calibrate the spherical chamber



Financial request for 2024

	Scope	Type of request	Cost
LNF	• Chemicals • ArduSipm • Calibration ionization chamber • Xray spectrometer	Consumables	13 k
LNF	• Multi-channel analyser and digitalizer	Equipment	12.6 kE (offer)
LNF	• Bologna for calibration • Lecce for crystal growth	Travel	2 kE

- Possible variation of ~30%
- For 2025 10 kE expected

FTE

LNF	FTE	Activity
M. Testa (RN)	0.2	Coordination, testing
A. De Santis (RL)	0.3	Testing, Radiation hardness
G. Tinti	0.1	Testing Xrays
C. DiGIulio	0.1	BTF support, analysis from BTF
L. Foggetta	0.2	BTF support, analysis from BTF
N. Di Giovenale	0.1	BTF support, analysis from BTF
A. Russo	0.2	Xray tube characterization in LEMRAP lab

Futuro AR finanziato PRIN 100%

FTE

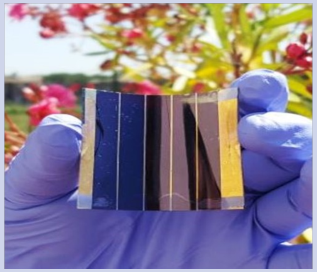
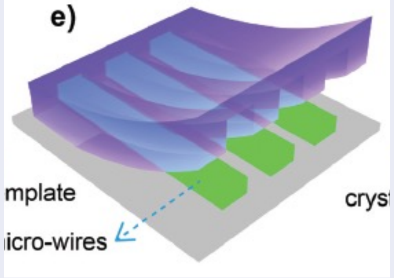
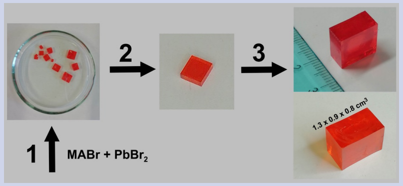
Associate LNF		FTE	Activity
CNR-NANOTEC	I. Viola	0.3	Crystal growth through microfluidics and dewetting technique, Photo-luminiscuence
CNR-NANOTEC	Mastria, Zizzari Bianco,	Tot 0.3	Crystal growth through microfluidics and dewetting technique
Dip. Ing. Elettr. Tor Vergata	F. Matteocci	0.2	Substrate pattern design and realization, contact deposition
Dip. Ing. Elettr. Tor Vergata	M. Auf der Maur	0.2	Modelling, data analysis
Dip. Chimica Universita' di Milano	S. Rizzato	0.2	Bulk crystal growth
CNR- Soft Matter	S. Sennato	0.1	Morphology, SEM, AFM
ENEA	Antonino Pietropaolo (ENEA)	0.2	Xray tube setup and calibration in LNF LEMRAP lab (Bedogni)

Stima richieste ai servizi 2024

		Activity
SEA	2MU	PCB design and realization, laboratory support, manual wire bonding
Officina	1MU	3D printing for mechanical supports

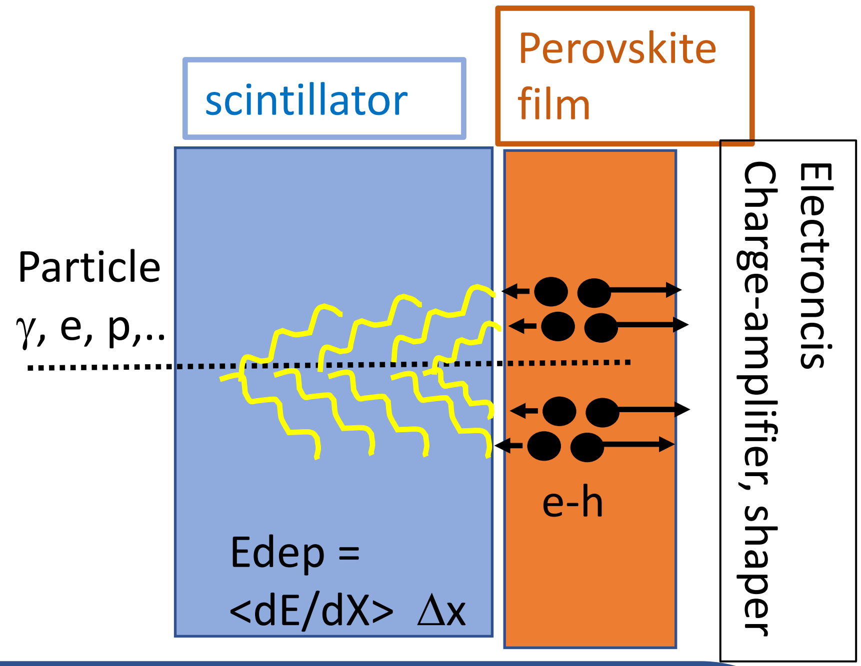
Backup

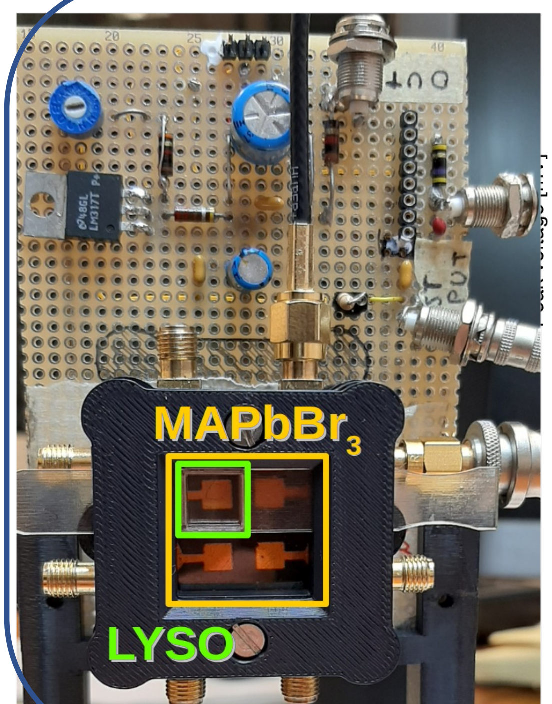
PEROV: Overview of CH_3PbBr_3 crystal growth

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

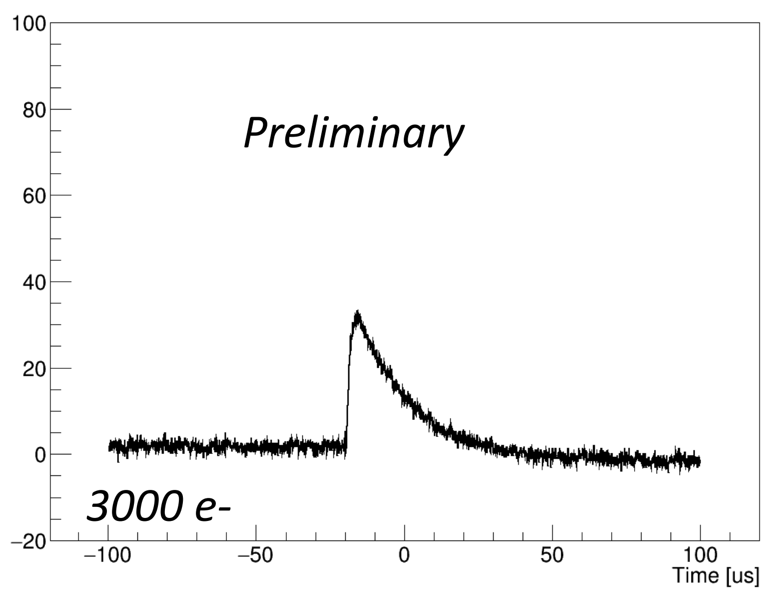
Film-based devices: application for radiation detection

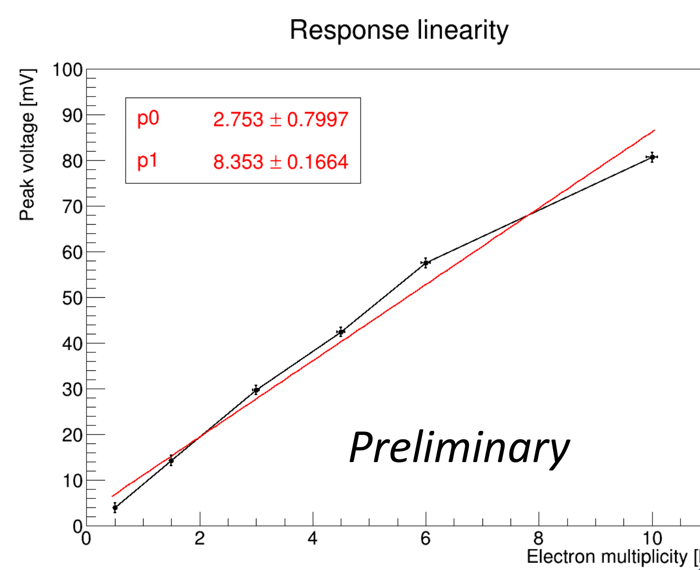
- Film devices can be used in combination with a scintillator (eg LYSO)
- Film not suitabble if sensitivity to single photon required (SiPM have gain ~10^6)
- If large areas need to be covered, light intesity is high and timing performance not stringent, films are good candidate





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

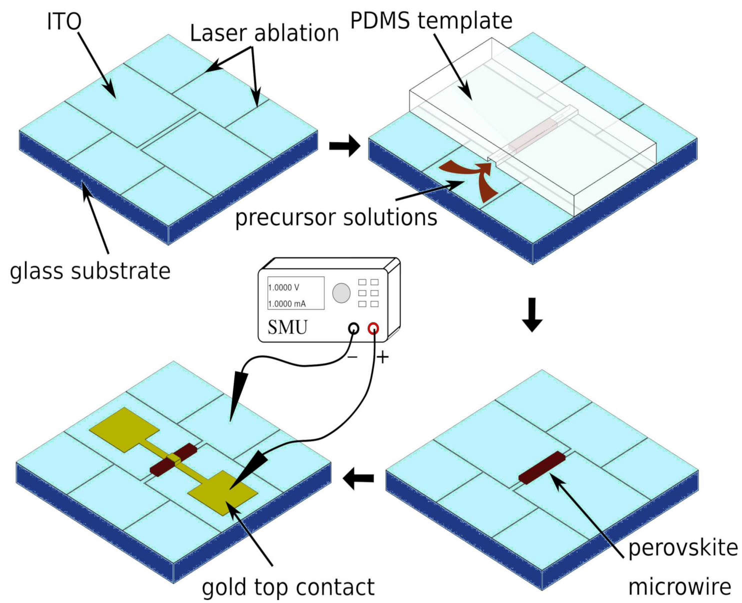




Micro-wires on patterned substrate

- 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

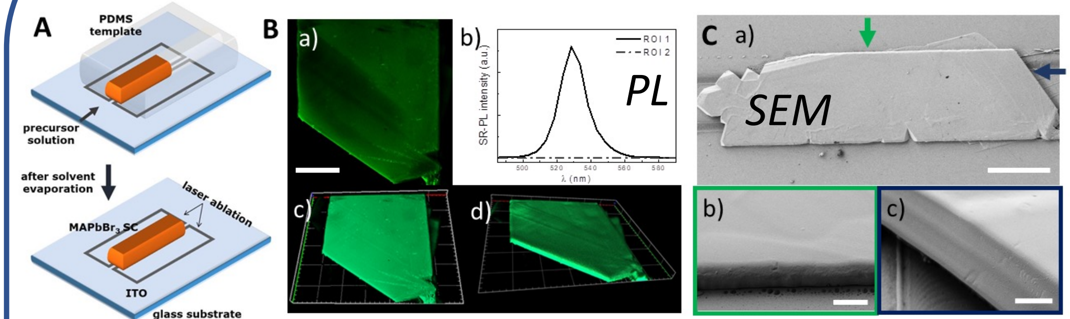
Fabrication steps



Advanced Material Technology

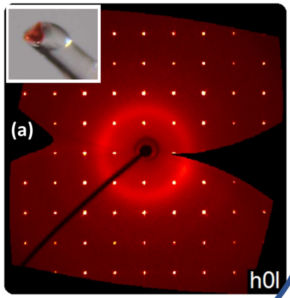
[10.1002/admt.202300023](https://doi.org/10.1002/admt.202300023)

Material Characterization

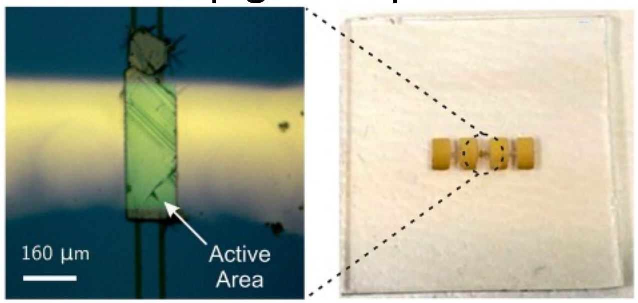


- homogeneous 3D crystalline microstructures, consistent with microchannel used for confinement
- typical photoluminescence of $MAPbBr_3$
- expected cubic phase with cell length a=5.927(2) Å

Xray diffraction



Top gold deposition

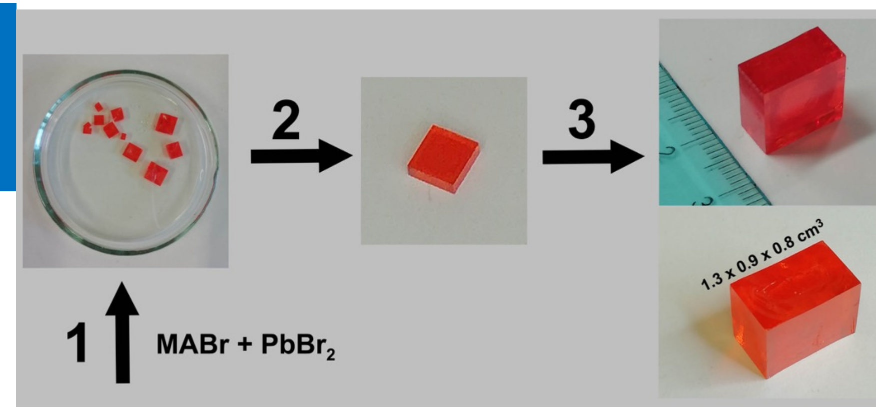


Final vertical device

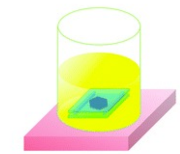
Deposited patent 102022000010469

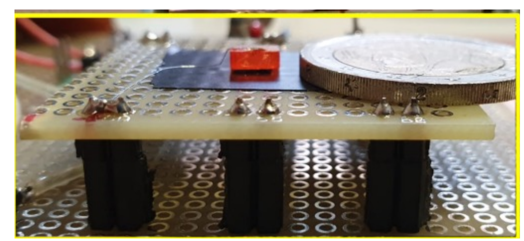
Large Single crystal

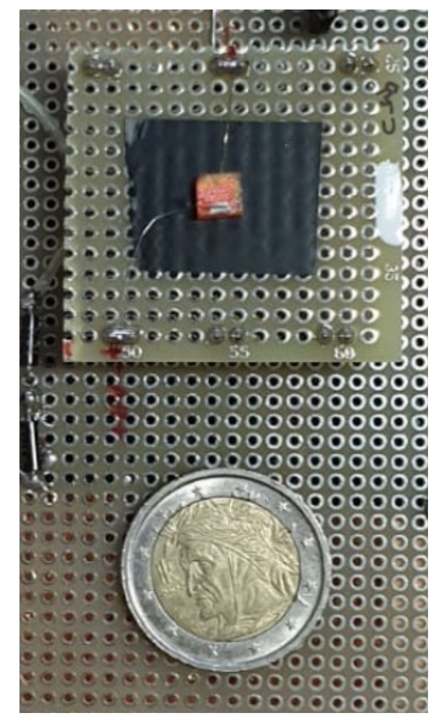
- Dimensions up to 1.0 x 1.5 cm^2 and up to 0.5 cm thick down to 300 µm by cutting the crystals along one of the {100}cubic planes
- Device realized with Indium Tin Oxide / $CH_3NH_3PbBr_3$ / Au
- Stable response measured
- Due to large thickness, suited for radiation detection (X-rays, charged particles)

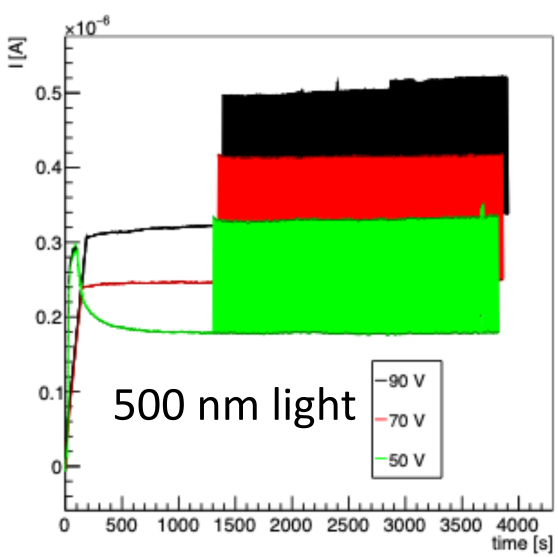


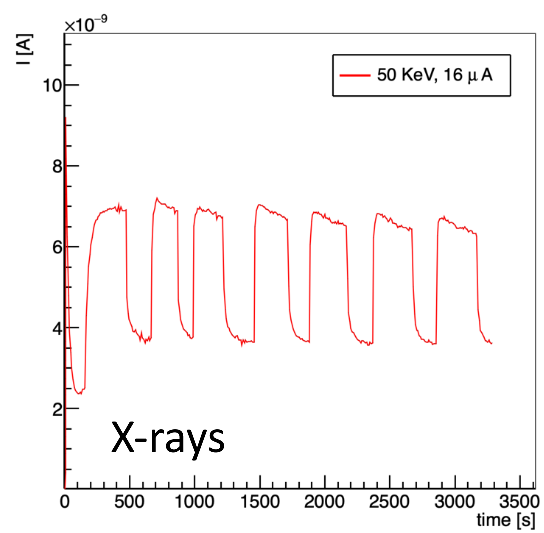
Seeding Techniques
Dip. Chimica Milano







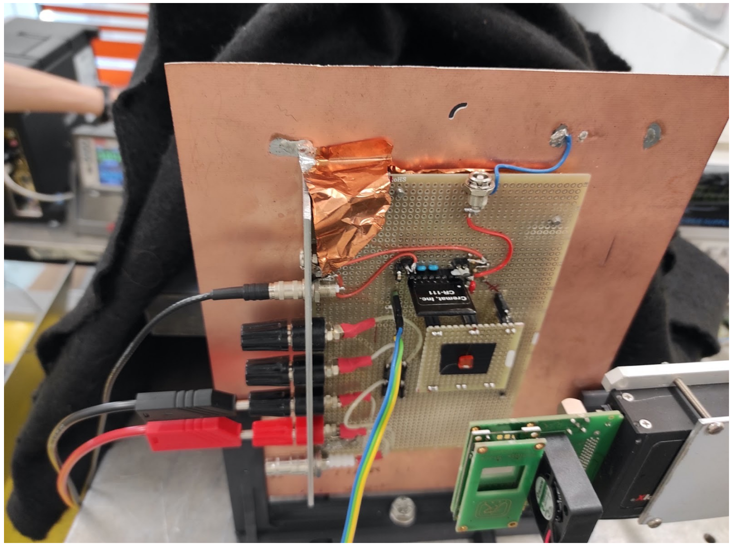


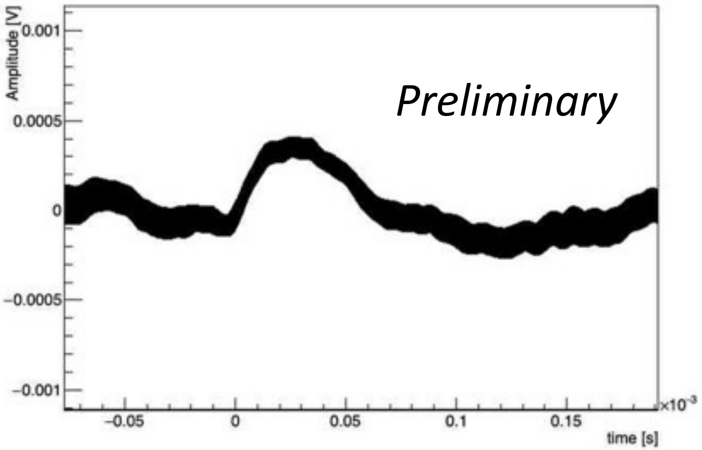


G. Tinti (LNF)

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

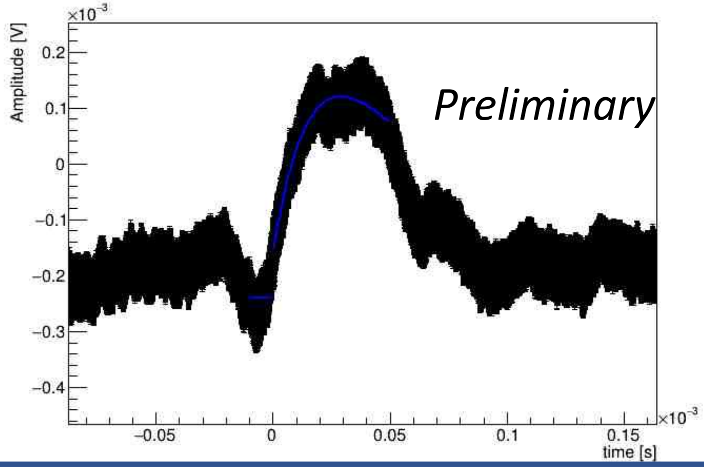




< Beam multplicity >= 1.4

- 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

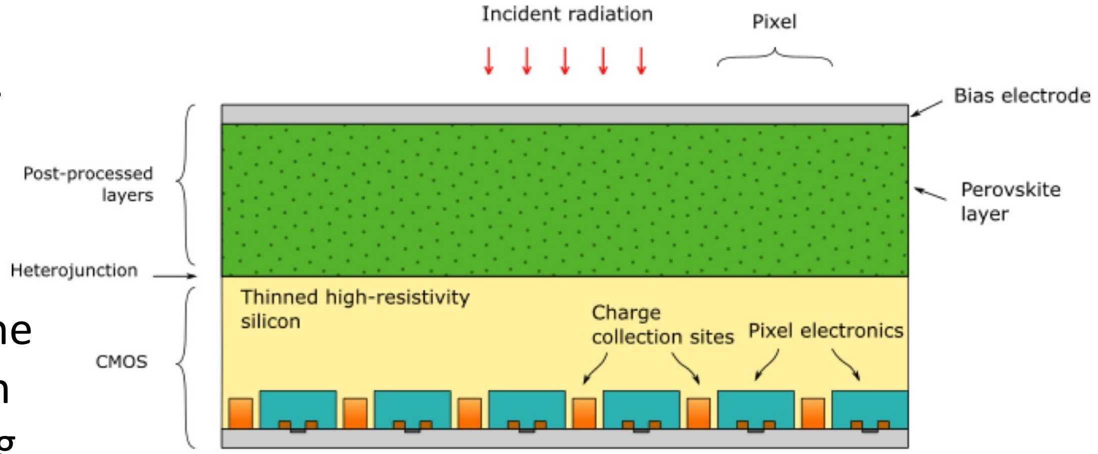
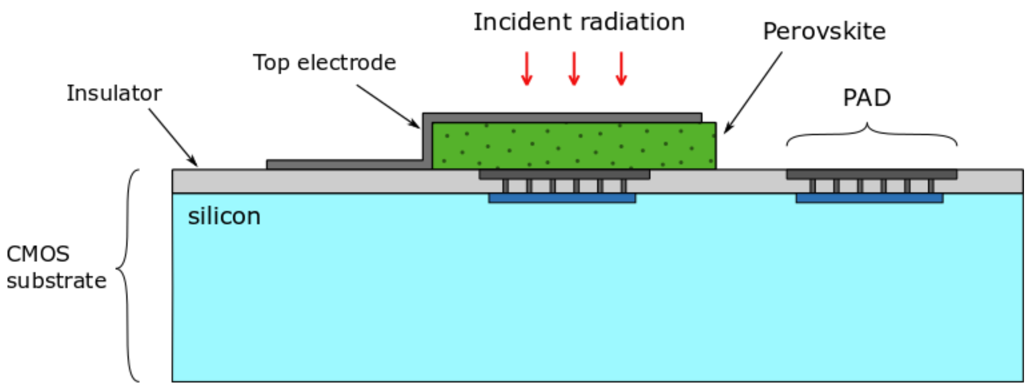


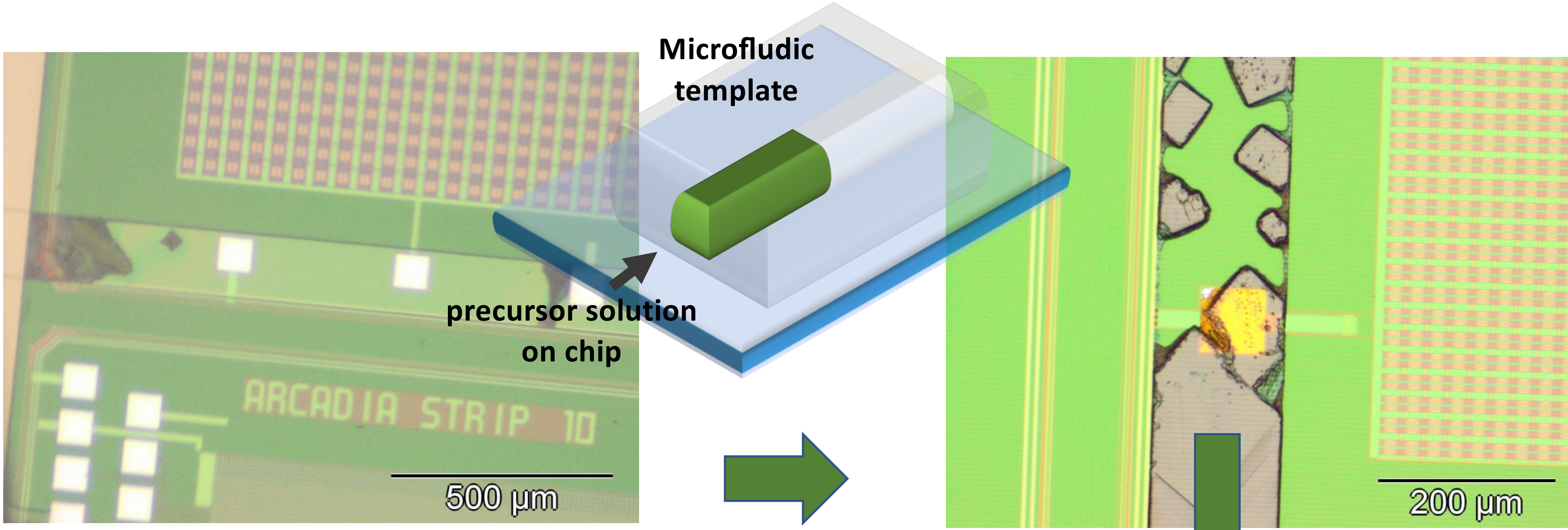
Figure 1. Simplified cross section of the proposed hybrid detector

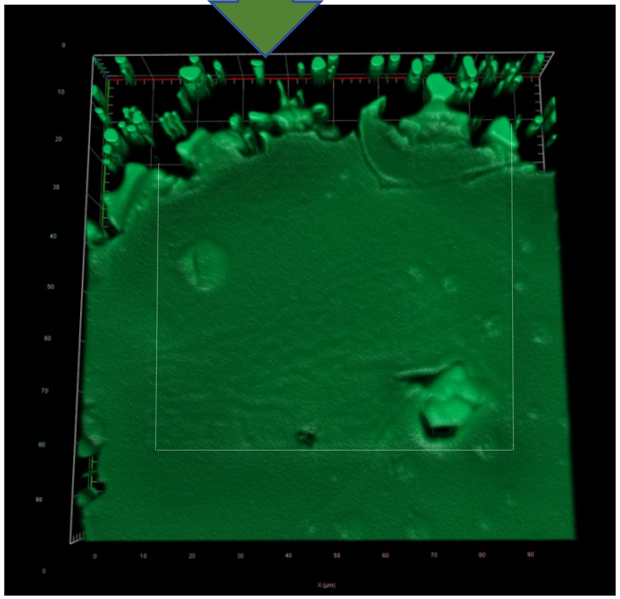
PRIN 2022 project granted
HyPoSiCX = Hybrid Perovskite on Silicon CMOS X-ray Detectors
L.Pancheri, M. Testa, I.Viola

- 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

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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