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 three 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 [3]. In 2022

1. Production and characterization of film-based device
   Film devices with 300 nm thickness and four 4x4 mm^2-area pads were characterized (Fig. 1). Among the produced batches, ∼6 devices showed a gain, with an incident photon to current efficiency (IPCE) larger than 100%. An analytic model including the impact ionization processes and the effect of mobile ions has been implemented, leading to the publication [1].

2. 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

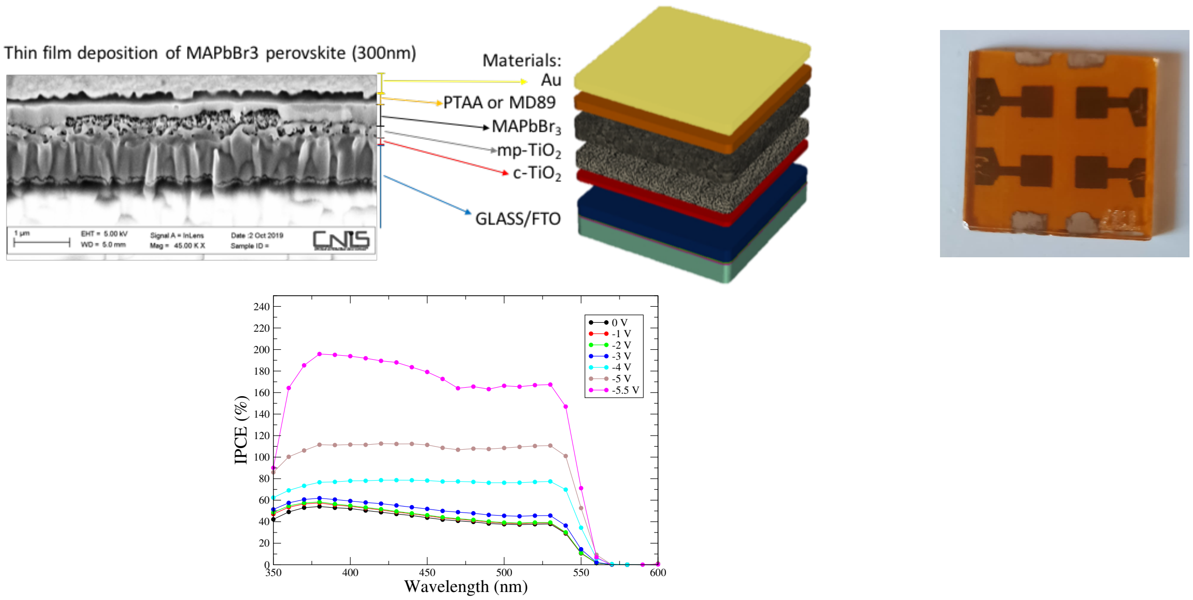

Figure 1: Film characterization. Top Left: Image of scanning electron microscopy and sketch of the device layers. Top Right: film-device. Bottom: incident photon to current efficiency (IPCE) as function of the wavelength at different bias voltage.

deposited [2] and a paper have been submitted to Advanced Material Technology journal. The devices show an IPCE 2 larger than 100%. The evaporation of the Au contact was possible through 3D printed masks realized by the LNF mechanic workshop.

3. 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 3)

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

3 Test Beam

During February and May 2022 two test beams were performed at the BTF, the Frascati beam test facility. The energy of the beam was 370 MeV in February and 450 in May. The beam profile, measured with FITPIX device, has approximately a round cross section with 3.5 mm width at the detector position. Two different setups have been tested with the beam:

- Film: pads of perovskite on ITO support and gold metallization;
- Single macroscopic crystal 4x4x1.6 mm^3 directly metallized with gold deposition on the surface;

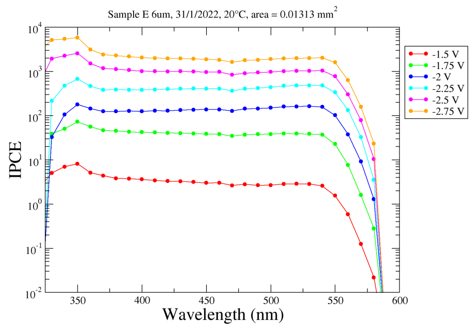

Figure 2: Incident photon to current efficiency (IPCE) of a micro-channel of dimensions (W x L x H) of 150 μm $\times$ 250 μm $\times$ 6 μm

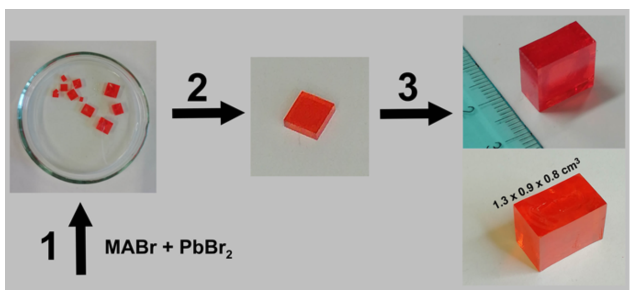

Figure 3: Large single crystals of $CH_3NH_3PbBr_3$ grown by temperature raising method.

For both devices the LNF electronic service realized ad-hoc boards. The film+LYSO setup linearity has been tested against the beam multiplicity ranging between 500 and 10k. In the fig. 4 the used setup is shown, together with the linearity as a function of beam multiplicity. The results are preliminary. The setup for the large single crystal, wave forms at different bias and the linearity

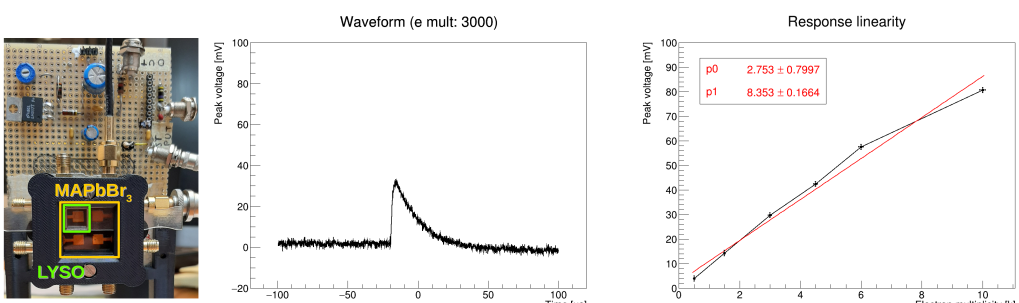

Figure 4: Left: Photo of the experimental setup used. In the central part the scintillator (LYSO crystal - the green box) is placed on top of the active detector perovskite film (the orange box). The four pads realised on the same ITO support are clearly visible. The setup allows to extract signal from one pad at the time. Center: waveform at the scope for the 1.5k particles/shot multiplicity. Right: linearity of the response of the setup (LYSO+Film) versus the beam multiplicity in the range between 500 and 10k particles/shot

are shown in the fig .5. This result represent the first usage of crystal perovskites as bulk detector for charged particles at high energy. In the test beam of May 22, we used bulk crystals of the second batch with improved response. Sensitivity down to a single particles has been observed. Analysis is on going.

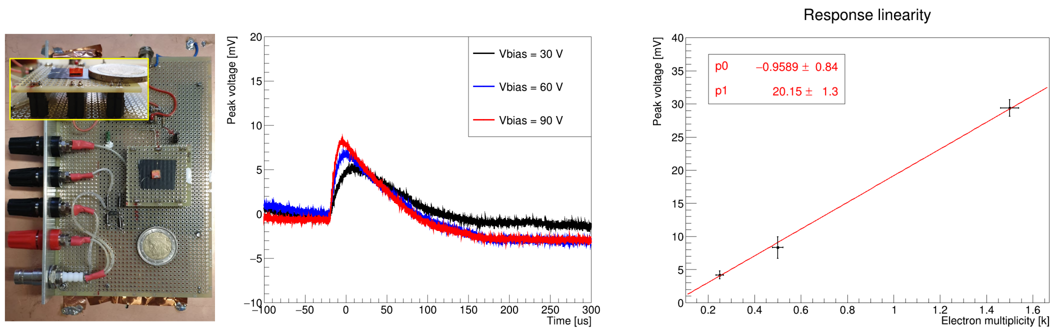

Figure 5: Left: picture of the crystal setup. The MAPbBr3 macroscopic crystal is metalized on the two largest surfaces and bonded on piggy board for easy mount and replacement on the main board. In the yellow box a detail that shows the thickness of the crystal. Center: waveform observed with the bulk crystal setup. The V_{bias} is ranging between 30 and 90 V while the multiplicity is kept constant at 250 particle/shot. On the top right the response linearity of the crystal with constant $V_{bias} = 30$ V as a function of the beam multiplicity.

4 List of Conference Talks by LNF Authors

1. M. Testa on behalf of PEROV coll., Frascati, PEROV: R&D for photo-detectors based on Organo-Metal halide Perovskite material, Workshop Quantum Materials for Quantum Technologies, Laboratori Nazionali di Frascati, February 2022

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

References

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. 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

3. 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