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

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1 Introduction

The organometal halide perovskites (OMHP) semiconductors combine the advantages of organic and inorganic semiconductors. Due to their crystalline structure and band-like electronic properties, they present low exciton binding energy and high charge-carrier mobility. As high Z material, they have a high absorption coefficient that makes a thin layer of material sufficient for almost complete light absorption. The main advantage with respect to the III-V semiconductor technologies is the possibility to scale up over large area substrates by using several printing techniques such as spin and blade coating. These processes typically work at low temperatures and under ambient conditions and allow to fabricate thin film devices on large areas of several square centimeters. Therefore they are attractive to build large area photodetectors with possibility for curved shapes. OMHP can also be grown in large and high–quality single crystals with seeding techniques or with unconventional lithographic techniques (such as soft-lithography, microfluidics or dewetting-driven deposition).These latter offer less scalability as printing techniques, but provide higher purity which, depending on the application context, may be of higher priority.

A prerequisite to use OMHP semiconductors to detect low intensity signals is the presence of a gain. This latter has been described in literature in association with a slow time response, related to the presence of traps in the OMHP film. The main goal of the PEROV project is to find out whether OMHPs exhibit also fast internal avalanche multiplication. The second goal is to study the stability of perovskite devices.

2 Device production and characterization

In the PEROV project various classes of devices have been realized through a dedicated optimization of the perovskite-crystal growth. Xray diffraction and Scanning Electron Microscopy have been used to measure the quality and morphology of the crystals. All the device have been electrically characterized. The perovskite with Bromide has been chosen due to a larger band gap with respect to that with Iodide and due to its larger defect activation energies [5]. In 2022 a paper was published on the film-based devices [2]. In 2023 the activity has been focused on:

1. Micro-fluidics assisted single-crystals production
   Microwires of $CH_3NH_3PbBr_3$, realized by a microfluidic deposition technique, with total dimensions (W x L x H) of 150 × 250 × 2(6) μm^3 were deposited. A patent has been deposited [3] and a paper have been published to Advanced Material Technology journal [1]

2. Single crystals production with seeding techniques and characterization
   We employed different crystallization techniques to grow high-quality single crystals of $CH_3NH_3PbBr_3$ in order to compare their efficiency and suggest practical criteria for their use. $CH_3NH_3PbBr_3$

exhibits inverse solubility in dimethylformamide with respect to the temperature. The heating protocol was accurately designed to control nucleation, crystal size and morphology of the crystals (figure 1 top)

3. Micro-pads production and characterization
   Micro-pads are grown directly on pattered ITO substrate through a dewetting technique, with total dimensions (W x L x H) of approximately $250 \times 500 \times 100\ \mu m^3$ (figure 1 bottom).

For all the devices the LNF electronic service realized ad-hoc boards for the time-resolved electrical measurements.

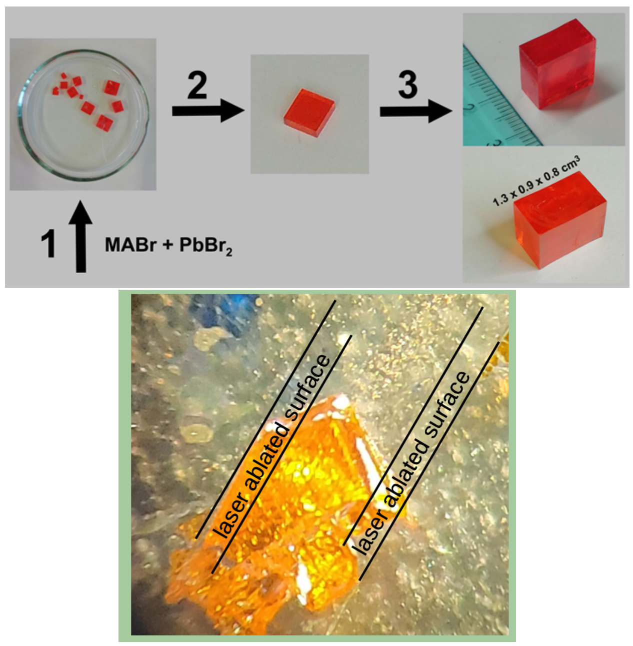

Figure 1: Top: Large single crystals of $CH_3NH_3PbBr_3$ grown by temperature raising method. Bottom: Micro-pad of $CH_3NH_3PbBr_3$ directly gorwn on ITO patterned substrate

3 Test Beam

During July and November 2023 two test beams were performed at the BTF, the Frascati beam test facility. The energy of the beam was aound 400 MeV. Two different setups have been tested with the beam:

- Single macroscopic crystal with approximate dimensions of 4x4x1.6 (W x L x H) mm^3 directly metallized with gold dand ITO deposition on the surface;
- micro-pads of perovskite grown directly on patterned ITO support with approximate dimensions of 200x500x100 (W x L x H) μm^3

For both devices the LNF electronic service realized ad-hoc boards.

The setup for the large single crystal, wave forms at different bias and the linearity have been studied, are shown in fig .2. as preliminary results. This result represents the first usage of crystal perovskites as bulk detector for charged particles at high energy. A paper is expected to be soon submitted. A patent [4] has been deposited. The preliminary results from the test beam with the micropad perovskite are shown in fig. 3.

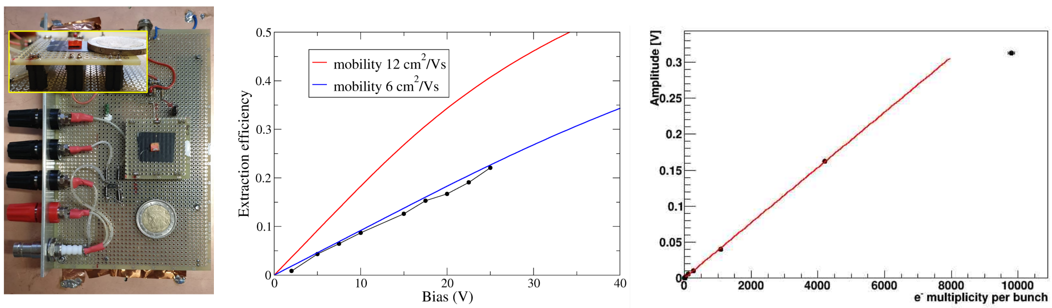

Figure 2: Left: picture of the crystal setup. The MAPbBr3 macroscopic crystal is metalized on the two largest surfaces and bonded on piggy board for easy mount and replacement on the main board. In the yellow box a detail that shows the thickness of the crystal. Center: amplitude of signal as a function of the bias voltage . On the top right the response linearity of the crystal with constant $V_{bias} = 2$ V as a function of the beam multiplicity.

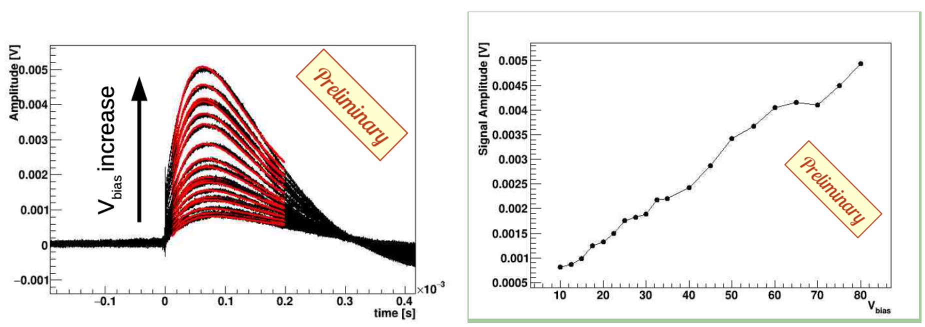

Figure 3: Left: Waveforms recorded during the test beam using a perovskite micro-pad with voltage bias from 10 V to 80 V. Right: amplitude of the signal as a function of the bias voltage

The project RADPEROV in the context to the RADNEXT EU call has been funded in 2023. Its goals is high-dose irradation of perovskite crystals with protons.

4 List of Conference Talks by LNF Authors

1. M. Testa on behalf of PEROV coll., talk at High Precision X-ray Measurement, Jun 19-23 2023 Frascati, title "PEROV project: perovskite devices for visible light and potential for X-ray detection"

2. M. Testa, Dipartimento di Ing. Elettronica Università di Tor Vergata, Seminari at Chose Scientific Cafè 20 Marzo 2023, title "PEROV project: perovskite devices for visible light and radiation detection"

3. A. De Santis on behalf of PEROV coll,. Frascati 15 November 2023, Seminar: Overview of the PEROV results

5 Publications

1. Testa M, Auf der Maur M, Matteocci F, Di Carlo A (2022). Reverse bias breakdown and photocurrent gain in CH3NH3PbBr3 films. APPLIED PHYSICS LETTERS, vol. 120, ISSN: 0003-6951, doi: 10.1063/5.0082425

2. I. Viola, F. Matteocci, L. De Marco, L. Lo Presti, S. Rizzato, S. Sennato, A. Zizzari, V. Arima, A. De Santis, C. Rovelli, S. Morganti, M. Auf der Maur, M. Testa, Microfluidic-Assisted Growth of Perovskite Single Crystals for Photodetectors. Adv. Mater. Technol. 2023, 8, 2300023. https://doi.org/10.1002/admt.202300023

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1. I. Viola, F. Matteocci, L. De Marco, L. Lo Presti, S. Rizzato, S. Sennato, A. Zizzari, V. Arima, A. De Santis, C. Rovelli, S. Morganti, M. Auf der Maur, M. Testa, Microfluidic-Assisted Growth of Perovskite Single Crystals for Photodetectors. Adv. Mater. Technol. 2023, 8, 2300023. https://doi.org/10.1002/admt.202300023

2. Testa M, Auf der Maur M, Matteocci F, Di Carlo A (2022). Reverse bias breakdown and photocurrent gain in CH3NH3PbBr3 films. APPLIED PHYSICS LETTERS, vol. 120, ISSN: 0003-6951, doi: 10.1063/5.0082425

3. Deposited patent 102022000010469 “Confined growth of perovskite single-crystal on patterned conductive substrate for broad imaging applications” , M. Testa, M. Auf der Maur, F. Matteocci, I.Viola, L. Di Marco

4. Deposited patent 102023000012477 “Dispositivo di rivelazione e tracciamenti di particelle cariche basato su perovskiti e sistema comporendente detto dispositivo per monitoraggio di fasci di aprticelle”, M. Testa, A. De Santis, G. Felici, G. Papalino, S. Rizzato, L Lo Presti,. Rovelli;

5. J. M. Azpiroz et al., Defects Migration in Methylammonium Lead Iodide and their Role in Perovskite Solar Cells Operation, Energy Environ. Sci., 2015,8, 2118-2127