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प्लाज़्मा अनुसंधान संस्थान  
Institute for Plasma Research

Facilitation Centre for Industrial Plasma Technologies  
Institute for Plasma Research

# Plasma Processing Update

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#### Important Highlights

- Lead-free hybrid perovskite material
- Self-powered electron/hole conductor free device
- High performance photodetector
- Low light sensitivity
- Long environmental stability

#### Other team members

- Mukesh Ranjan

## Research Focus - Fabrication of Lead-Free Perovskite based Self-Powered Photodetector

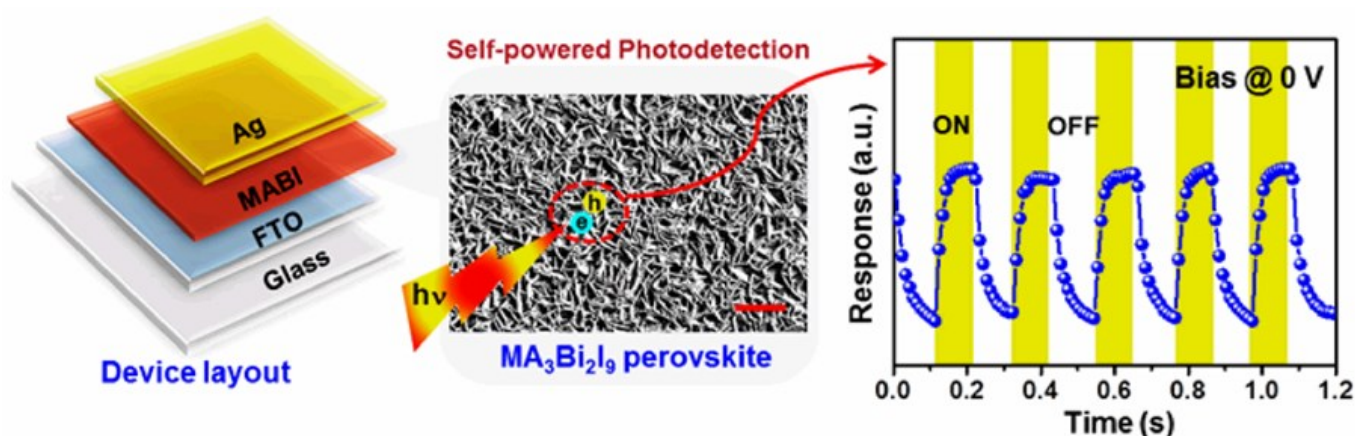
Optoelectronics is the junction of optics and electronics which uses the physics of optics and electronics on the same platform. Efficient utilization of various light radiations such as ultraviolet (UV), visible, and infrared (IR) sources for accurate photodetection in any optoelectronic devices is being brought into ever sharper focus.

For the past few decades, extensive research has been devoted to developing high performance photodetectors based on inorganic materials such as PbTe, GaN, ZnO, HgCdTe, *etc.* which can compete in the optoelectronic market.<sup>1,2</sup> Apart from the growing progress in photodetector fabrication with inorganic materials, the perovskite materials have laid the grounds framing the key objectives for investigating their applications in optoelectronic devices.<sup>3,4</sup> In particular, their prime importance drives in developing small-scale perovskite based optoelectronic devices including photodetectors, light emitting diodes, and phototransistors. Recently, various research groups have projected the applicability of hybrid lead (Pb) halide perovskite materials for optoelectronics applications, specifically in photodetectors.<sup>5</sup> In spite of the rapid progress in the field of Pb halide perovskite photodetectors, there remain two open questions related to the stability of the device at ambient condition and the use of Pb in the perovskite structure which hinders its use for industrialization. Therefore, in order to avoid the use of Pb in the device geometry, progressive research is directed towards synthesizing stable lead-free perovskite materials with comparable performance with that of Pb halide perovskites. Highlighted by A. Waleed *et al.*, lead-free perovskite nanowire arrays based on tin (Sn) provides improved photodetector stability.<sup>6</sup> Apart from Sn, researchers have also explored to incorporate Mn<sup>7</sup> and Bi<sup>8</sup> in the perovskite structure to be utilized in photodetectors. It is found that the as-substituted materials (Sn, Bi, Mn) in the photodetector geometry works under applied operating voltages ranging from 1 – 30 V. Also, the illuminated light intensity for photo-detection is high (0.2 – 3 mW/cm<sup>2</sup>) with a very small device active area (0.03 – 0.0006 cm<sup>2</sup>).

Therefore, it is of utmost importance to fabricate competitive photodetectors that should not only sense low optical signal but also of large area for practical realizations, for instance, in military surveillance, civil-fields, industry automation control and space based applications.

It is worth mentioning that these photodetectors can work under low operating voltages or in self-powered mode which will ultimately make a compact and portable circuitry.

Considering all these issues and after gaining rich inputs from the literature, here, it is aimed to address the issues related to the use of Pb in the perovskite structure as well as the device stability. In the present study, we have demonstrated the fabrication of one of the few lead-free perovskite photodetectors reported till date.<sup>9</sup> In particular, we have fabricated the photodetector based on methylammonium bismuth iodide, MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> (MABI) structure that works under the self-powered mode of operation (Figure 1). The optoelectronic properties of the photodetector are investigated systematically. The photoresponse of the photodetector is carefully studied and compared, which demonstrates the capability of MABI structure for detecting light at very low incident irradiance of 10  $\mu\text{W}/\text{cm}^2$ . Also, the photodetector exhibited fast and reproducible response speed (26.81/41.89 ms) along with high photosensitivity ( $\sim 10^5$ ) and detectivity ( $\sim 10^{12}$  Jones) at low operating voltages (0 and 0.8 V) where the effective device area is large. It is also revealed that the MABI photodetector has good stability even after storage for two months at ambient conditions.



**Figure 1** Self-powered photodetector based on MABI perovskite

It is worth mentioning that the performance of the present photodetector is compared with other hybrid perovskite photodetectors (Table 1) where it is found that our result shows a proper balance of all the critical parameters on which the performance of a photodetector relies. It is therefore concluded that the impact of the photodetector fabricated with MABI perovskite structure using a simple geometry has great potential to improve further the optoelectronic properties when proper electron/hole transporting layers will be fused for proper charge extraction. This will have significant benefits for next-generation cost-competitive optoelectronic technology to address the scalability issue.

PD (Photodetector)	$P^{a)}$ (mW/cm <sup>2</sup> )	$\lambda^{b)}$ (nm)	$S^{c)}$ (cm <sup>2</sup> )	Opt. volt. <sup>d)</sup> (V)	$R_{\lambda}^{e)}$ (A/W)	$D^{*f)}$ (Jones)	$\tau_r^{g)}$ (ms)	$\tau_d^{h)}$ (ms)	Ref. Year
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	0.01	400 – 700	0.25	0 0.8	1.76 m 0.16	$1.3 \times 10^{12}$ $4.6 \times 10^{12}$	26.81 34.77	41.98 39.46	This work
<i>Lead-free halide perovskite photodetectors</i>									
CsBi <sub>3</sub> I <sub>10</sub>	0.2	650	$6 \times 10^{-4}$	1	21.8	$1.9 \times 10^{13}$	0.33	0.38	2017
MASnI <sub>3</sub>	1.1	Halogen lamp	0.0314	2	0.47	$8.8 \times 10^{10}$	1500	400	2017
(RNH <sub>3</sub> ) <sub>2</sub> (CH <sub>3</sub> NH <sub>3</sub> ) <sub>n-1</sub> MnX <sub>3n+1</sub>	3	White light	-	30	13 m	-	10	7.5	2016
<i>Lead halide perovskite photodetectors</i>									
MAPbI <sub>3</sub> NPs	0.01	365	$1.5 \times 10^{-3}$	3	3.49	-	200	200	2014
MAPbI <sub>3</sub> NWs	0.08	650	0.0525	2	1.32	$2.5 \times 10^{12}$	0.2	0.3	2015
Graphene - MAPbI <sub>3</sub> -Au	0.014	532	-	1	223.5	-	1500	1500	2016
TiO <sub>2</sub> -MAPbI <sub>3</sub>	100	AM 1.5G	-	3	0.49 $\mu$	-	20	20	2014
CsPbBr <sub>3</sub>	1.01	442	-	10	0.18	$6.1 \times 10^{10}$	1.8	1	2016
CsPbBr <sub>3</sub> - CsPb <sub>2</sub> Br <sub>5</sub>	1.7	365	-	5	0.375	$2.9 \times 10^{11}$	0.28	0.64	2017
Au-CsPbBr <sub>3</sub>	0.4	532	-	8	0.01	$1.6 \times 10^9$	0.2	1.2	2016
MAPbI <sub>3</sub> -PDPP3T	0.5	365	0.33	1	10.7 m	$6.1 \times 10^9$	-	-	2016
CsPbCl <sub>3</sub> MWNs	0.7	405	-	10	14.3 m	-	3.212	2.511	2018
CsPbBr <sub>3</sub>	0.001	405	-	2	1.33 m	$0.8 \times 10^{12}$	-	-	2018

<sup>a)</sup> Incident intensity, <sup>b)</sup> Wavelength, <sup>c)</sup> Effective illuminated area, <sup>d)</sup> Operating voltage, <sup>e)</sup> Responsivity, <sup>f)</sup> Detectivity, <sup>g)</sup> Rise time, <sup>h)</sup> Decay time

**Table 1** Comparison of the MABI perovskite photodetector performance with the best reported values of other lead-free and lead based perovskite photodetectors.

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#### Important Highlights

- Uniform glow discharge
- Air discharge, no other gas such as Helium or Argon used
- World's first large scale air plasma system
- Environment friendly solution for textile processing
- Low cost power supply
- Array of plasma discharges

#### Other team members

- Nisha Chandwani
- Adam Sanghariyat
- Kushagra Nigam
- Nimish Sanchaniya
- Sudhir Kumar Nema

## Technology Focus - Design and development of Plasma System for Inline Treatment of Textile

Under the financial support from DST, New Delhi, a plasma system was successfully designed and developed at FCIPT, IPR for inline treatment of textile. In this system, uniform dielectric barrier discharge plasma (commonly known as DBD plasma) is generated using just ambient air as plasma generating gas. There are 72 numbers of plasma discharges, with each discharge of 2.5 metres length, for treating technical textile on an industrial scale. Each of the DBD plasmas was powered by an individual and identical indigenously developed low cost power supply. Architecture of this power supply is very novel in the context of generating uniform glow discharge plasma, particularly in air at atmospheric pressure. The system was demonstrated to industries during a recent workshop on “Applications of Plasma for Textile Processing (AFTP)”, held at FCIPT. Later, this system was successfully installed and commissioned at MANTRA (Manmade Textile Research Association), Surat. This system, at MANTRA, will be used for carrying out various experiments on textiles and also to demonstrate the same to the industry. To the best of our knowledge, based on literature survey, the system developed under this project activity is the world's first large scale air plasma treatment system for inline processing of textiles.



Plasma System for Inline Treatment of Textile installed at MANTRA, Surat



Demonstration of the system to industry and researchers during AFTP workshop



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#### Important Highlights

- Eco-friendly process
- Absence of white layer formation

#### Other team members

- Ghanshyam Jhala
- Keena Kalaria
- Suryakant Gupta
- Alphonsa Joseph

## System Focus - Installation of Plasma Nitriding System at, Dimapur, Nagaland

Plasma nitriding is a technique in which nitrogen plasma is produced and nascent nitrogen is allowed to diffuse into the surface of the substrate to be nitrided, typically steel alloy. This process helps in improving its tribological properties. Plasma nitriding is carried out in a vacuum chamber where high-voltage electrical energy is used both to generate the plasma and to accelerate the nitrogen ions towards the substrate. These ions recombine near the surface of the substrate and nitrogen atoms diffuse into it and form hard compounds. The continuous ion bombardment also heats the substrate, cleans its surface, and provides a hardened surface after nitriding.

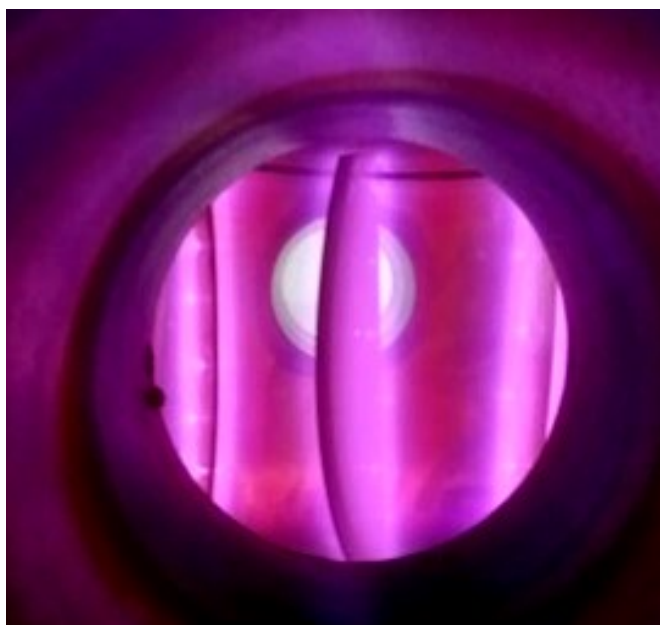
Plasma nitriding technique offers the following major advantages over conventional techniques:

- ‘Post-heat treatment’ grinding operation is not required
- Accurate process control is possible
- Process can be performed at lower temperatures
- Less distortion of the substrates
- Reduced time cycles
- Eco-friendly process

Considering the above advantages, Department of Science and Technology has awarded a project to the Plasma Surface Engineering Division (PSED), Institute for Plasma Research; for the development and commissioning of a plasma nitriding facility at Dimapur, Nagaland. This plasma nitriding facility will be used for surface hardening of agricultural tools used in Nagaland and surrounding regions of North-East India. Surface hardening of agricultural tools will finally lead to improved service life without compromising on the sharpness of the tools. PSED division of IPR has successfully designed and developed a Plasma Nitriding System for the nitriding of agricultural tools and equipment used in hill areas. Photograph of the Plasma nitriding system, installed and commissioned at Dimapur Nagaland is shown in the next page.



Plasma nitriding system installed at Dimapur Nagaland



Plasma nitriding of agricultural blades



Plasma nitrided agricultural blades



## Past Events

### *Visit to FCIPT of* **Shri. Gopal Baglay, Joint Secretary, PMO**

Shri. Gopal Baglay, Joint Secretary to PM, visited FCIPT on 12<sup>th</sup> April 2019. He was accompanied by Dr. Shashank Chaturvedi, Director IPR, Shri. Ujjwal Baruah, the then Dean IPR, Dr. Nirav Jamnapara, Head of the Plasma Technology and Transfer Section and few other dignitaries from Space Applications Centre, ISRO. During his visit, he toured various labs and facilities and took keen interest in the scientific, technological and industrial activities being carried out by APD and PSED divisions of IPR at FCIPT campus.



Visit to Nano Lab



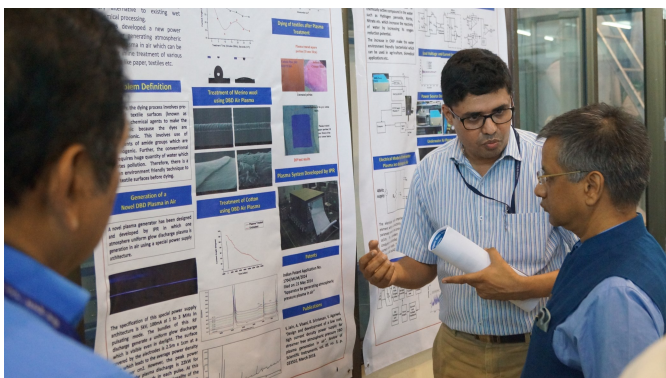
Visit to Nitriding Facility



Visit to PECVD Lab



Visit to Physical Vapor Deposition Lab



Visit to Textile Lab



Visit to Pyrolysis Facility



Visit to Denim Fading Facility



Visit to Solar Lab



**Students' visit to FCIPT as a part of Outreach activities of IPR**

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