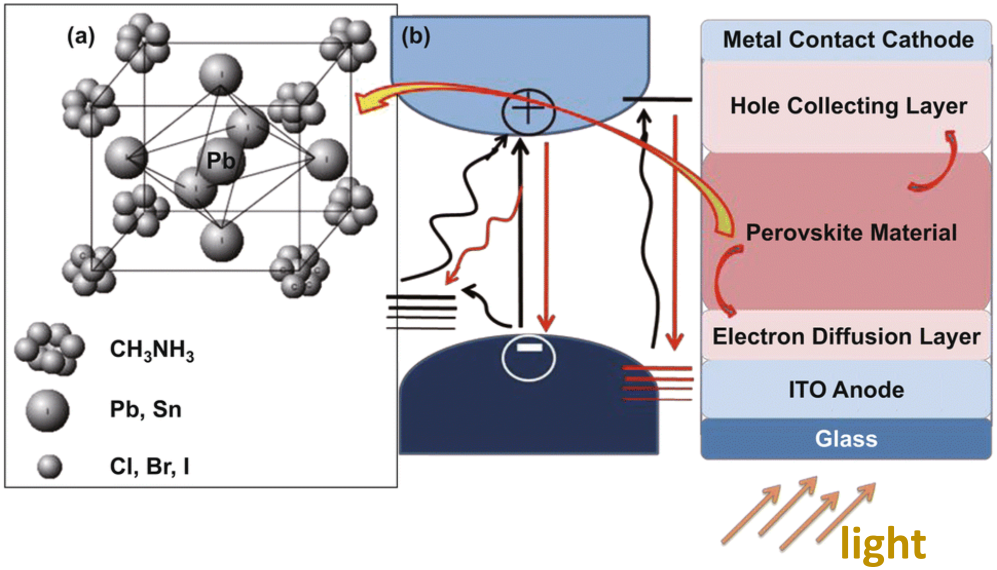
PEROV

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

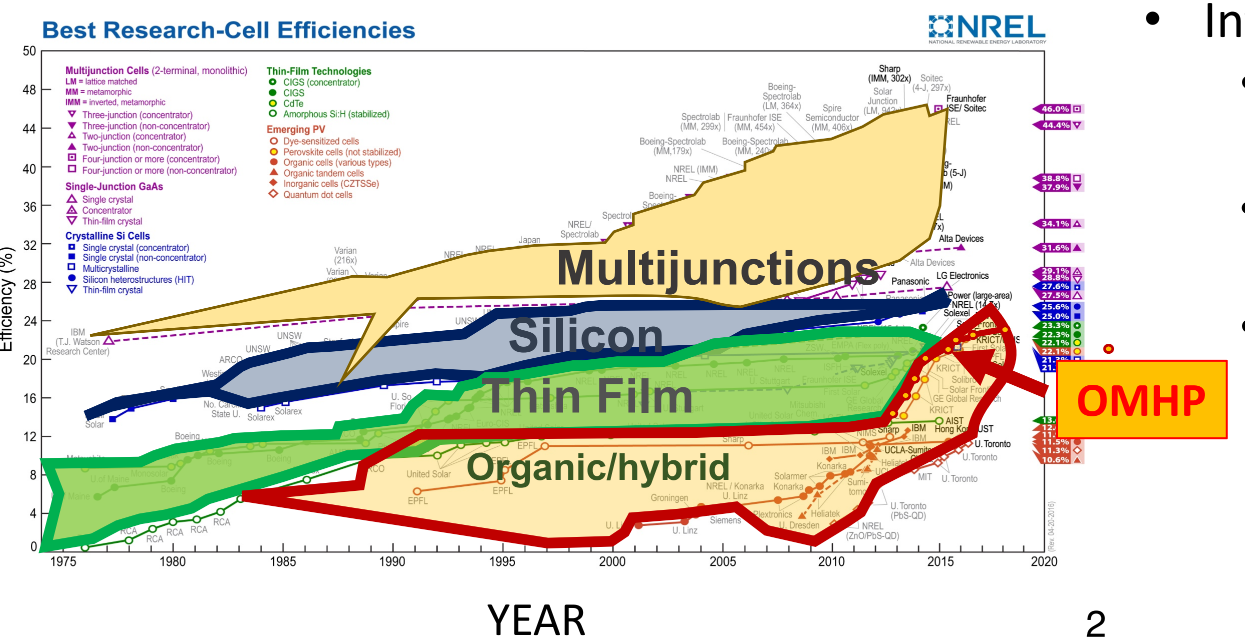
- LNF-INFN (Resp. Naz.)
- INFN Sezione di Roma 1 and Università di Roma "La Sapienza"
- Uniroma2 – Dipartimento Ingegneria Elettronica
- UniMi– Dipartimento Chimica
- CNR – NanoTec,ISR,ISM

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 ~9 years
  - OMHP are emerging as new generation photovoltaic material
  - performance comparable to commercial Si cells
  - **promising candidate as <u>large area and flexible</u> sensitive photodetectors**

  → **interest for HEP 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	$CH_3NH_3Pb(I,Br)_3$
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)

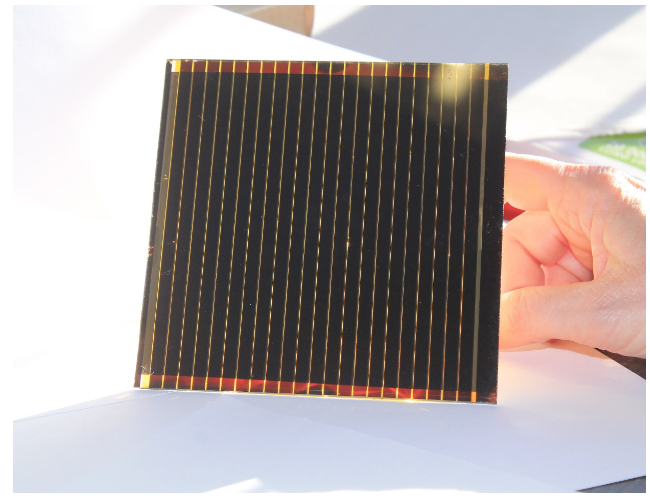
- OHMP band gap tunable changing halide (I,Br,Cl)
- OMHP contain highly mobile defects and have instabilities issues

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
3. thinner sensors wrt silicon-based sensors, due to higher Z

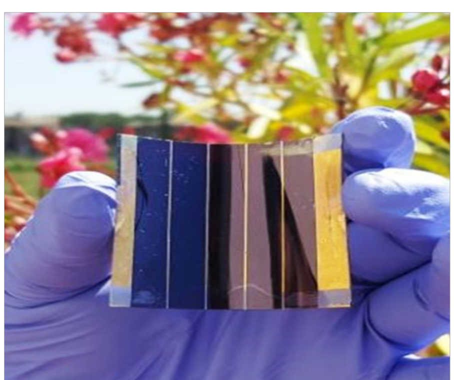
Interesting for calorimetry, neutrino/dark matter experiments



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

- Several devices developed, with different contact interfaces and architectures
- Two classes developed:
  - Devices without gain, reasonably fast
  - Devices with gain, slow
    - the underlying mechanisms are still not completely understood.
    - proposed so far is the trap-assisted charge-tunneling

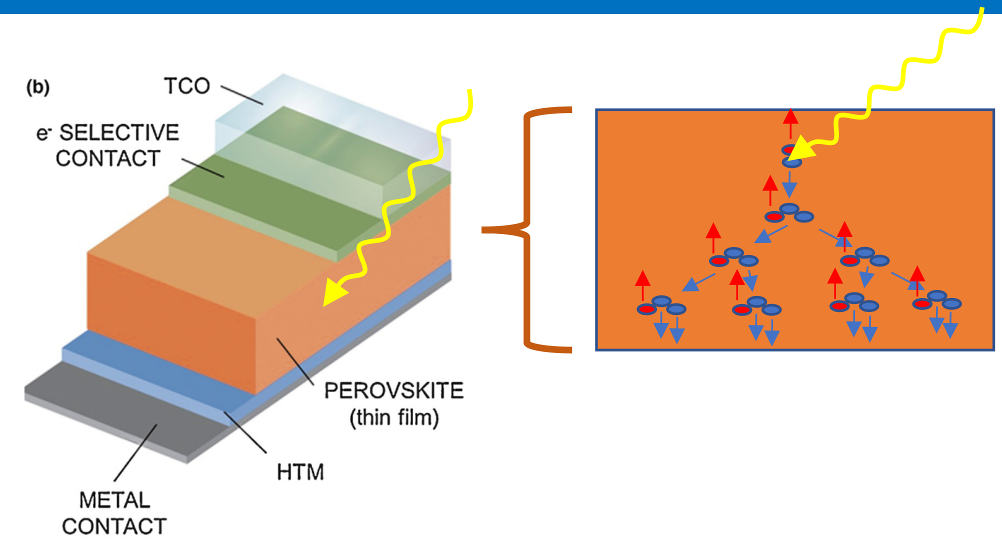
film device with O(ns) time resolution and gain not yet developed

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]

Adv. Sci. **2018**, *5*, 1700256

PEROV Goals in 2020 (Dot Gr5)

1) **Observation or exclusion of internal avalanche multiplication** in OMHPs



- not yet observed so far
- no first principle preventing it
- expected to be a fast process
- may be masked by mobile ions

- **Methodology**
  - purchase/fabricate single OMHP mono crystals of thickness 1μm – 10 um
    - thickness not limited by purity
    - Less defects / traps states compared to films
  - measure gain vs Vbias with led
  - compare with gain in OMHP films

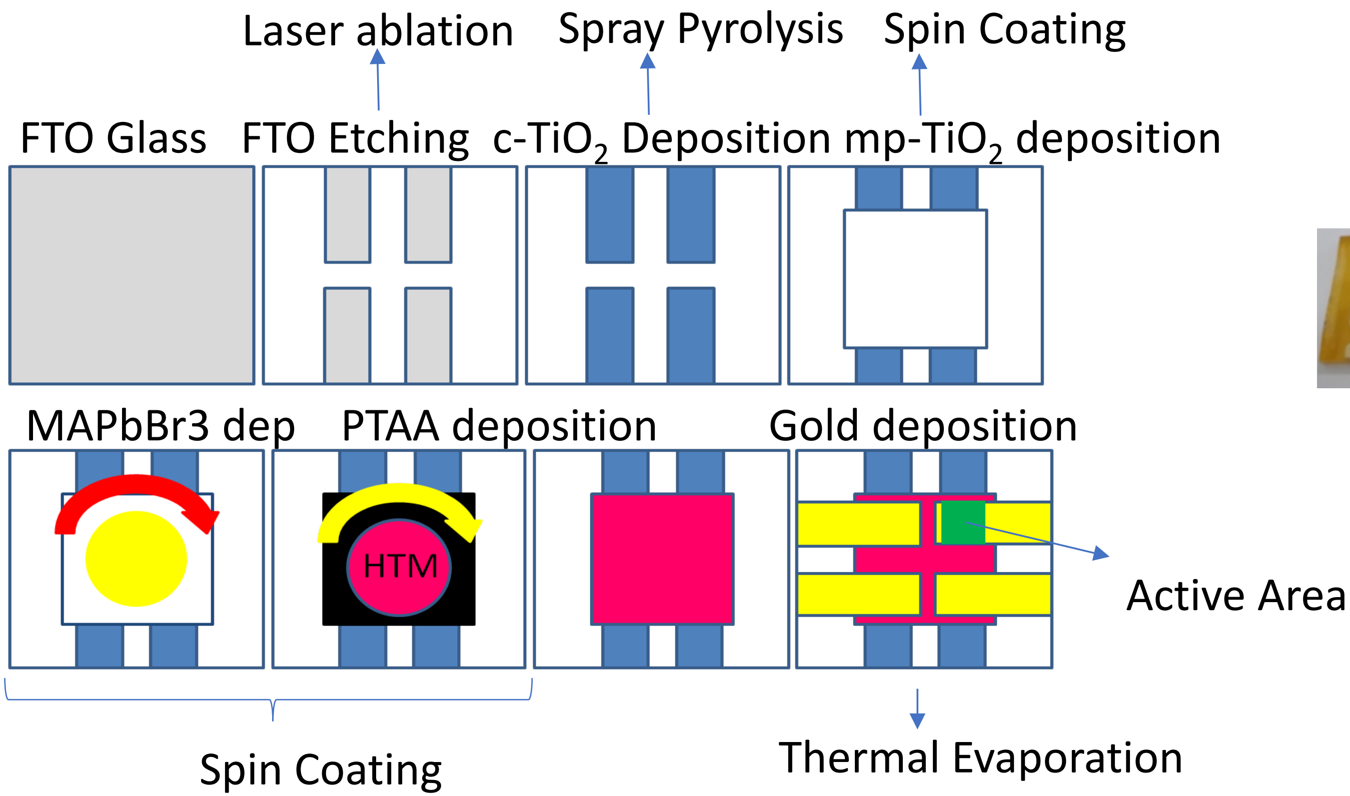
2) **Radiation hardness** under synchrotron radiation at DAFNE

Current Status

1. Film-based devices:
   - fabrication, characterization, simulation ✓
2. Single crystals devices:
   - started collaboration with Dip. Chimica of Milano and CNR NANOTEC ✓
     - will join PEROV in 2021
     - first test on single crystals fabrication
3. Radiation Hardness studies not yet done ✓

- Severe limitations from covid-19
  - all labs closed during lockdown
  - currently not all labs restarted. Generally limited availability

Film-based devices production

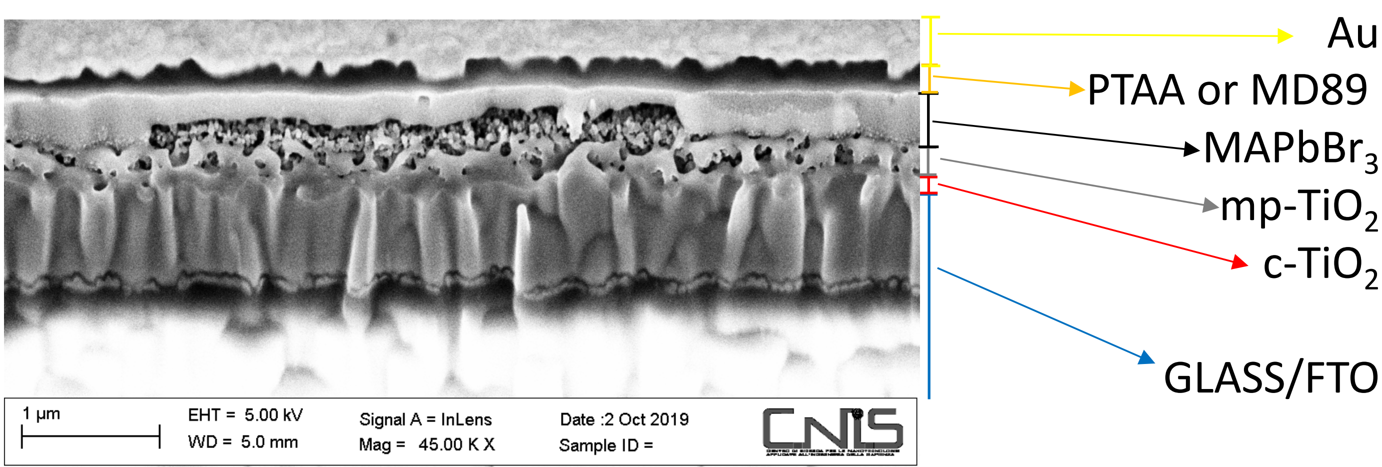


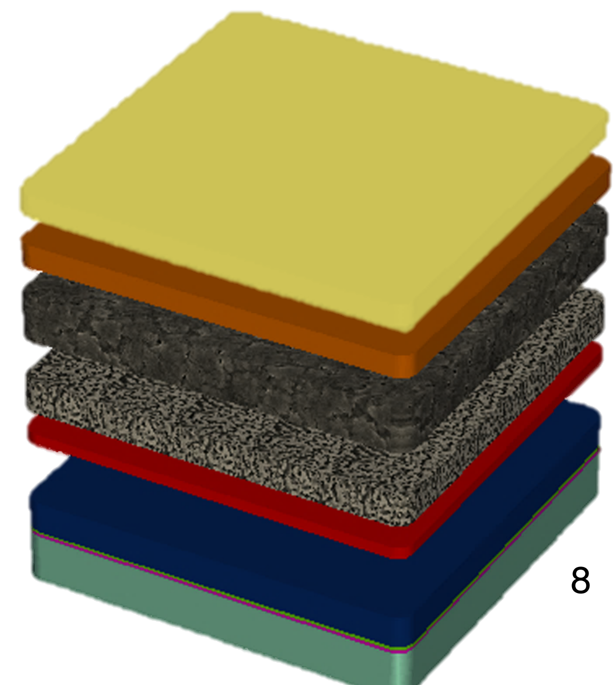
Ready devices with different Optical Band-Gap

CHOSE lab
Dip Ing. Elettronica RM2

Thin film deposition of MAPbBr3 perovskite (300nm)

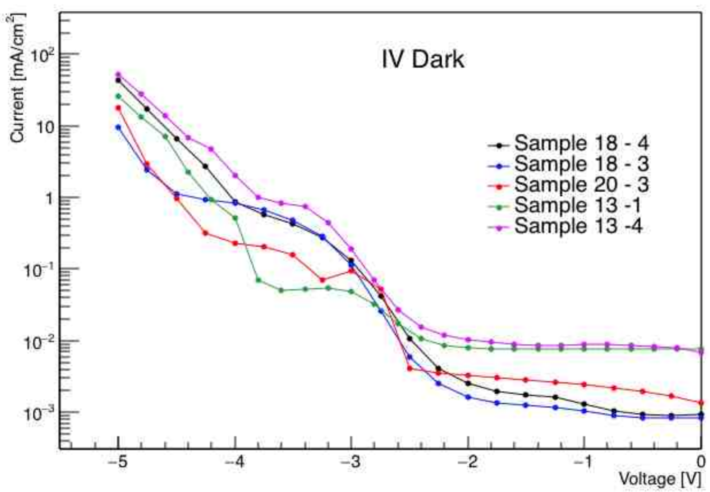
Materials:

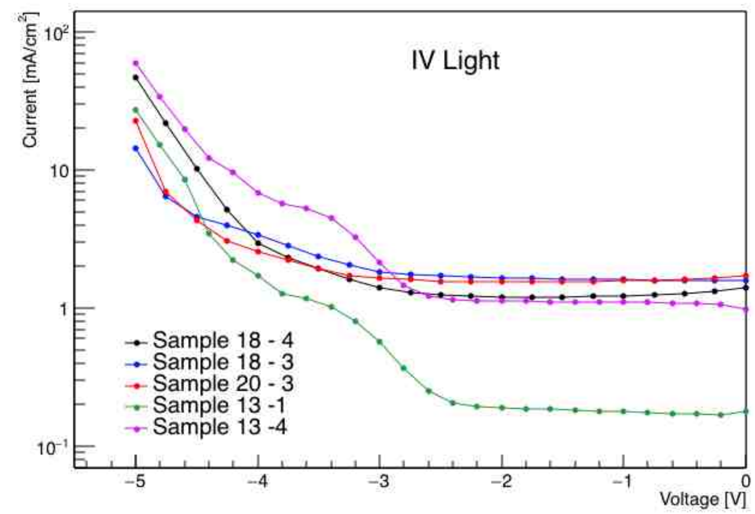




IV and gain measurement on 300nm films

Setup: pulsed LED
varying V_{bias}





- Gain observed in a fraction of devices
  - Not dependent on different hole transport layers (HTL), PTAA or MD89

- Significant differences among devices and pixels on the same devices
  - SEM and AFM to understand morphological differences among devices

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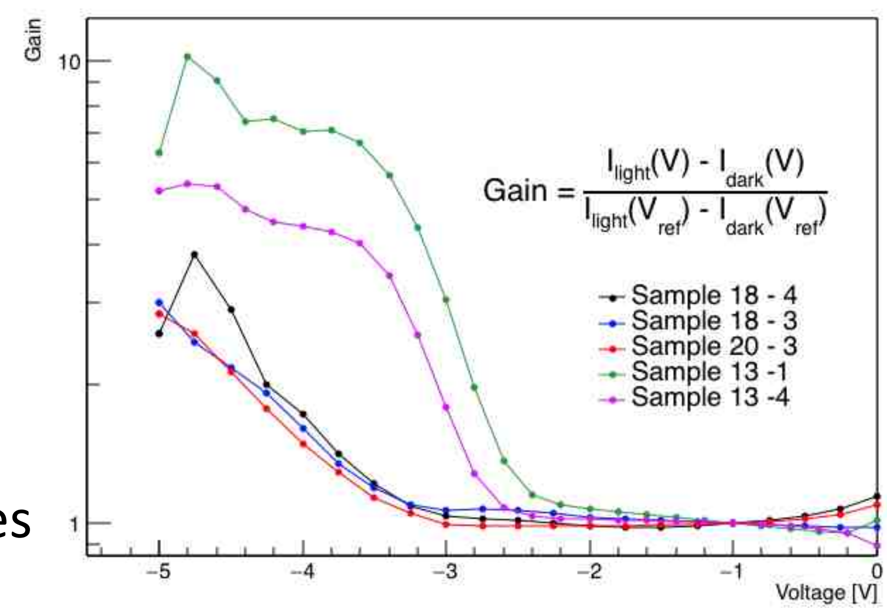
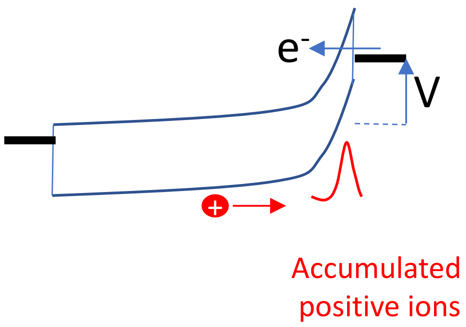


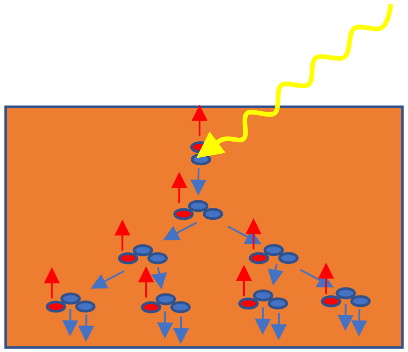
Modelling and Simulation

Observed gain could be explained by two different mechanisms:

1. Mobile ions in OMHPs (I, Br and vacancies) move in electric field and accumulate at interfaces ⇒ modification of injection barrier, tunneling
    - slow process O(ms)



2. Impact Ionization (i.e. avalanche generation)
    - Generation Rate $G = \alpha_n j_n + \alpha_p j_p$
        - Ionization coefficient $\alpha_{n,p}$ = inverse of mean free path
        - j_n, j_p *electron and hole flux*
        - fast process O(ns)
        - Overstraeten – de Man model:
            - $\alpha(E) = \gamma a e^{-\gamma(T) b/E}$ E= electric field
    - To compare with data: vary or fit *a*, *b* parameters, using TCAD simulation and analytical models



Results interpretations

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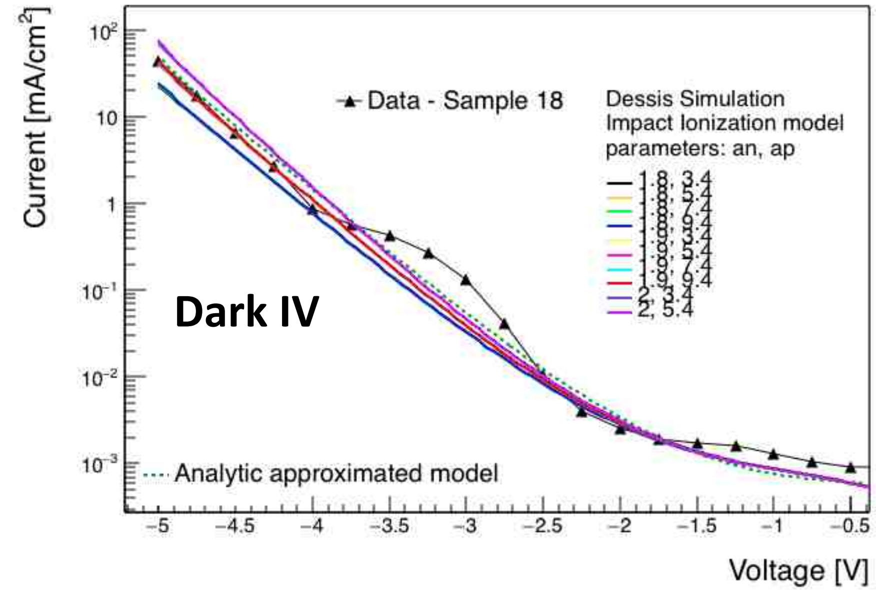
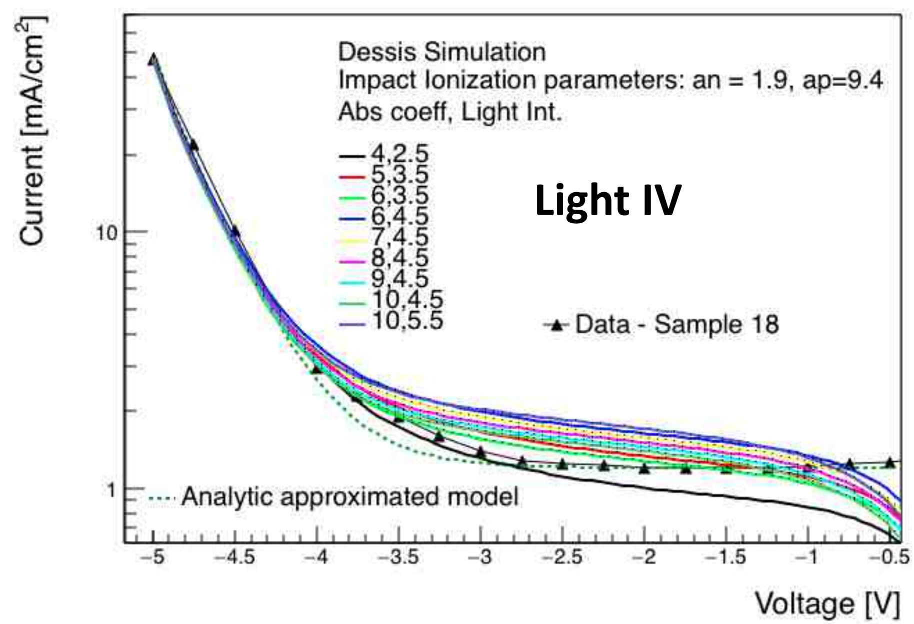
- Dark IV:
  - Reasonable agreement between data and simulation, both using TCAD simulation and analytic model



- Light IV:
  - Use parameters best modelling Dark IV
  - Uncertainty on light intensity and absorption coefficient taken into account



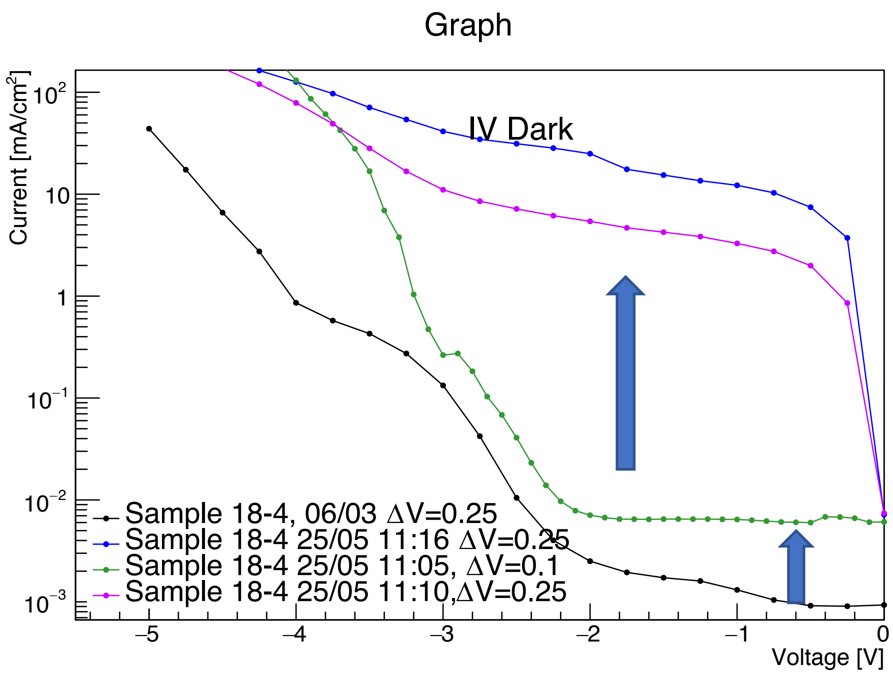
Modelling of ion mobility on going

Degradation with reverse bias 300nm films

Degradation observed under reverse bias:

- after time 3 months → larger dark current
- after finer ΔV scans → ohmic behavior

PEROV Preliminary



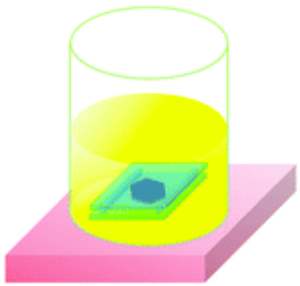
- Instability of OHMP is a known and hot topic for solar cells application
- Study on stability under reverse bias at large V_{bias} for photodetector application not yet studied so far

Need to systematically study the stability under reverse bias before any radiation hardness study

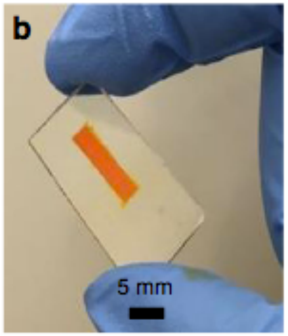
Single crystal productions

Complementary techniques

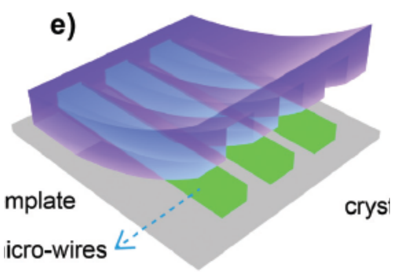
1. **Serial seeding technique**
   - Good for very large bulk OMHP crystals
   - need cut along proper cleavage crystallographic planes to fit the device shape and thickness requirements



2. **confined growth technique**
   - growth directly conductive substrate
   - microcrystalline layer with the desired thickness.



3. **Microfluidic-assisted crystallization** next 3 slides



Collaboration with
- Chemistry Department of Università degli Studi di Milano for techniques 1) and 2)
  - Delays for covid-19, restart in September
- Collaboration with CNR NANOTEC technique 3)
  - Activity recently re-started; preliminary results in the next slides

Microfluidic-assisted perovskite crystallization

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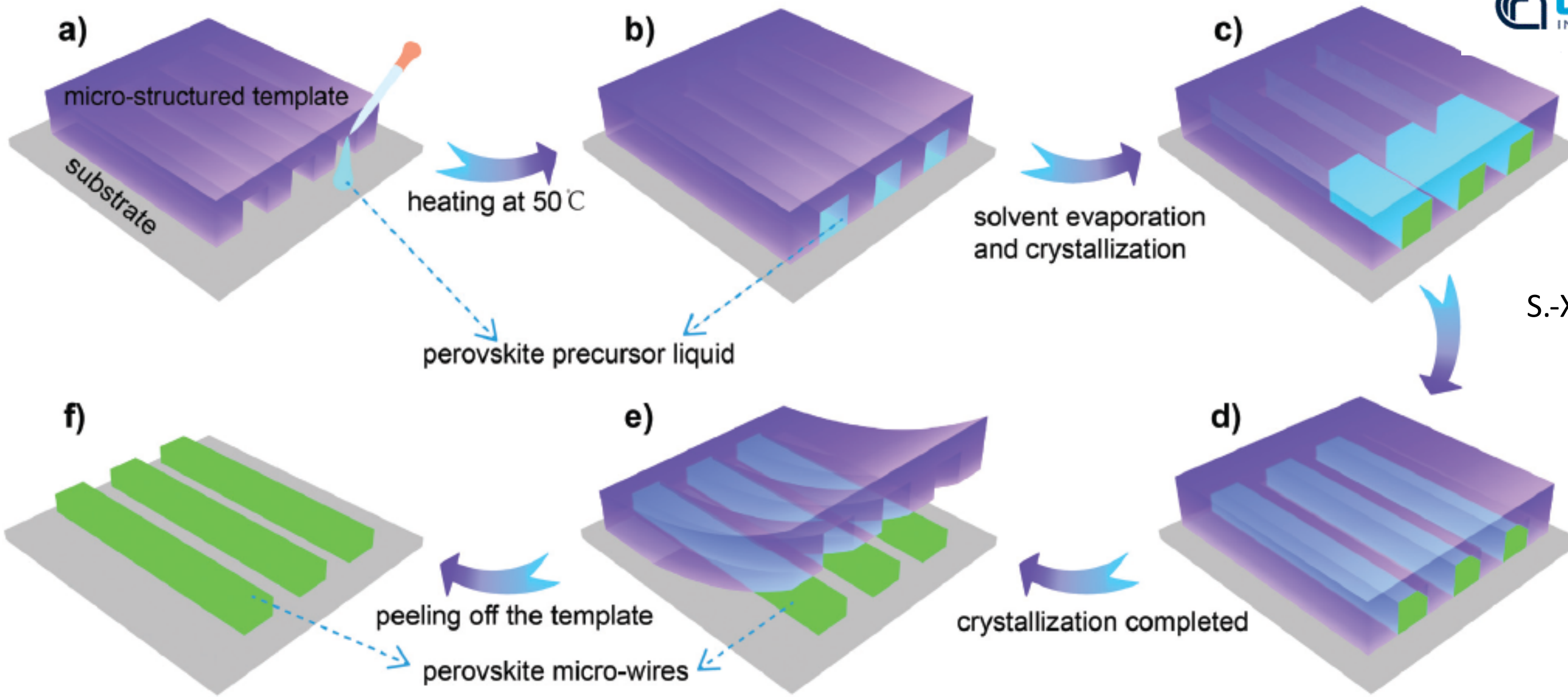


S.-X- Li, Nanoscale, 11, **2019**

- manipulation of fluids at the microscale
- high control over the crystallization kinetics

↓

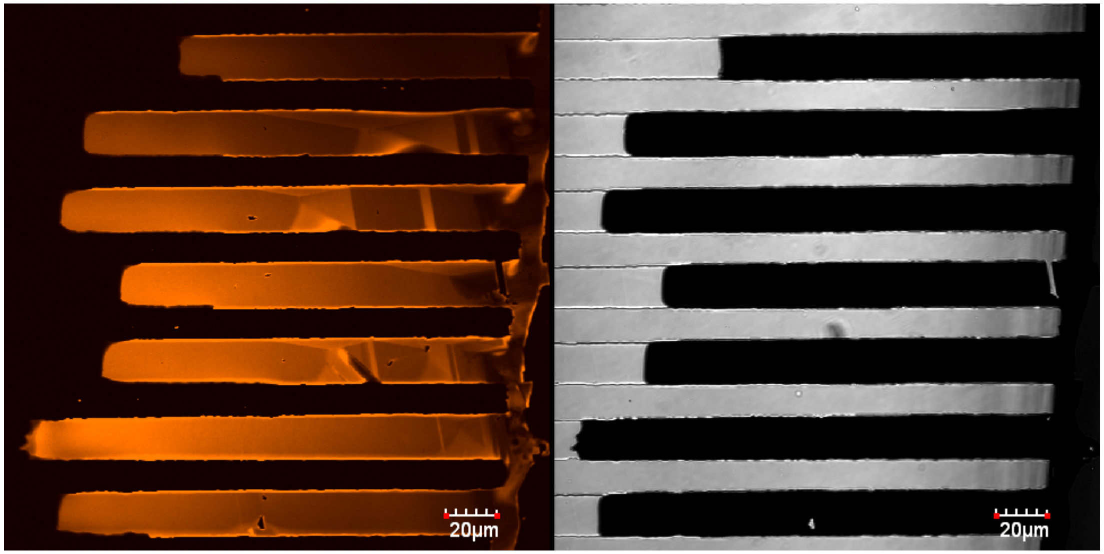
- Excellent uniformity, crystallinity and structural quality due to the reduced density of defects and grain boundaries

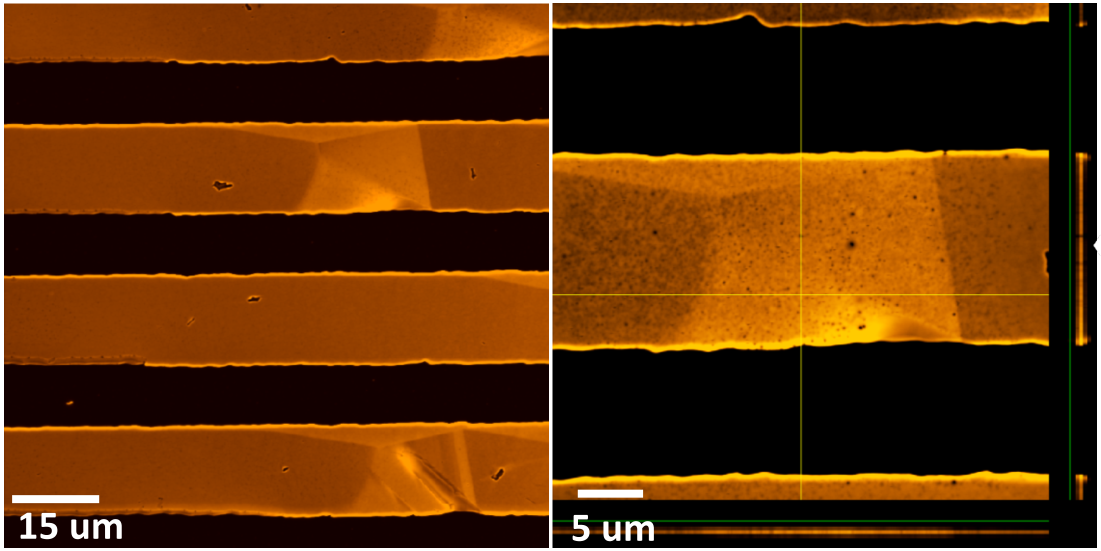
- Allow perovskite crystallization on functional device
- Reduce significant batch-to-batch variability
- Allow patterning over large area, on nonplanar surfaces, with sub-micrometer resolution

Preliminary experimental results : $MAPbBr_3$ microcrystals

Confocal image

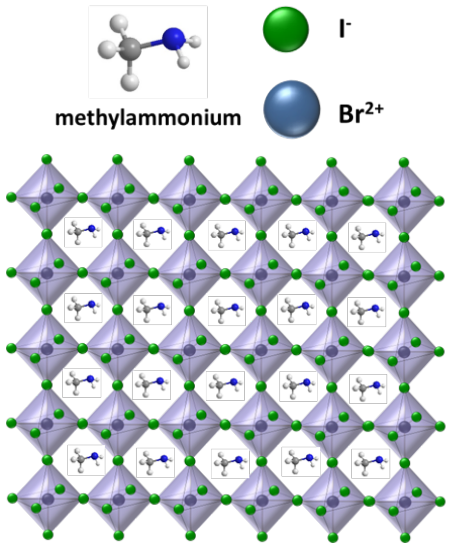
Trasmission image

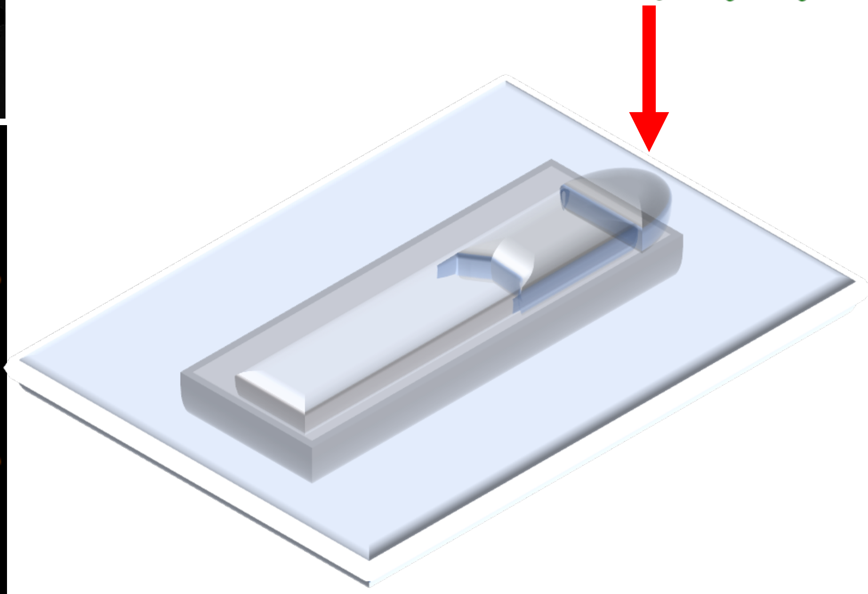




HR 3D – Z stack projection with profiles

$MAPbBr_3$





Microfluidic polymeric channels

w= 15 µm; h= 1 µm

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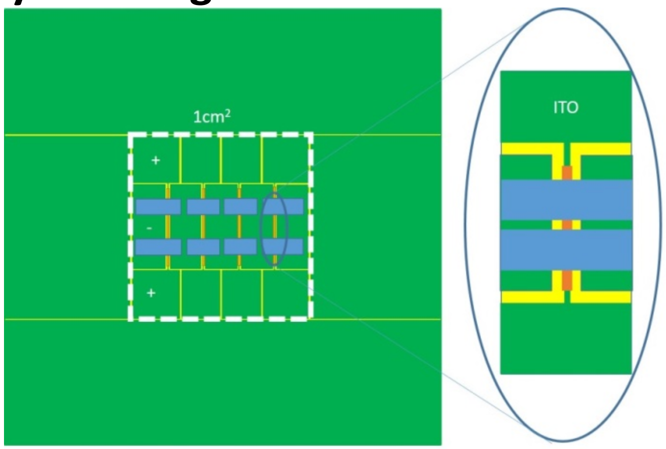
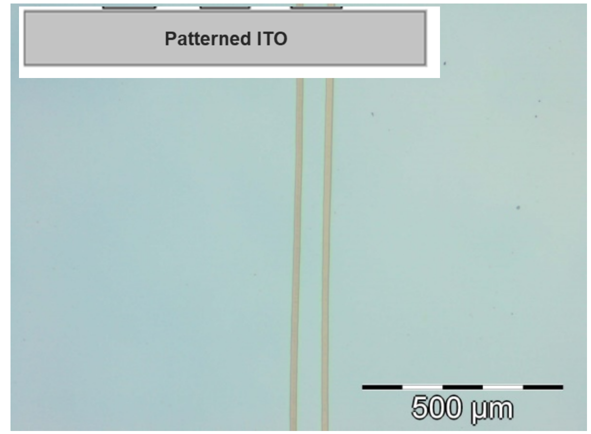
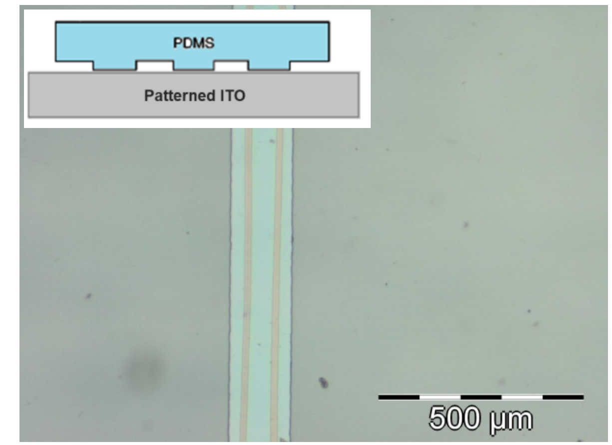
De Marco L., Viola I. preliminary results

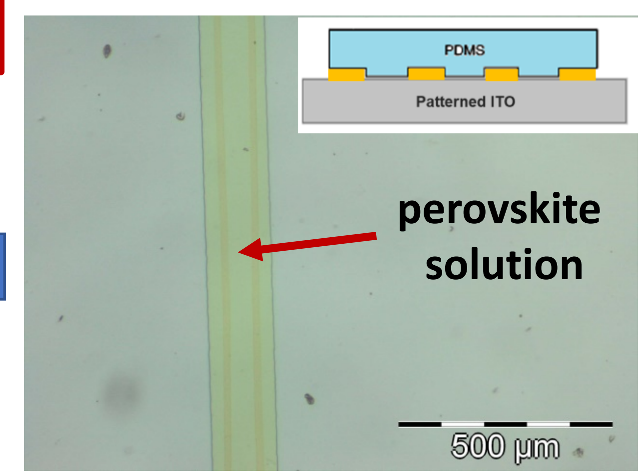
Preliminary experimental results: $MAPbI_3$ on patterned ITO

Layout designed at CHOSE for PEROV





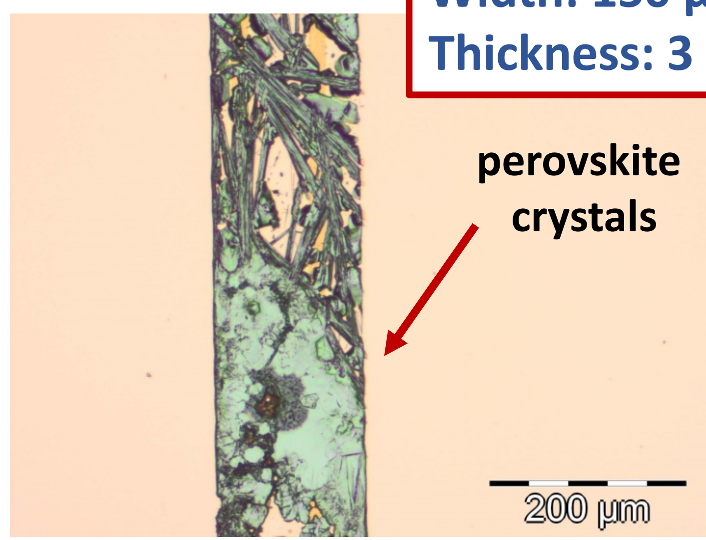


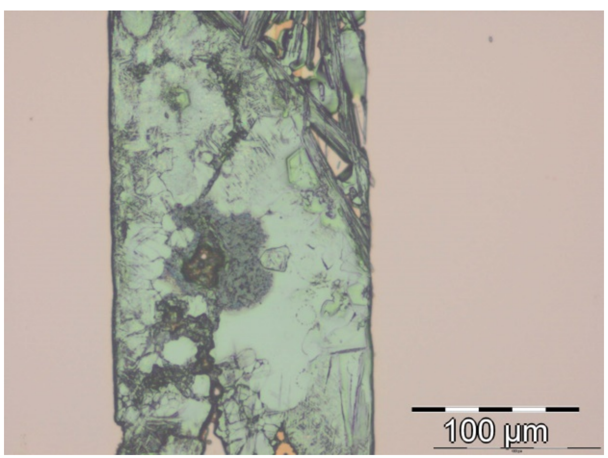


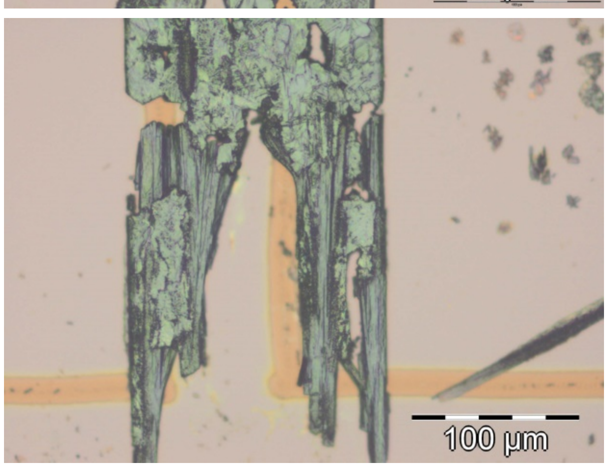
perovskite solution

Width: 150 µm
Thickness: 3 µm

perovskite crystals







De Marco L., Viola I. preliminary results

to be optimized …
(solution concentration, temperature)

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2021-2022 plan

- Extend project to 2 years
  - complete 2020 program
  - new studies emerged from 2020 results
  - more time to optimize single crystal productions

- Plan
  - Proof/Exclusion of Avalanche Multiplication
  - Test stability under reverse bias (*before* radiation hardness) **new**
  - Separate effect from avalanche multiplication (fast) from effect of Ion mobility (low) **new**
    - Timing characterization
    - Low temperature measurement
  - SEM/AFM characterization **new**
  - Radiation hardness

MIlestones
- 04/2021: Monocrystal and film fabrication and characterization
- 10/2021: Stability of monocrystals/films under reverse bias
- 02/2022: Proof/Exclusion of Avalanche Multiplication in films and/or mono crystals
- 06/2022: Radiation Hardness study
- 12/2022: Optimized layouts

Man power for 2021

M. Testa LNF	*0.2*	*Samples characterization, coordination*
A.De Santis LNF	*0.2*	*Radiation hardness*
S. Morganti RM1	*0.1*	*Stability measurements, characterization with sources*
C.Rovelli RM1	*0.1*	*Stability measurements, characterization with source*
M. Auf der Maur - Dip Ing Tor Vergata	*0.2*	*Simulation, Theory*
F. Matteocci - Dip Ing Tor Vergata	*0.1*	*Fabrication, characterization*
Al. Di Carlo – CNR ISM	*0.1*	*Theory, Supervision*
Silvia Rizzato - Dip Chimica Unimi	*0.2*	*Chemical synthesis and crystallization*
Leonardo Lo Presti - - Dip Chimica Unimi	*0.2*	*Crystallographic characterization*
Ilenia Viola – CNR Nanotec	*0.25*	*Microfluidic-assisted synthesis of perovskite single crystals*
Luisa De Marco – CNR Nanotec	*0.1*	*Microfluidic-assisted synthesis of perovskite single crystals*
Simona Sennato – CNS ISC	*0.15*	*SEM/AFM characterization*

FTE>1 → open "sigla"

Financial request for 2021 year

	Scope	Type of request	Cost
Roma2, UNiMi, CNR (associati a LNF)	• Fabrication of single OMHP crystal • Fabrication of OMHP films	Consumables	2 kE
CNR ISC (associato a LNF)	• Probes for AFM	Consumables	500 Eu
Roma1	• transimpedance amplifier for characterization with low intensity sources	Consumables	2kE
CNR NanoTec (associato a LNF)	• Realization of substrates at CHOSE RM2 for microcrystals from Lecce, with both experts	Travel from Lecce to Roma2	500 Eu

Estimate for 2022: ~ 4kE

Backup

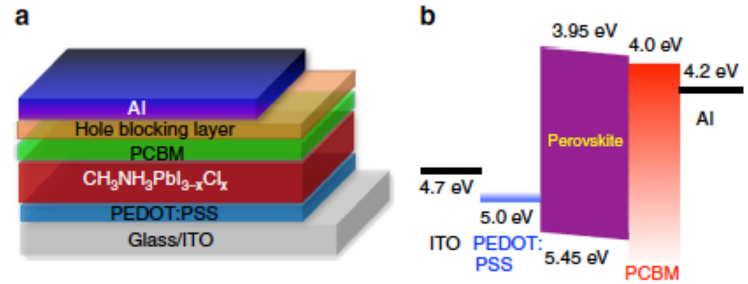
Facilities

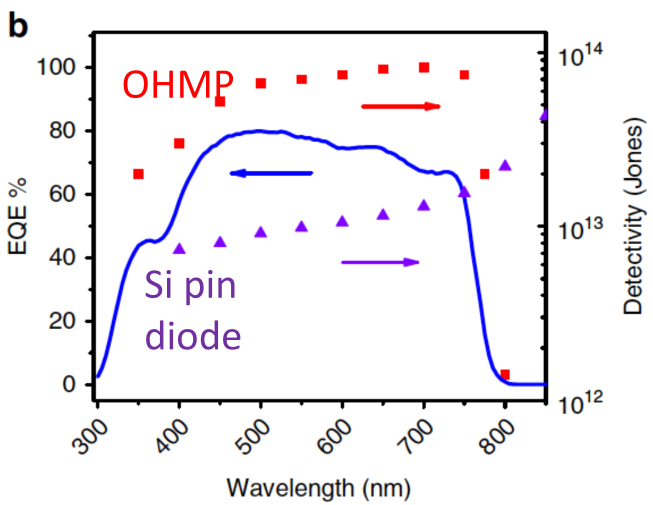
	Facilities/Services	Activity
Roma2	CHOSE laboratories	Fabrication of OMHP films and characterization with led
		Theory expertise in OMHP
Roma1	Lab Segre' Equipment for test with led/laser/radioactive sources	Stability measurements, characterization with radioactive sources, Simulation
LNF	DAFNE, X rays tubes	Radiation hardness
CNR Nanotec	Soft and Living Matter Laboratory, Rome and HOPV Laboratory, Lecce	Microfluidic-assisted synthesis of perovskite single crystals
CNR ISC	AFM, SEM	Morphological characterization
Dip.Chimica UniMi	Laboratories at Chemistry Department	growth and crystallographic characterization of OMHP single crystals

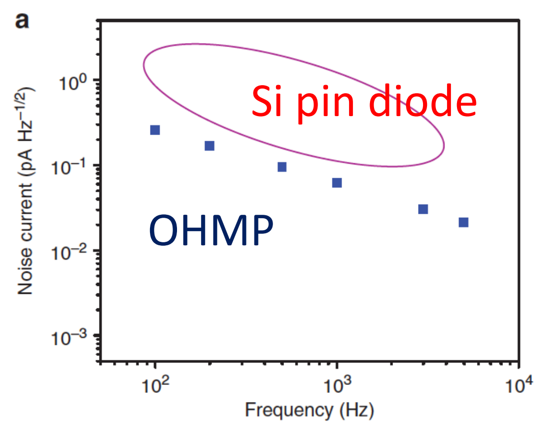
State of art: OMHP photodetector (no gain)

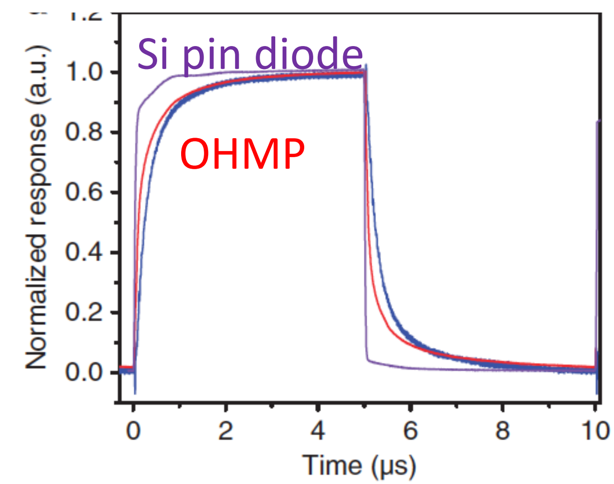
Dou, Y. Yang e al Nat. Commun. 2014, 5, 5404.

- 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, 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

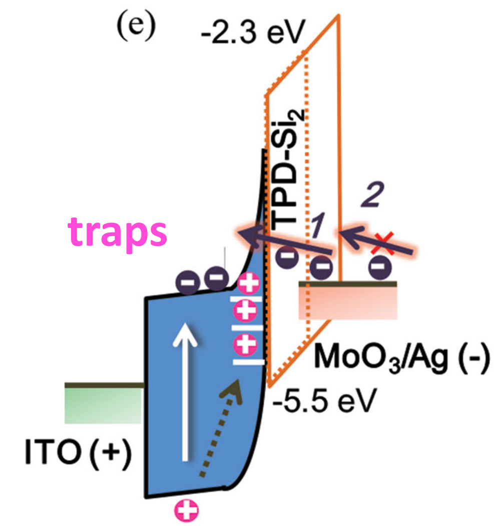
State of art: OMHP photodetector (gain)

- 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.

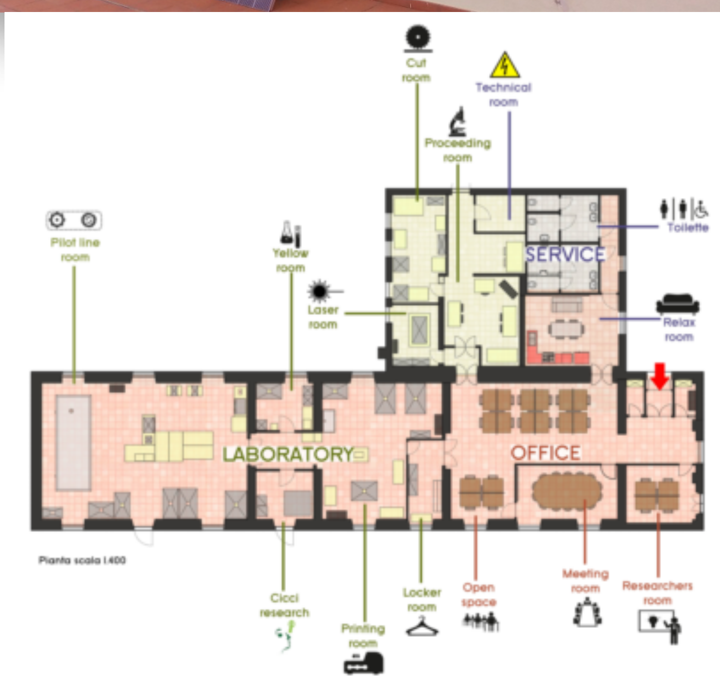


Examples: ITO/$MAPbI_3$/MoO 3 /Ag

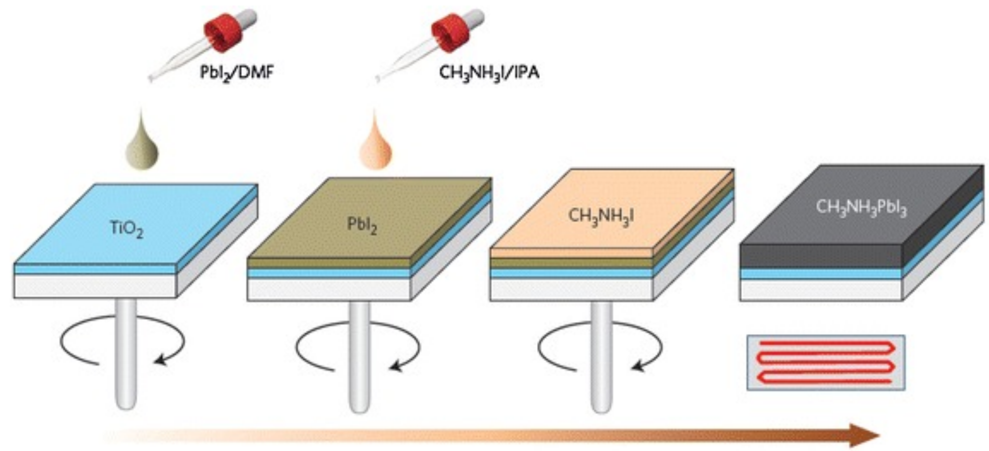
- Gain ~490
- $\tau_{rise/decay}$ ~10 us ☹
- Area 6 mm^2 .

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)

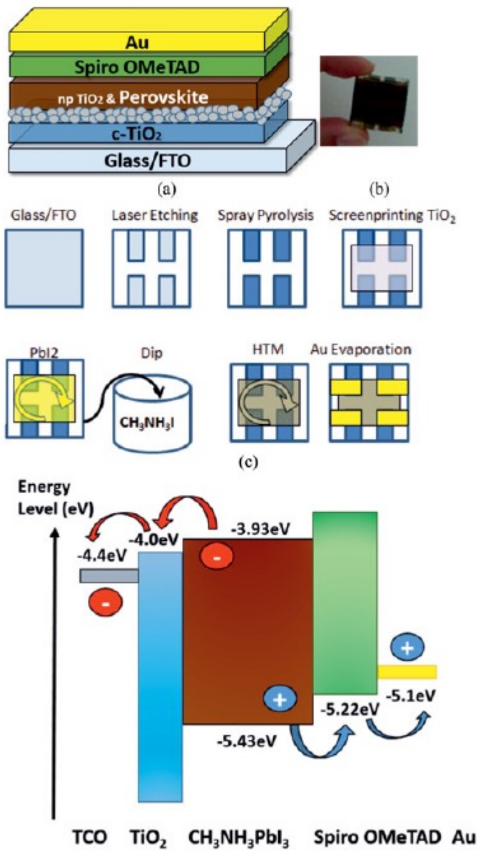


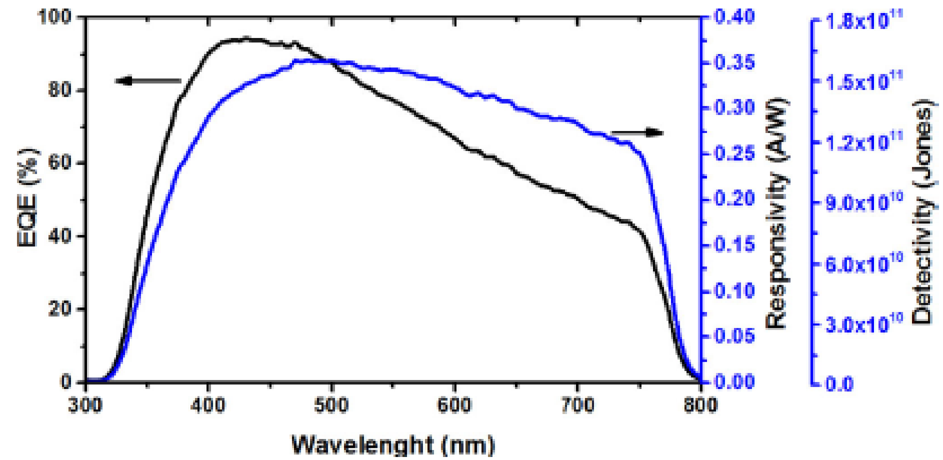
Spin coating technique

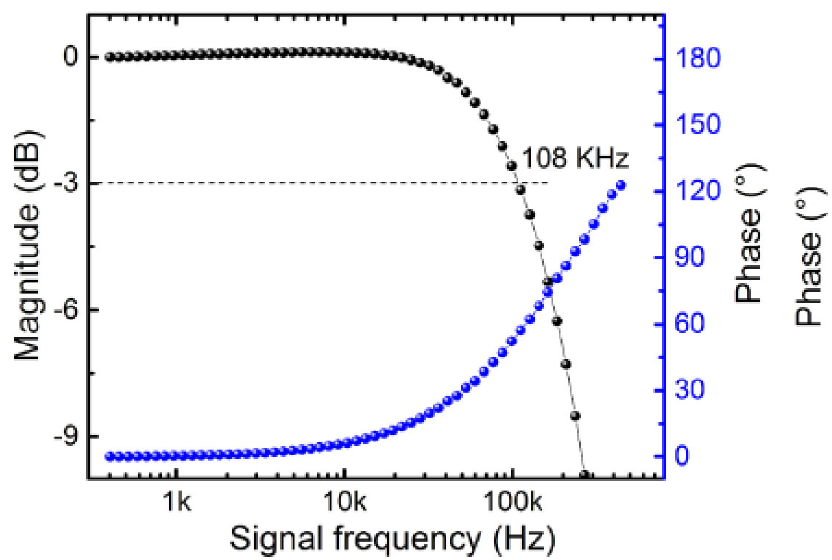


Spin coater

Already experience with fabrication of OMHP photodetectors



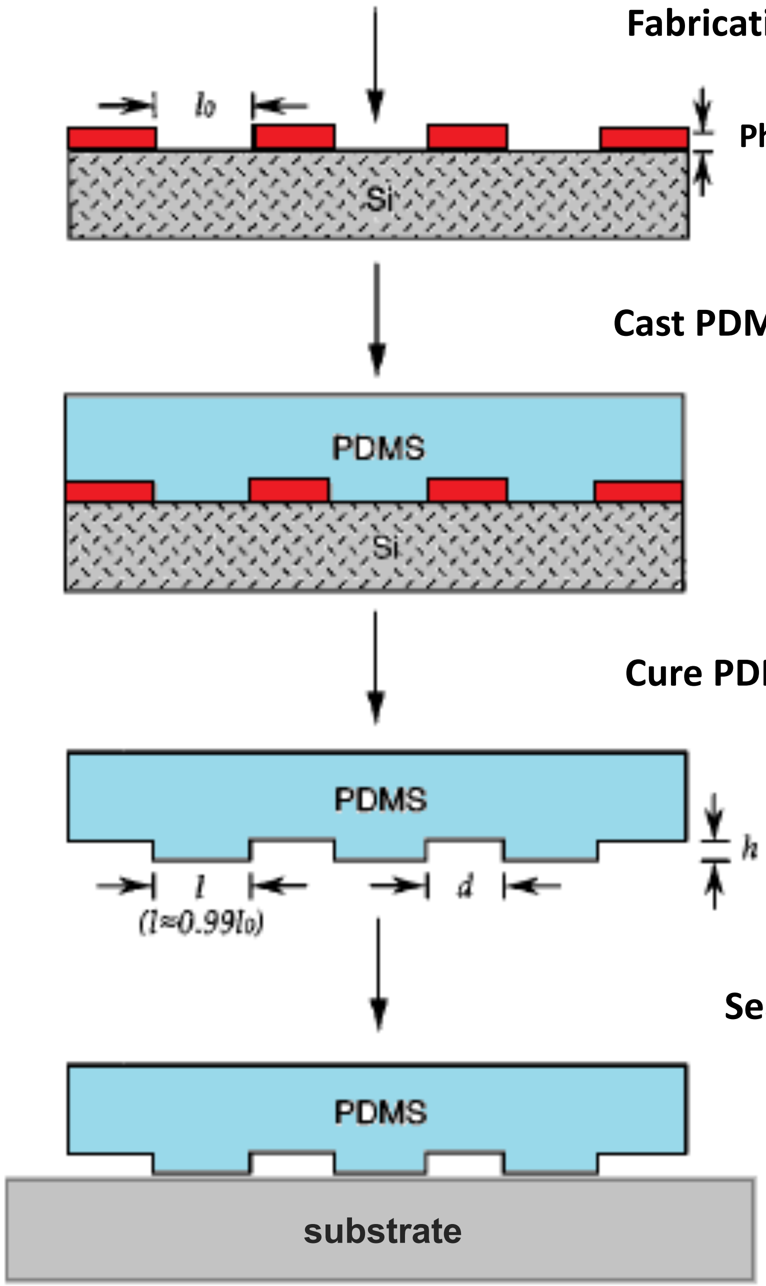




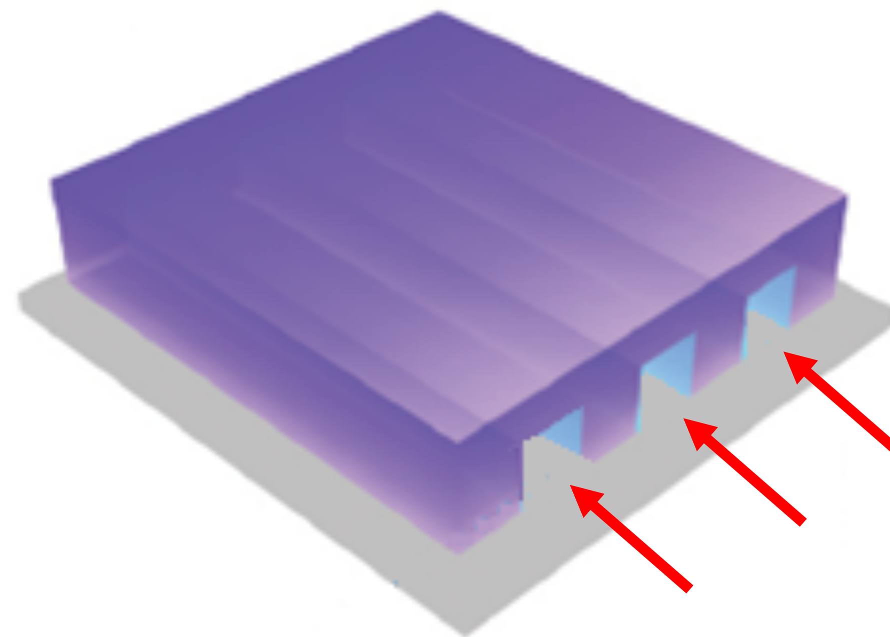
S. Casaluci et al. IEEE TRANSACTIONS ON NANOTECHNOLOGY, VOL. 15, NO. 2, MARCH 2016

Microfluidics: Soft-Lithography fabrication technique

PHOTOLITHOGRAHY



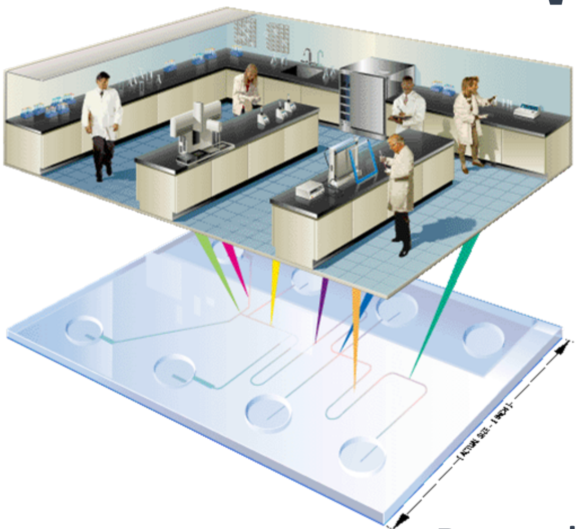
MICROFLUIDIC DEVICE

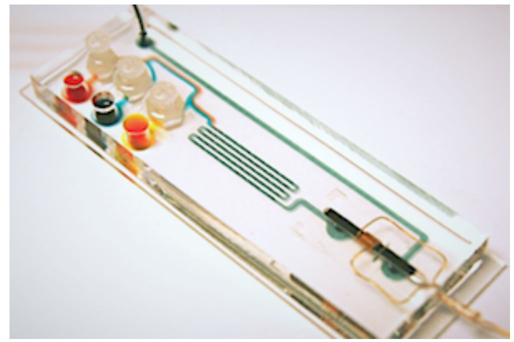


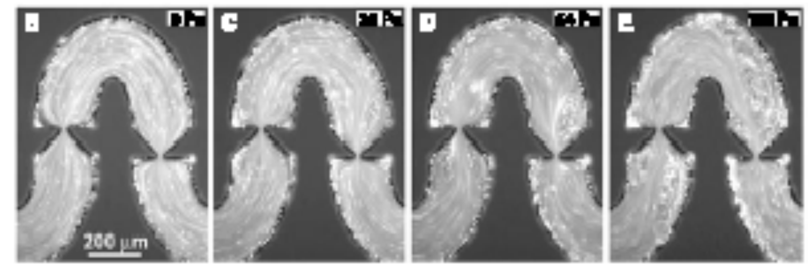
Y. Xia, G.M. Whitesides, **Ann. Rev. Mater. Sci**, 28, 1998

I.Viola et al., **Anal. Chem.**, 77, 2005

Why Microfluidics ?







Prevalent TOOL for the local control of liquid flows

Manipulation of gas and liquid inside the confined environment of micro-networks

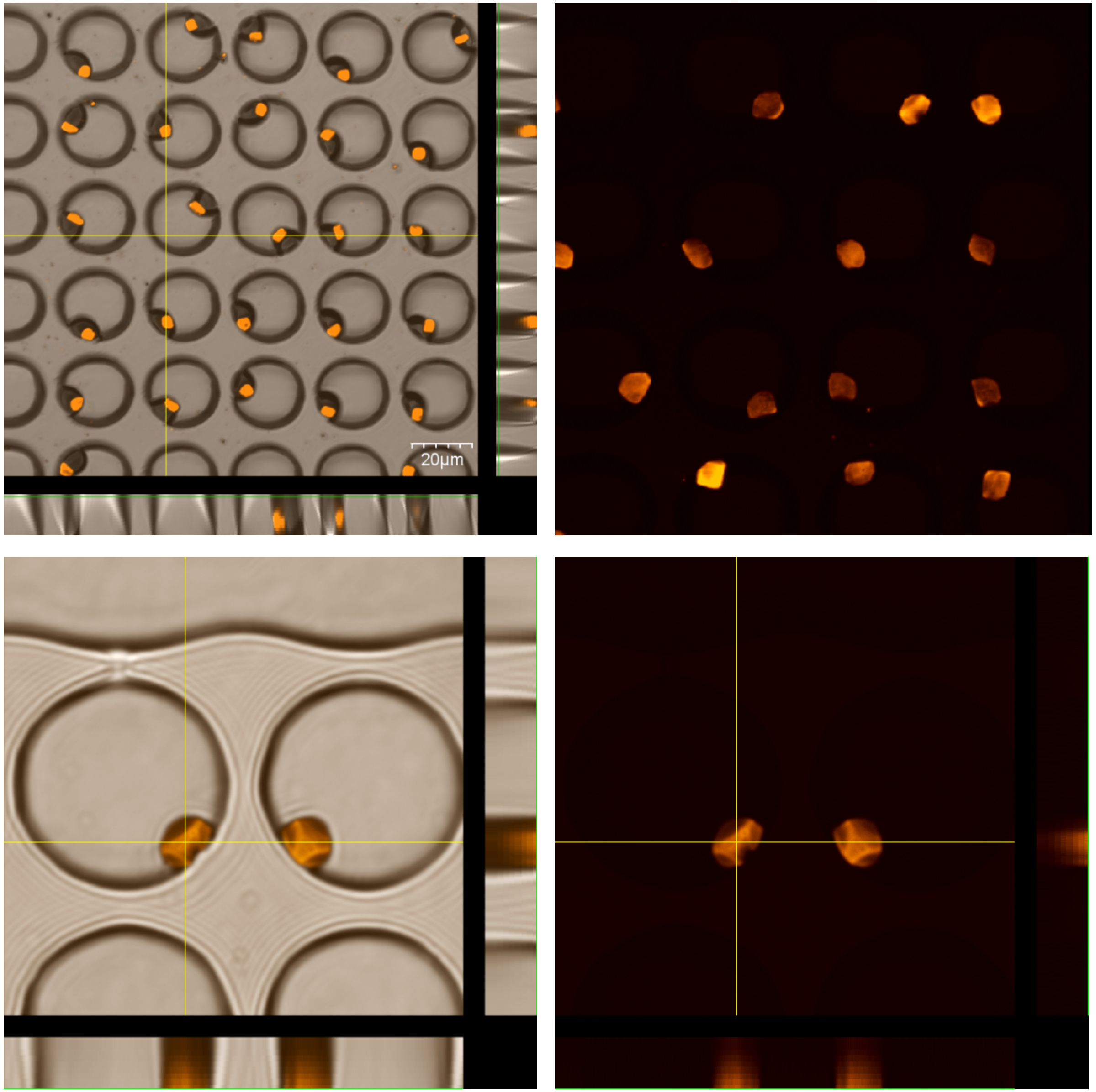
Fabrication of miniaturized devices and micro-array

Integration of functional components (Mixers, Valves, Filters and Pumps) for OptoElectronics, Chemistry and Biology

A. Groisman et al., Science, 300, **2003**

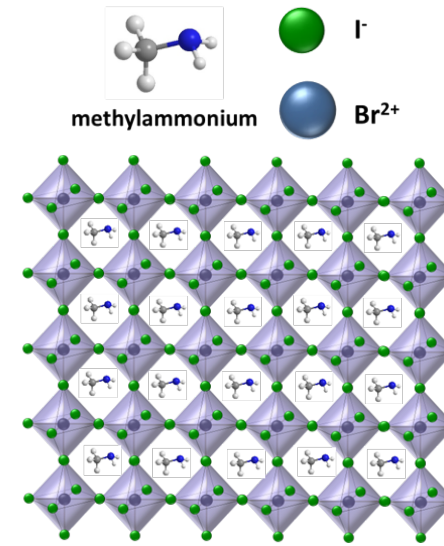
CNRNANOTEC
INSTITUTE OF NANOTECHNOLOGY

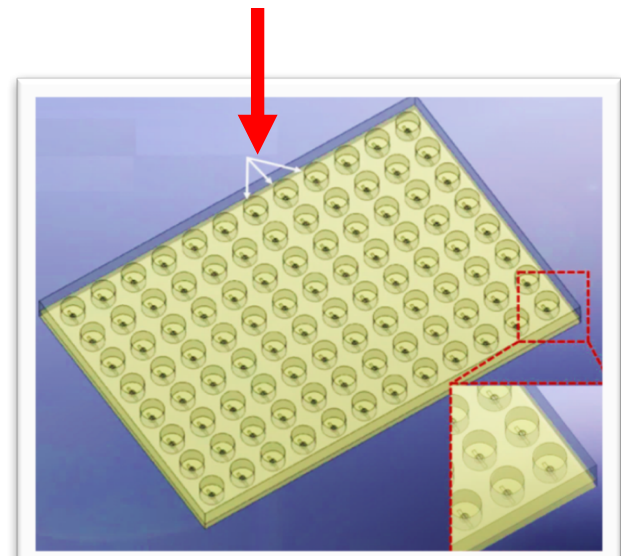
Preliminary experimental results: $MAPbBr_3$ micropixels



Confocal Z-stack with sections

$MAPbBr_3$



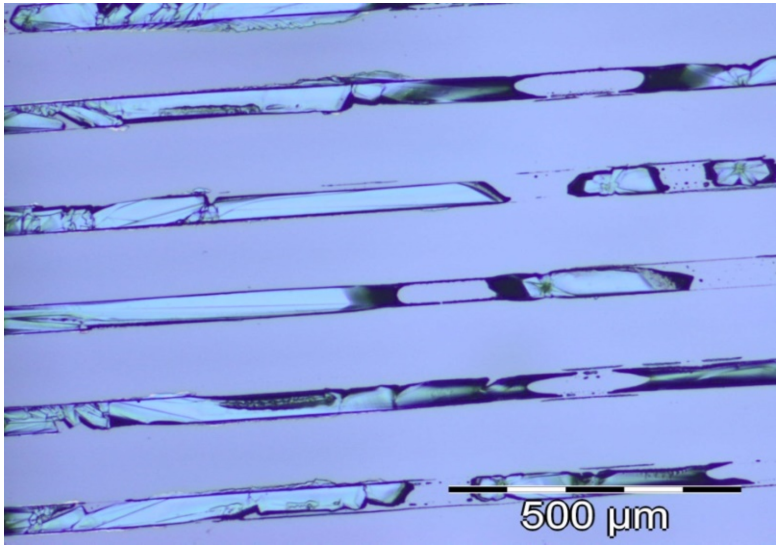


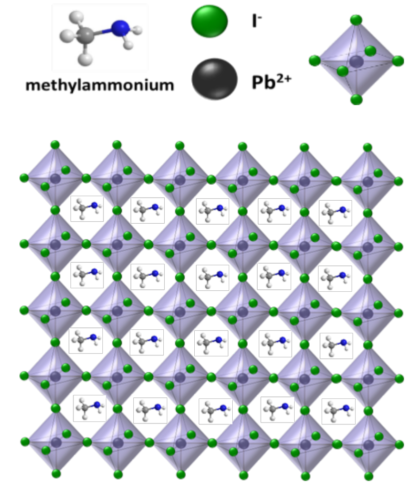
Micropillars polymeric device

CNRNANOTEC INSTITUTE OF NANOTECHNOLOGY

De Marco L., Viola I. preliminary results

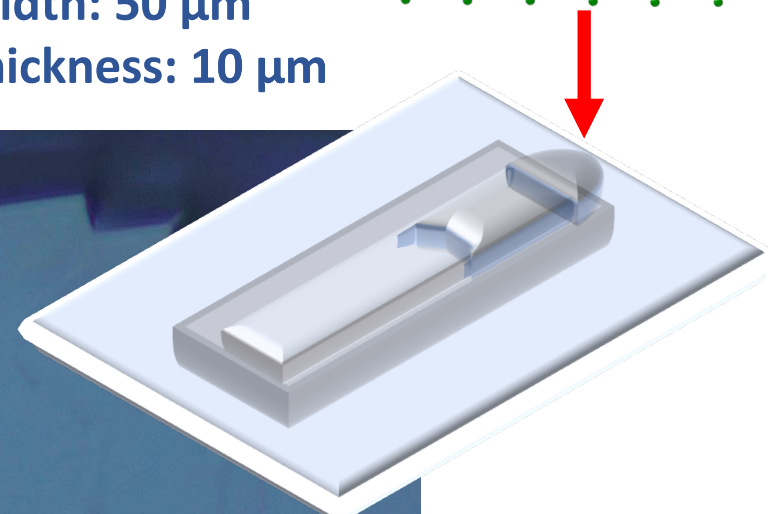
Preliminary experimental results: $MAPbI_3$ on glass

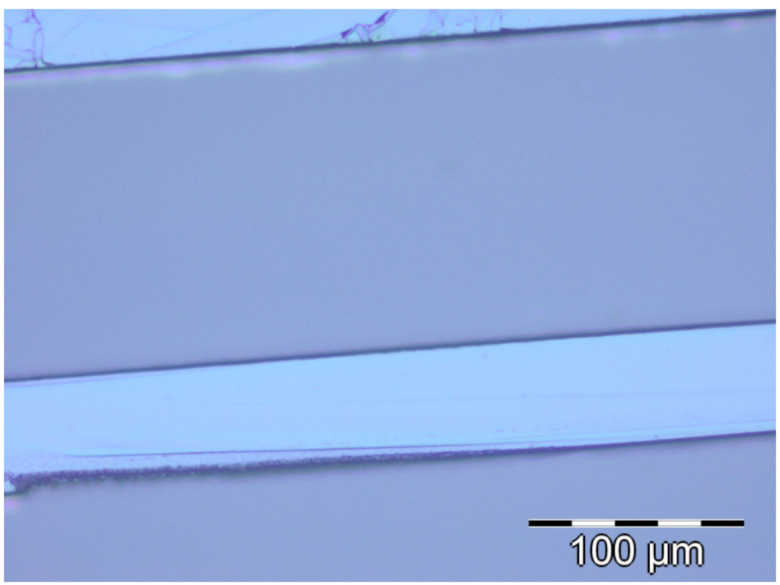


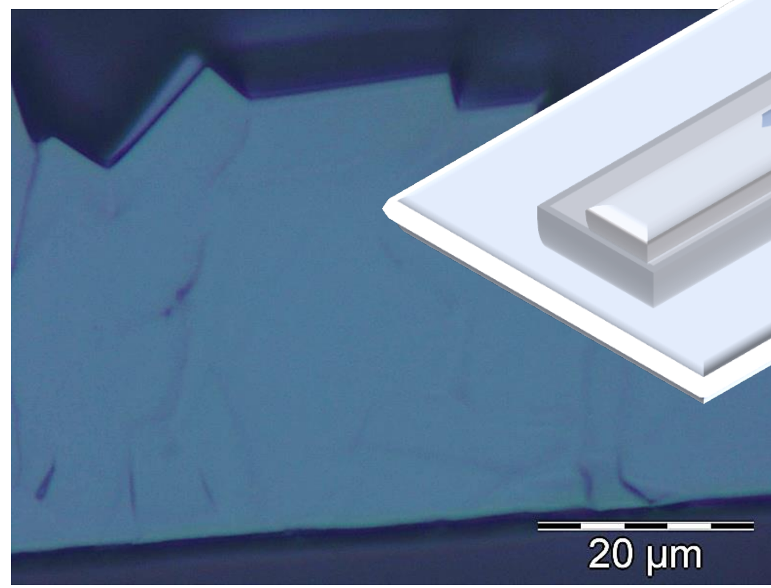


$MAPbI_3$

Single crystals Width: 50 µm
Single crystals Thickness: 10 µm







to be optimized…

CNR NANOTEC INSTITUTE OF NANOTECHNOLOGY

De Marco L., Viola I. preliminary results

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

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