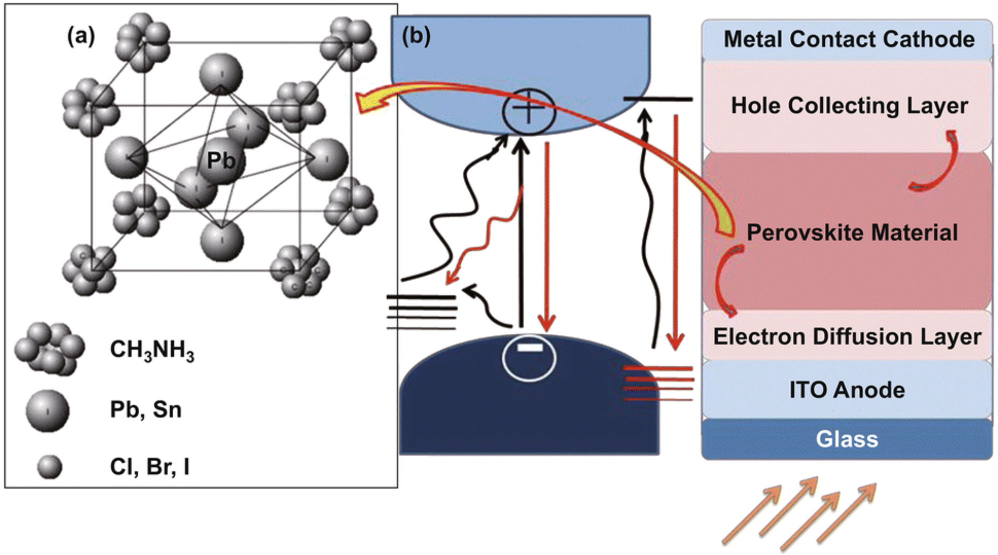
R&D for photodetectors based on Organo-Metal Halide Perovskite material

- LNF-INFN
- INFN Sezione di Roma 1 and Università di Roma "La Sapienza"
- Uniroma2 – Dipartimento Ingegneria Elettronica

Organo-Metal Halide Perovskite (OMHP)

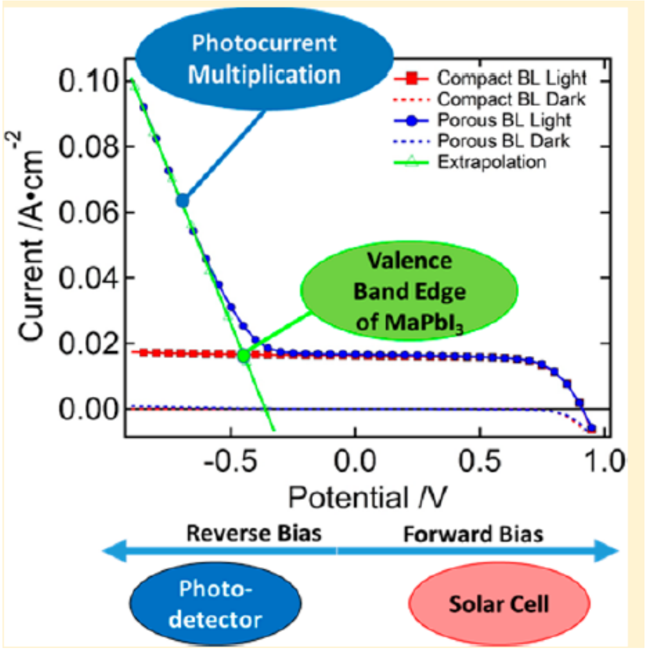
- **Organo Metal-Halide Perovskites** are a class of hybrid organic-inorganic semiconductor materials with a perovskite unit-cell structure **ABX_3** with
  - A = $CH_3NH_3^+$, B = metallic cation (Pb^{2+}), X = halide anions (Cl^-, Br^-, I^-)



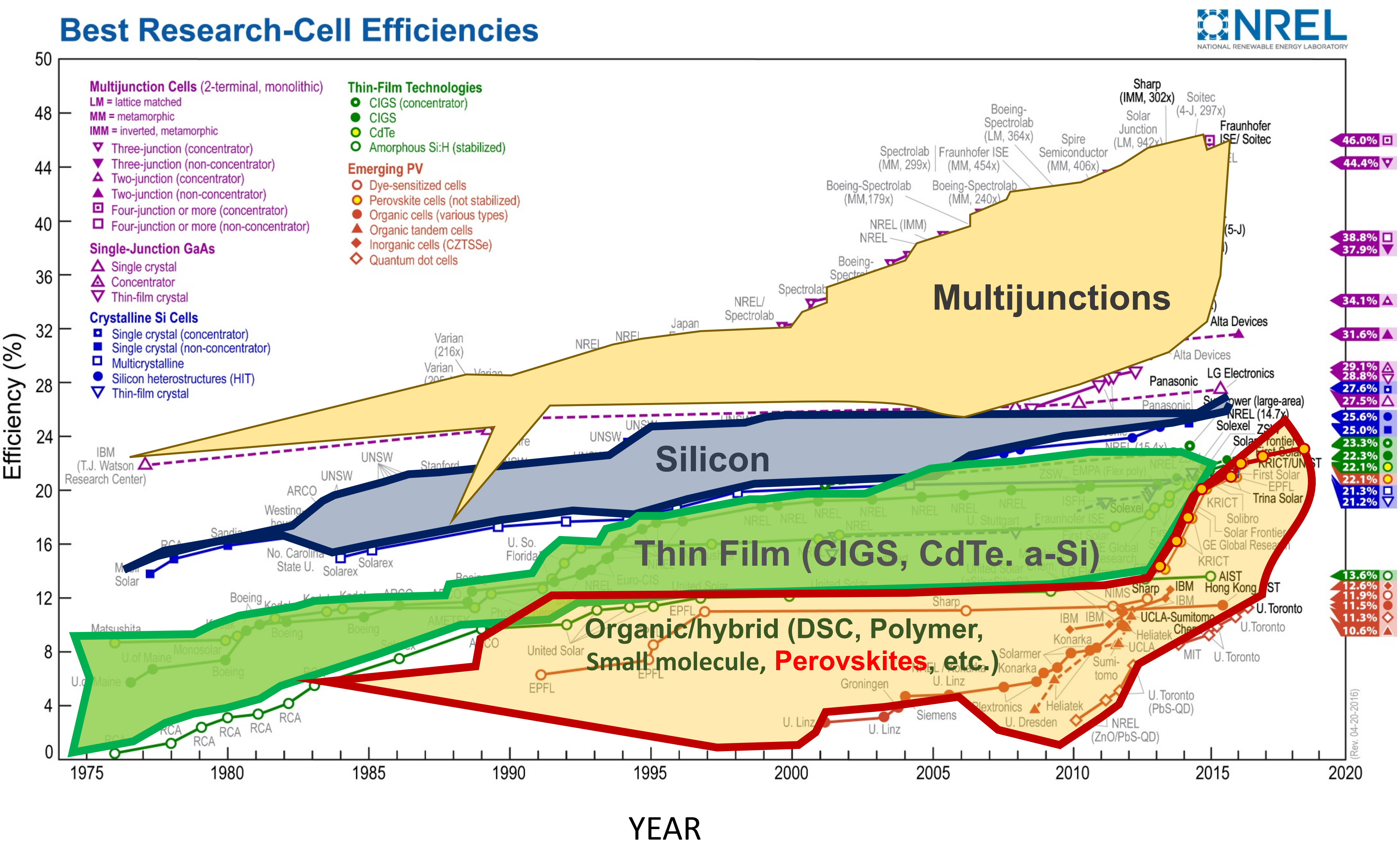
- opto-electronic properties combine **advantages from organic and inorganic semiconductors**

- intense R&D in the last ~8 years
- OMHP are emerging as
  - new generation photovoltaic
    - already performance comparable to commercial Si cells
  - **promising candidate as <u>large area and flexible</u> sensitive photodetectors**

  → **interest for HEP detectors !**



Rapid R&D as solar cells



Perov skite

profit of and influence this engineering R&D for application in particle detectors

OMHP 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:

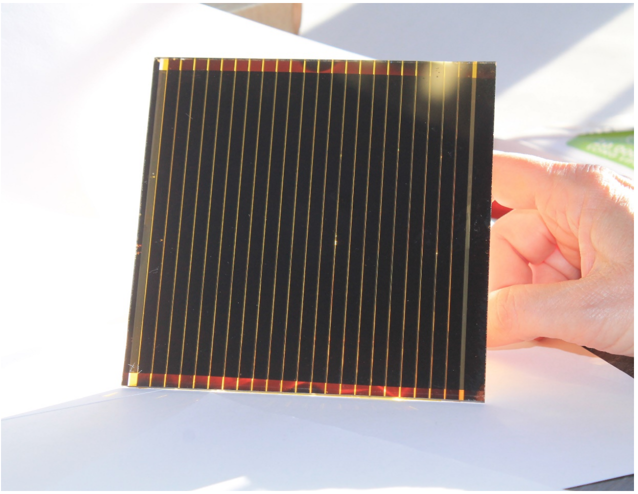
- **Ordered periodic crystal ⇒ band structure**
- **Delocalized Bloch states**
- **band transport ⇒ high mobility**
- Usually wafer based technology
- Costly, high temperature processes

		Silicon	**$CH_3NH_3PbI_3$**
Density		2.33 g/cm^3	4.15 g/cm^3
Band gap (eV)		1.12 (indirect)	1.5-1.6 (direct)
Mobility (cm^2/Vs)	electrons	1400	< 70
	holes	450	< 160
Absorption (cm^{-1})		< 10^4	> 4×10^4
Threshold energy for impact ionization (eV)		1.2	~2 (estimated)
Mean free path (nm)		≤ 100	~100 (theory)

OMHP advantages for particle detectors

Most attractive feature of OMHP files for detectors for particle physics experiments

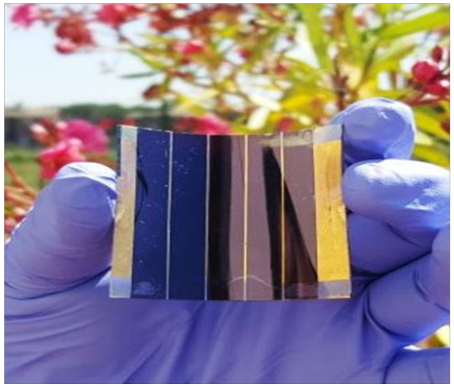
1. possibility to build large area device
2. flexible devices



Active Area=110cm^2
Efficiency=13.4%

large area device

Active Area = 12 cm^2,



Flexible device

Fabrication through solution processes

State of art OMHP photodetectors

- A lot of devices developed, with different contact interfaces
- Generally two classes developed:
  - Devices without gain, reasonable fast
  - Devices with gain slow

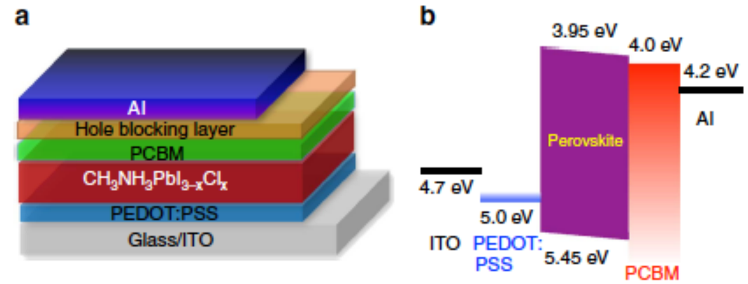
film device with O(ns) time resolution and gain not yet developed

Device architecture	R [A W^{-1}]	$D^* \times 10^{12}$ [Jones]	EQE [%]	On/off ratio	G [$\times 10^3$]	LDR [dB]	NEP [pW cm^{-2}]	t_{rise}/t_{decay} [ms]	Ref.
Pt/$MAPbCl_3$/Ti/Au	0.0469	0.012	–	–	–	–	–	24/62	[145]
FTO/ETL/ $MAPbI_3$/HTL/Au	620	–	2.4×10^5	–	2.4	–	–	100–200	[146]
ITO/HTL/perovskite/ETL/Al	–	7.4	≈90	–	–	94	0.6	1.2×10^{-4}	[92]
ITO/perovskite/MoO_3/Ag	242	–	–	–	0.489	85	0.18	0.01/0.006	[35]
Au/perovskite/Au	320	–	–	10^4	0.01–0.1	–	–	<0.01	[25]
ITO/HTL/perovskite/ETL/LiF/Al	–	>1	50–70	–	–	170	200	0.005/0.003	[147]
ITO/TiO_2/perovskite/P3HT/MoO_3/Ag	0.339	4.8	84	–	–	100	–	≈10^{-4}	[148]
ITO/perovskite/ITO	4×10^3	>10	–	–	>10	–	–	0.025	[97]
ITO/ $MAPbCl_3$/ITO	18	1	–	–	0.1	–	–	0.001	[95]
ITO/HTL/perovskite/ETL/Al	0.321	–	60	–	–	84	–	0.004/0.003	[78]
Pt/perovskite/Pt	–	0.13	–	10^4	–	–	–	90/20	[81]
ITO/perovskite/ITO	1640	10	10^5	–	2.5	70	–	0.03/0.02	[149]
Au/perovskite/Au	2.36	1.5	639	>10^3	–	–	–	<4	[150]
Au/perovskite/Au	10.33	–	–	10^5	–	–	–	0.02/0.01	[62]
Au/ $MAPbI_3$/Au	953	–	2.2×10^5	224	–	76	–	0.07/0.06	[100]
ITO/ $MAPbI_3$/ITO	3.49	–	1.2×10^3	324	–	–	–	<200	[80]
ITO/HTL/perovskite/ETL/Al	–	100	–	–	–	100	4.6	6×10^{-4}	[32]
Au/perovskite/Au	1.9×10^4	–	4.9×10^6	–	53	–	–	<450	[151]
Au/ $MAPbI_3$/Au	7.92			130				<200	[152]

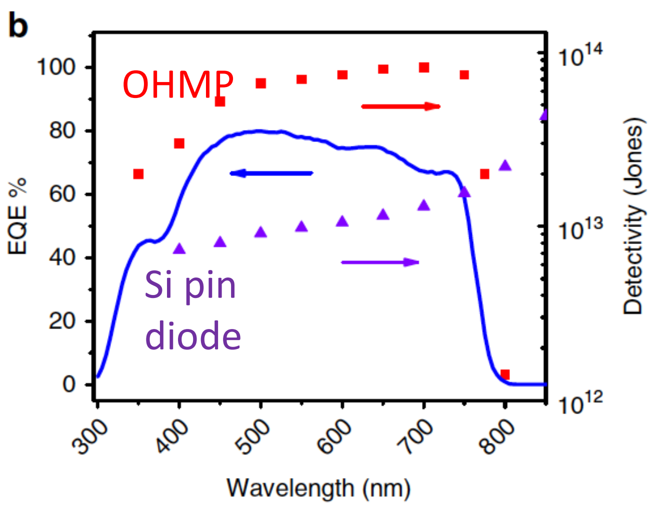
Jiachen Zhou and Jia Huang Adv. Sci. **2018**, *5*, 1700256

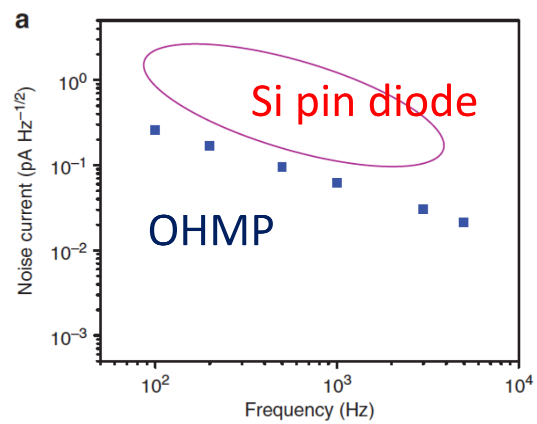
State of art: OMHP photodetector (no gain)

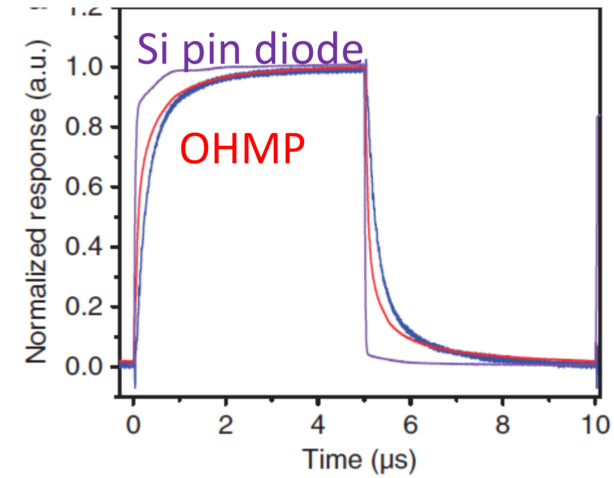
Dou, Y. Yang e al Nat. Commun. 2014, 5, 5404.



- Example of device with no gain: (*)
  - External quantum efficiency max 80%
  - ~180 ns rise/time decay with area = 0.01 cm ^{2}







Other devices with no gain

Structure	Bia [V]	D^* [cmW^{-1}Hz$^{1/2}$]	Rising/falling time	Stability	Ref.
PEDOT:PSS/$MAPbI_{3-x}Cl_x$/PCBM	0	3×10^{11}	180/160 ns	(*)	33
OTPD/$MAPbI_3$/PCBM/C_{60}	0	7.4×10^{12}	120 ns		37
PTAA/$MAPbI_3$/C_{60}/BCP	0	7.8×10^{12}	0.95 ns		41
PTAA/$MAPbBr_3$ SC/C_{60}/BCP	0	1.5×10^{13}	100 ns		39
PTAA/$MAPbI_3$ SC/C_{60}/BCP	0	1.5×10^{13}	295 ns		39
PTAA/PEIE/$CsPbIBr_2$/PCBM/BCP	0	9.7×10^{12}	20 ns	>2000 h	25
PTAA/PEIE/$CsPbBr_3$/PCBM/BCP	0	6.0×10^{12}	62 ns	>2000 h	25

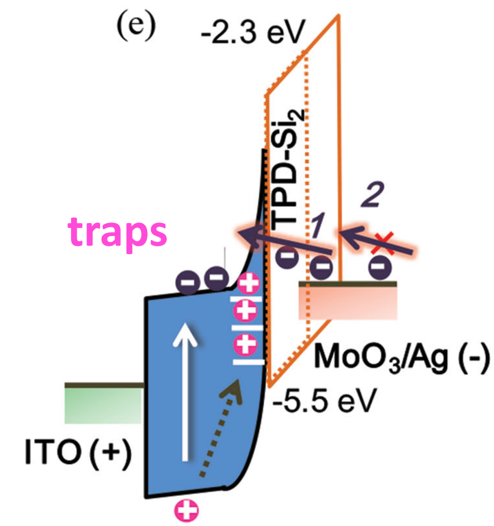
State of art: OMHP photodetector (gain)

- So far, photoconductive gain observed:
  - under illumination, there are charges injected by the electrodes under an applied bias
    - Schottky junction → ohmic contact

  - the underlying mechanisms are still not completely understood.
  - proposed so far is the trap-assisted charge-tunneling:
    - Traps induces band bending in the perovskite layer close to one of the electrodes

    →Reducing the Schottky junction thickness

    →allowing the injection of the opposite charges under reverse bias.

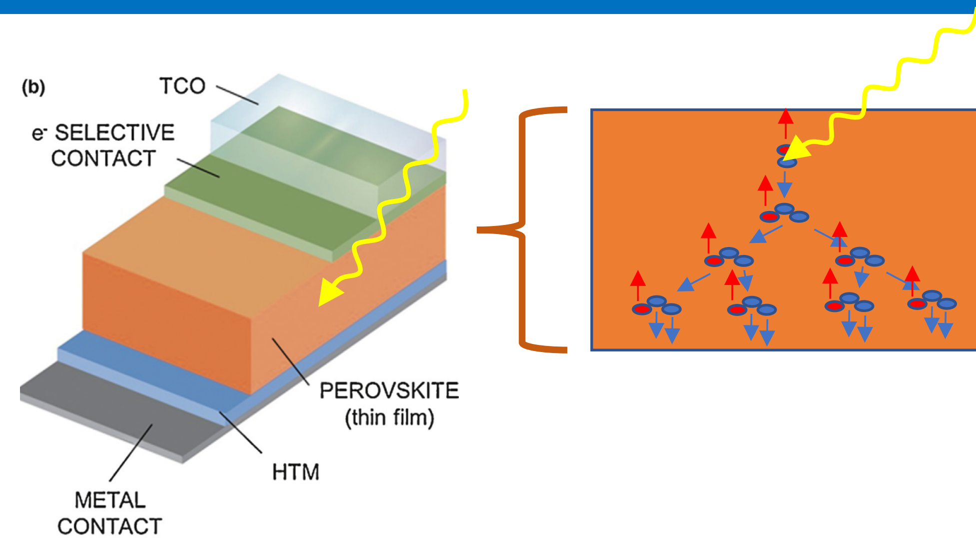


Examples: ITO/$MAPbI_3$/MoO 3 /Ag

- Gain ~490
- $\tau_{rise/decay}$ ~10 us ☹
- Area 6 mm^2 .

Proposed R&D (1)

Goal: understand if **internal avalanche multiplication** is possibile in OHMP



- not yet observed so far
- no first principle preventing it
- expected to be a fast process

Methodology

- purchase/fabricate single OHMP mono crystal thick 10μm – 1mm
  - thickness not limited by purity
  - no gain related to electronic traps states in films

- measure gain vs Vbias with led
- if gain observed, measure gain in OMHP films
- characterization with radioactive sources

Proposed Study (2): radiation hardness

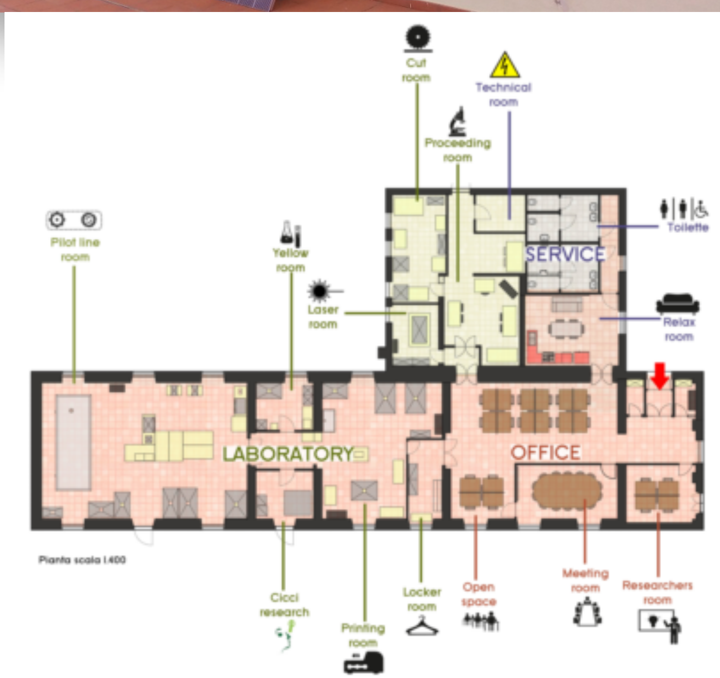
Goal:
study radiation hardness under synchrotron radiation and X-rays exposure

Measurements before/after radiation
- I-V characteristics in darkness and under illumination
- photo-current vs dose-rate
- time-resolved photocurrent under illumination

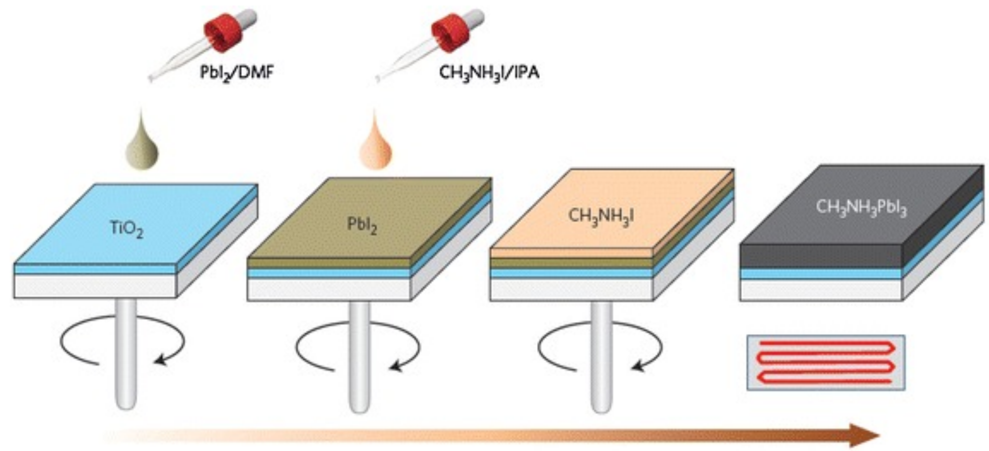
State of art:
- radiation hardness studied for applications in solar cells needed for spaceships or satellites
- Irradiations with electrons or protons and have shown a good tolerance of perovskite cells
- missing systematic study for particle physics applications

CHOSE Lab, Roma2 Dip Eng. Elettr.

- Devices will be fabricated in the CHOSE laboratories of Roma2 Electronic Engineering Dep.
- **No cost** for film production (only consumables)

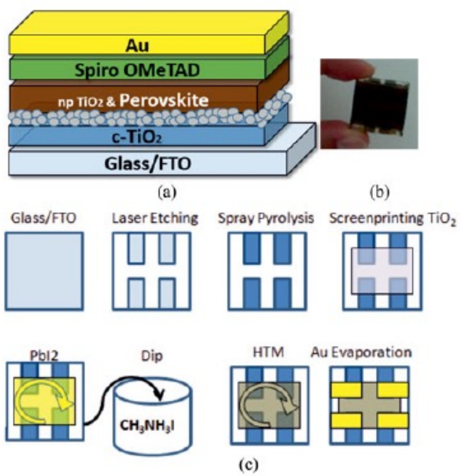


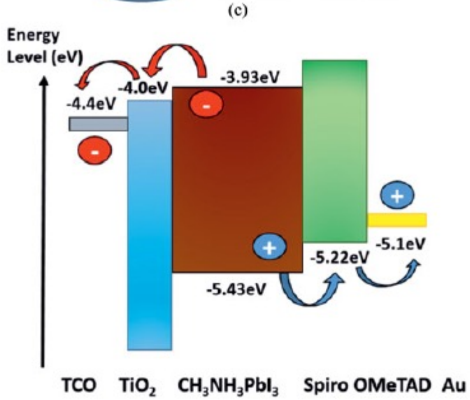
Spin coating technique

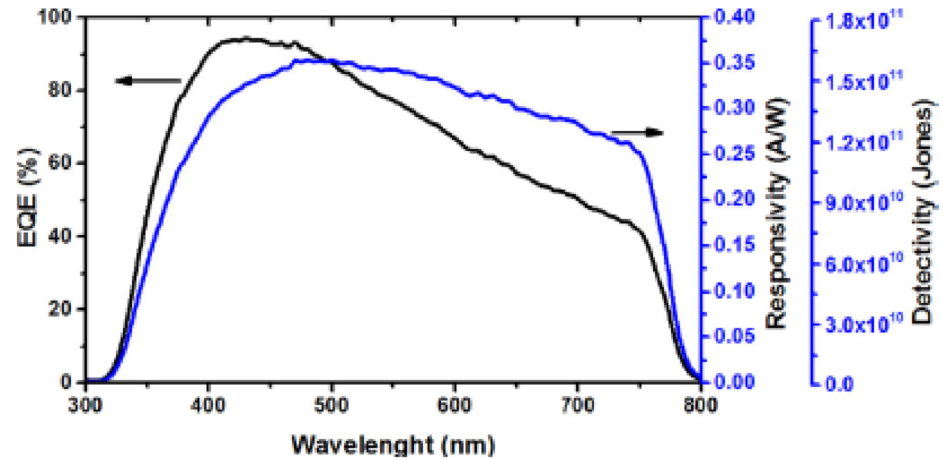


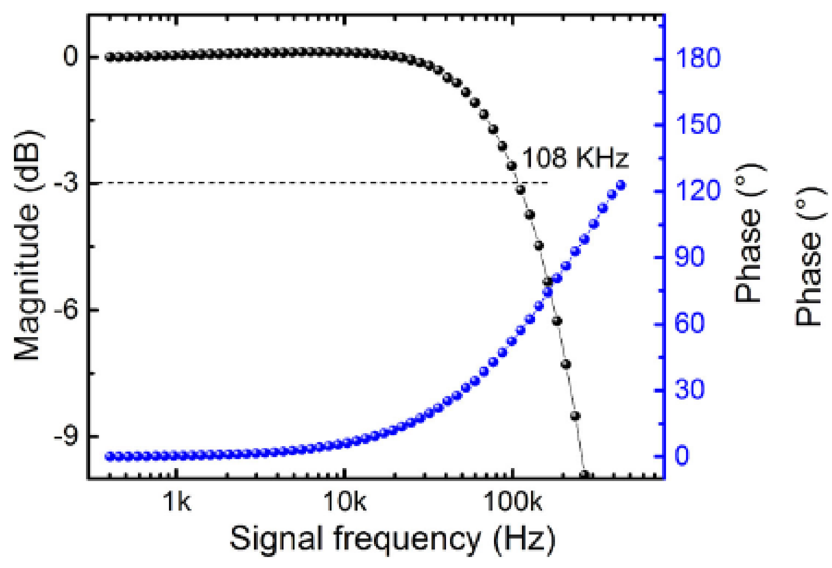
Spin coater

Already experience with fabrication of OMHP photodetectors









S. Casaluci et al. IEEE TRANSACTIONS ON NANOTECHNOLOGY, VOL. 15, NO. 2, MARCH 2016

Facilities and workflow

	Facilities/Services	Activity
Roma2	CHOSE laboratories	Fabrication of OMHP films and characterization with led
		Theory expertise in OMHP
Roma1	Lab Segre' Equipment for test with led/lase/Radioactive sources	Characterization of devices with radioactive sources
LNF	DAFNE, X rays tubes	Radiation hardness

Man power

	FTE (%)	Note
M. Testa LNF	0.15	Measurements, Coordination
A. De Santis LNF	0.2	Radiation hardness
C. Rovelli Roma1	0.1	Measurement with sources, exp setup
S. Morganti Roma1	0.1	Measurement with sources, exp setup
F. Matteocci Roma2 – Dip Ing Elettronica (*)	0.1	Fabrication, Characterization
M. Auf der Maur Roma2 – Dip Ing Elettronica (*)	0.2	Simulation, Characterization
A. di Carlo Roma2 – Dip Ing Elettronica (*)	0.1	Theory, Supervision

(*) associazione a LNF in corso

Financial request for 1 year

	Scope	equipment	Cost
Roma2 (associati a LNF)	• Purchase/Fabrication of single OHMP crystal • Fabrication of OMHP films	Consumables	2 kE
Roma1	Characterization of devices with radioactive sources	Electronics procurement -transimpedance amplifier	2kE
LNF	Radiation hardness test at DAFNE	Adjustable mechanical support for device	1kE

Backup

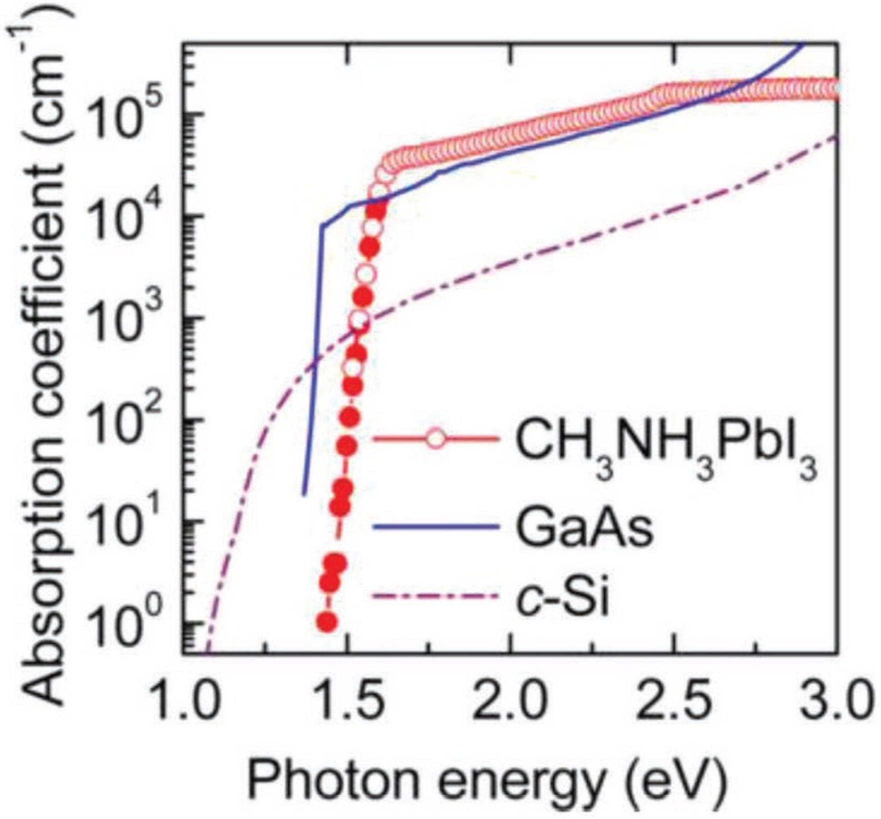
State of art: Silicon based photodetectors

PDG2018: "**Except for applications where coverage of very large areas** or dynamic range is required, solid-state detectors are proving to be the better choice."

Type	λ (nm)	$\epsilon_Q\,\epsilon_C$	Gain	Risetime (ns)	Area (mm^2)	1-p.e noise (Hz)	HV (V)	Price (USD)
APD	300–1700	$\sim$0.7	10–10^8	$O(1)$	10–10^3	1–10^3	400–1400	$O(100)$
PPD	320–900	0.15–0.3	10^5–10^6	~ 1	1–10	$O(10^6)$	30–60	$O(100)$

Example: APD used in CMS crystal Gain=50

Absorption coefficient



State of art: OMHP photodetector (gain)

- So far, photoconductive gain observed:
  - under illumination, charges injected by the electrodes under an applied bias, besides the photogenerated charges.
- the underlying mechanisms are still not completely understood.
  - proposed so far: the trap-assisted charge-tunneling
- This gain is associated to slow time performance O(ms)

Matreial	Bia [V]	D^* [cmW^{-1}Hz$^{1/2}$]	Rising/falling time	*EQE*	Ref.
$FA_{0.85}Cs_{0.15}PbI_3$ film	0	2.7×10^{13}	45/91 ns		67
$MAPbCl_3$ single crystals	15	1.2×10^{10}	24/62 ms		54
$MAPbI_3$ single crystals	3		74/58 μs	595%	55
$MAPbI_3$ nanowires	1	2.0×10^{13}	<0.1 ms		58
$MAPbI_3$ film	3		100/100 ms	1190%	8
$MAPbCl_3$ single crystals	5	10^{12}	1 ms		27
$CsPbBr_3$ nanocrystals	3	6.1×10^{10}	1.8/1 ms		45
$CsPbI_3$ nanocrystals	1		24/29 ms		28
$MAPbBr_{3-x}I_x$ film	10		20 μs		7
$CsPbBr_3$ nanoparticles	2	1.68×10^9	0.2/1.2 ms		44
$CsPb(Br/I)_3$ nanorod networks	8		680/660 ms		59
$CsPbBr_3$ nanosheets	5		19/25 μs	54%	46
$CsPbBr_3$ thin films	6	9×10^{12}	430/318 μs	16 700%	43
$CsPbBr_3$ nanoarrays	5		21.5/23.4 μs		3
$CsPbI_3$ nanoarrays	1	1.57×10^{12}	292/234 ms	16%	60
$CsPbBr_3$ nanosheets	10		16/380 μs	7488%	29
$CsPbBr_3$ nanoplatelets	1.5	7.5×10^{12}	0.6/0.9 ms	10^4%	56
$CsPbBr_3$ bulk single crystals	0	1.7×10^{11}	230/60 μs		49
$CsPbBr_3$ bulk single crystals	5		69/261 μs	460%	47
$CsPbBr_3$ microcrystals	3	1×10^{13}	0.5/1.6 ms	2×10^7%	50
$CsPbBr_3$ nanowires	3		252/300 μs		62
$CsPbI_3$ nanorods	2	5.17×10^{13}	50/150 μs	9×10^5%	63

Electronic 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]

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

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